METHOD OF COATING METAL SURFACES WITH A FLUORENE-CONTAINING POLYMER

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20 Claims

ABSTRACT OF THE DISCLOSURE

A method of coating a metal surface with a fluorine-containing polymer, comprising forming a chromium plating layer on a flat or roughened metal surface under various conditions, i.e. at an optimum electric current density of the metal surface lower than a predetermined value. The fluorine-containing polymer is then applied thereto, and then the plating layer is etched electrolytically to form a number of cracks or crevices therein. The surface of the flourene-containing polymer is coated thereto, followed by the application of an additional film of a continuous polymer. The resulting film is subsequently sintered and the binding strength is increased.

The present invention relates to a novel method of coating a metal surface with fluorine-containing polymers and more particularly relates to a method of forming a metal surface a rigidly bonded film of such fluorine-containing polymer which are poor in binding property. Fluorine-containing polymers such as polyethylene tetrafluoride, polyethylene trifluorochloride and ethylene tetrafluoride in particular have excellent chemical resistance, heat resisting property, electric property and mechanical property, but on the other hand, they are usually much inferior in binding property. Of these fluorine-containing polymers polyethylene tetrafluoride in particular has the advantages that it is most excellent in heat resisting property and chemical resistance, is least adhesive to other articles and has a very small frictional resistance, but on the other hand, those outstanding advantages make the binding of said polymer on metal surfaces extremely difficult.

In forming a coating of fluorine-containing polymer on a metal surface, two methods are mainly being employed at the present. Namely,

1. A method wherein a dispersion of fluorine-containing polymer is coated on a metal surface (by application method, dipping method or spraying method), dried and sintered.

2. A method wherein a film of fluorine-containing polymer is bonded to a metal surface by means of a binding agent.

However, the method (1) in many cases involves the steps of roughening the metal surface chemically or mechanically, applying a primer on the thus roughened metal surface, and drying and sintering said primer, before applying the dispersion of fluorine-containing polymer in order to obtain an improved binding strength between said metal surface and said polymer, and yet the binding strength of the coated polymer film thus produced is usually insufficient for the intended purposes. On the other hand, the method (2) has the disadvantages that the bonding strength of the fluorine-containing polymer film must be chemically treated beforehand to impart a binding property thereto and such treatment is not always simple because it not only necessitates the use of dangerous chemicals and special apparatus but also requires a technical skill, and that the binding strength produced between the fluorine-containing polymer and the metal surface is generally not sufficiently great and further the shape of an article to be coated is inevitably limited because the polymer is provided in the form of film.

In any event, these conventional methods are unsatisfactory, even when the complexity of the process is ignored, due to the fact that the binding strength of the films formed by the methods is insufficient and therefore the use of the methods for industrial applications or for the production of daily necessities is always accompanied by uneasiness at the binding strength of the resultant films.

The principal object of the present invention is to provide a method of coating a metal surface with a fluorine-containing polymer rigidly bonded thereto with a strength which has not been obtainable by the conventional methods described above.

Namely, the fluorine-containing polymer coating method according to the present invention comprises forming a chromium plating layer on a smooth or roughened metal surface under various conditions as will be described later, i.e. at an optimum electric current density or an electric current density higher than said optimum electric current density, electrolytically etching the surface of said chromium plating layer by reversing the polarities of electrodes to produce a number of pits, cracks or crevices therein, coating the resultant surface with a dispersion of a fluorine-containing polymer and sintering said polymer to form a continuous film of said polymer on said surface. The film is anchored to said surface by portions of the polymer filling the pits, cracks or crevices.

According to the second aspect of the present invention (hereinafter referred to as the second invention), there is provided a method of coating a metal surface with a fluorine-containing polymer as set forth above, wherein the surface of the chromium plating layer formed on the roughened metal surface is further superposed by a chromium plating layer at a lower plating bath temperature and then the surface of the top chromium plating layer is electrolytically etched by reversing the polarities of electrodes thereby to form more compound, finer and deeper cracks or crevices therein, and thereafter the resultant surface is coated with a dispersion of fluorine-containing polymer which is dried and sintered to form a film of the polymer thereon, whereby the binding strength between the fluorine-containing polymer coating and the metal is further improved by the so-called anchor affect of the polymer filling the pits, cracks or crevices.

According to the third aspect of the present invention (hereinafter referred to as the third invention), there is provided a method of coating a metal surface with a fluorine-containing polymer as set forth above, wherein the chromium plating operation is carried out at an electric current density higher than the electric current density optimum for the ordinary chromium plating operation so as to produce a chromium plating layer having projections thereon and then the surface of said chromium plating layer is etched electrolytically to form a number of cracks or crevices therein by reversing the polarities of
The coated films obtained by the methods of the present invention set forth above are rigidly bound on the metal surface without losing various inherent properties of the fluorine-containing polymer and the binding strengths therebetween are as great as has not been obtainable by the conventional methods. The important feature of the inventive coating methods resides in the fact that according to the methods fluorine-containing polymer, such as polyethylene tetrafluoride, which are poor in binding property, can be rigidly bound directly on a metal surface without necessitating a special treatment of the metal surface such as application of a primer. A further advantage of the methods of this invention is that the hardness and rigidity of a metal surface can be improved greatly by the chromium plating and the surfaces of even such metals as, for example, mild steel, copper, gun metal, aluminum or aluminum alloys, which are relatively low in hardness, can be made rigid by practicing the present methods. Thus, the present methods can very advantageously be used in various fields of application. The above-described advantages of the present invention are of great interest to the fact that the metal surface is coated with an electro-plated chromium. In this view, the formation of the chromium plating constitutes the most important step in the methods of the present invention.

In practicing the first and second inventions, the binding strength between the chromium plating and the metal surface is usually stronger when said metal surface has previously been roughened than otherwise. The roughening of the metal surface can be attained by any known mechanical or chemical method, such as sand blast method, shot peening method, scratch method or chemical etching method, and in the present invention any one of these methods can be selectively used optionally as the circumstances demand. Whether the metal surface is roughened or not, the metal surface must be subjected to pre-treatments, such as treatments for the purging of oxide film, removal of rust, and purging of rust, before the chromium plating operation, as is usually practiced.

Then, the metal surface thus treated is coated with a chromium plating. As a chromium plating bath, Sargent bath and a fluoro-silicate compound bath are known and either of them can be used in the present invention. With the Sargent bath containing, e.g. 250 g./l. of chromic anhydride and 2.5 g./l. of sulfuric acid, is used, the plating bath temperature is suitably selected relative to the electric current density as follows:

<table>
<thead>
<tr>
<th>Chromium plating bath temperature, °C</th>
<th>Electric current density, a./dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7-15</td>
</tr>
<tr>
<td>30</td>
<td>7-20</td>
</tr>
<tr>
<td>40</td>
<td>8-35</td>
</tr>
<tr>
<td>50</td>
<td>15-80</td>
</tr>
<tr>
<td>60</td>
<td>25-150</td>
</tr>
</tbody>
</table>

The thickness of the chromium plating formed may be varied optionally by adjusting the current conducting period but is usually preferably from 0.001 to 2 mm. This is because a thickness not greater than 0.001 mm will result in an insufficient binding strength between the metal surface and the fluorine-containing polymer, whereas a thickness not smaller than 2 mm will result in consumption of an extremely lengthy time, which is disadvantageous economically.

When the chromium plating layer has been electrolytically deposited rigidly on the metal surface in the manner described above, the polarities of electrodes are reversed for the electrolytic etching of said layer. Namely, the deposited layer of chromium plating is partly dissolved electrolytically leaving a number of pits, cracks, or crevices in the surface of said layer. In this case, since the solution velocity is at least 5 times the electrodensation velocity, current conducting period can be made shorter than in the case of electroplating. The number of pits, cracks or crevices per unit area is variable depending upon the temperature of the plating bath used and usually it becomes smaller as the bath temperature rises. The size and depth of the pits, cracks or crevices are determined mainly by the bath temperature, electric current density and current conducting period employed for the electro-deposition of the chromium plating layer. With the current conducting period fixed, it is usual that the size and depth of the pits, cracks or crevices and the interspace therebetween become greater as the bath temperature and electric current density becomes higher. Thus, it will be understood that by properly selecting the plating bath temperature and electric current density for the electro-deposition operation, pits, cracks or crevices of the desired size, depth and interspace can be obtained.

Upon completion of the chromium plating process in the methods of the first and second inventions described above, a glossy hard chromium plating (which will hereinafter be referred simply as "glossy chromium plating") is produced by each method and the electric current density for the production of such glossy chromium plating has an optimum range as specified previously. In the third invention, however, use is made of a current density higher than said optimum range. In this case, fine projections are formed on the surface of the resultant chromium plating and a glossy surface cannot be obtained. These projections which are generally referred to as "frost" or "burning" in the art, are semi-spherical or spherical in shape, with a part thereof having a needle-like shape. The plating surface with such projections thereon presents a greyish color and would be rejected when a glossy plating is desired. However, the present inventors have found that when the surface of such a chromium plating is etched electrolytically by reversing the polarities of electrodes opposite to those for the ordinary plating operation, thereby to dissolve the plating layer partially, pits, cracks or crevices are formed in the semispherical or spherical projections and a fluorine-containing polymer film superposed on said plating surface will produce an extremely strong binding strength between it and the plating layer. In this case, since the solution velocity is at least 5 times as high as the electro-deposition velocity, the current conducting period can be much shorter than in the case of electro-deposition. The number of pits, cracks or crevices per unit area is variable depending upon the temperature of the plating bath used and usually it becomes smaller as the bath temperature becomes higher. The size and depth of the pits, cracks or crevices are determined mainly by the bath temperature, electric current density and current conducting period employed for the electro-deposition of the chromium plating layer. With the current conducting period fixed, it is usual that the size and depth of the pits, cracks or crevices and the interspace therebetween become greater as the bath temperature and electric current density becomes higher. Thus, it will be understood that by properly selecting the plating bath temperature and electric current density for the electro-deposition operation, pits, cracks or crevices of the desired size, depth and interspace can be obtained.

In practicing the method of the third invention, a thin chromium plating layer may be formed on the metal surface by electro-deposition at an optimum electric current density, described previously for the formation of a glossy chromium plating, prior to the chromium plating etching in the first invention. The formation of such thin chromium plating layer is advantageous, though not essential, in producing an improved binding between the metal surface and the chromium plating layer having the projections, which will subsequently be formed on said metal surface. The metal plate used in the method of the
third invention must also be subjected to pre-treatments, such as treatments for the purging of oxide film, removal of fat and purging of rust, before the chromium plating electrodeposition operation, as well as in the case of ordinary plating operation.

For a fuller understanding of the present invention, reference will now be to the following detailed description taken in connection with the accompanying drawings, in which:

FIGS. 1 to 10 inclusive are cross sectional views diagrammatically showing various states of chromium platings formed on a metal surface by the methods of the present invention;

FIGS. 3' to 7' inclusive are fragmentary cross sectional views diagrammatically showing in enlargement the states of the respective chromium platings shown in FIGS. 3 to 7; and

FIGS. 9' and 10' are fragmentary cross sectional views diagrammatically showing in enlargement of the respective chromium platings shown in FIGS. 9 and 10.

First of all, the methods of the first and second inventions will be described.

FIGS. 1 to 5 and FIGS. 3' to 5' inclusive are views diagrammatically showing the cross sections of a metal substrate and a plating layer formed therein. Of the figures, FIGS. 1 and 2 are the case wherein the metal substrate has been previously roughened. FIG. 1 is a view of a metal substrate 1 with a chromium plating layer 2 formed therein, whereas FIG. 2 is a view of the chromium plating layer 2 on the metal substrate 1 after pits, cracks or crevices 3 formed therein by electrolytic etching. FIGS. 3 to 5 inclusive show the case wherein the chromium plating layer is formed on a roughened metal surface and FIGS. 3' to 5' are enlarged view of the chromium plating layers shown in FIGS. 3 to 5 respectively. FIGS. 3 and 3' are views of the metal substrate 1 whose surface 4 has previously been roughened by mechanical or chemical means, whereas FIGS. 4 and 4' are views of the metal substrate whose roughened surface has not previously been roughened, and it will be appreciated that the former is advantageous for binding a fluorine-containing polymer.

The surface of the metal having the cross section shown in FIG. 2 or FIG. 5, which is obtained in the manner described, is suitable for being coated with a fluorine-containing polymer. According to the second invention, such surface is further coated with the aforesaid chromium plating and the resultant layer of chromium plating is etched electrolytically by reversing the polarities of electrodes, whereby finer and more complex pits, cracks or crevices are provided on the surface of the metal and accordingly the binding strength between the metal and the fluorine-containing polymer coating formed therein is further improved. In this case, the second chromium plating operation may be carried out in the same manner as the first chromium plating operation but where the pits, cracks or crevices are to be produced by the following electrolytic etching are desired to be finer than those produced by the first electrolytic etching operation, the bath temperature for the second plating operation is preferably at 10°C lower than the bath temperature for the first plating operation. The operation for the formation of the second chromium plating layer (indicated at 5 in FIG. 6) must be stopped before the pits, cracks or crevices 3 in the first chromium plating layer 2 are filled with said second chromium plating layer. Upon completion of this, the polarities of the electrodes are reversed, whereby finer pits, cracks or crevices (indicated at 6 in FIG. 7) are formed.

FIGS. 6, 7 and FIGS. 6' and 7' are views diagrammatically showing the cross sections of the metal and chromium plating, which are obtained in different stages of treating the surface of the chromium plating layer shown in FIG. 2 in the manner described above. In the figures, reference numeral 5 designates the chromium plating layer newly formed and 6 designates the fine pits, cracks or crevices formed therein as a result of electrolytic etching. The same treatment may be made on the surface of the chromium plating layer shown in FIG. 5 to obtain a further complicated surface. The formation of the double layers of chromium plating on the metal surface as described above is advantageous not only in that the binding strength therebetween can be improved as described previously but also in that the electrodeposition velocity of the first chromium plating layer can be made higher than in the case of a single layer. This is because of the following reason. Namely, when an excessively high electro-deposition velocity is used for the formation of a single chromium plating layer on a metal surface, only a small binding strength is obtained between the metal surface and a fluorine-containing polymer film provided on said metal surface after the electrolytic etching of said chromium plating layer and for this reason the electrodeposition velocity must be maintained below a predetermined value by controlling the bath temperature and the electric current density used. Such restriction is not imposed on the operation of forming the double layers of chromium plating.

The surface of the chromium plating thus formed no longer has the gloss inherent to metallic chromium and appears gray in most cases, and a variety of fluorine-containing polymer coatings can be formed directly thereon.

The methods of the first and second inventions can be operated with any type of fluorine-containing polymer but are most advantageously used with a fluorine-containing polymer in particular which are poorly adhesive to other substances. For coating a metal surface with fluorine-containing polymers, any conventional method can be employed but by employing the methods of the present invention there is brought about the advantage that the fluorine-containing coating operation can be simplified because the methods of the present inventions do not necessarily involve the use of a primer on the metal surface which has heretofore been required before coating such fluorine-containing polymer in particular as polyethylene tetrafluoride and polyethylene chlorotrifluoride in the form of dispersion or enamel, for improving the binding property of said polymer.

Next, the method of the third invention will be explained.

The cross sections of a metal and a plating layer formed thereon in various stages of the operation according to this method are diagrammatically shown in FIGS. 8 to 10 and FIGS. 9' and 10' inclusive. FIGS. 9' and 10' are fragmentary enlarged view of FIGS. 9 and 10 respectively. FIG. 8 shows a metal substrate 1 with a thin chromium plating layer 2 formed on the substrate 1 at an optimum bath temperature and optimum current density. When the current density is raised successively after the formation of the thin chromium plating layer, projections are formed on said plating layer as shown in FIGS. 9 and 10.

FIGS. 9 and 10 show the condition of the chromium plating surface which has been subjected to electrolytic etching effected by reversing the polarities of electrodes after formation of the projections shown in FIG. 9. Namely, FIGS. 10 and 10' show pits, cracks or crevices 4 formed in the projections 3.
The surface of the chromium plating thus formed is gray or grayish white in color. When fluorine-containing polymer is applied on the surface of the chromium plating, the fluorine-containing polymer fills the interstices between the projections and pits, cracks or crevices to produce the so-called anchor effect, and as a result a binding effect is obtained which is unexpectedly remarkable as compared with that obtainable by treating the metal surface mechanically or chemically. The method of this invention is extremely effective for coating a metal surface with the aforementioned fluorine-containing polymer, such as polyethylene tetrafluoride, polyethylene chlorotrifluoride and ethylene tetrafluoride-propylene hexafluoride copolymer, which are poor in binding properties. For coating a metal surface with fluorine-containing polymer, any conventional method can be employed but by employing the method of this invention there is brought about the advantage that the coating operation can be simplified because the method of the invention does not necessarily involve the step of applying a primer on the metal surface which has heretofore been required before coating such polymer in particular as polyethylene tetrafluoride and polyethylene chlorotrifluoride in the form of dispersion or emulsion, for improving the binding property of said polymer.

The present invention will now be illustrated by way of examples. Of the following Examples 1 and 3 exemplify the method of the first invention, Example 2 exemplifies the method of the second invention and Example 4 exemplifies the method of the third invention.

EXAMPLE 1

The surface of a soft steel plate was treated, before forming a chromium plating thereon, in the following manner for the purging of an oxide film and removal of stain and fat. Namely, the surface of the soft steel plate was (1) polished with Alundum, lapping powder No. 600, and then with lapping powder No. 100, (2) washed with water, (3) subjected to electrolytic etching at 80° C. in an electrolyte containing 50 g./l. of sodium carbonate and 50 g./l. of caustic soda, (4) washed with water, (5) dipped in a dilute hydrochloric acid solution for the removal of rust, and then (6) subjected to electrolytic etching for 2 seconds in a chromium plating bath by reversing the polarities of electrodes.

The surface of soft steel plate thus treated was plated with chromium in a chromium plating bath consisting of 250 g./l. of chromic anhydride and 2.5 g./l. of sulfuric acid for 3 hours at a bath temperature of 50° C. and a current density of 50 a./dm², whereby a glossy chromium plating was formed on said surface. Successively thereafter, the polarities of electrodes were reversed to effect electrolytic etching of the plated surface for 15 minutes under the same conditions and a grayish surface was obtained. A microscopic observation of the cross section of the surface revealed that a number of pits were formed in the surface of the plating layer in depths of 22 to 32 μ. A dispersion containing 60% by weight of polyethylene tetrafluoride was sprayed on the surface of the chromium plating layer thus formed, dried under an infrared lamp and sintered at about 380° C. This operation was repeated 10 times and thereby a polyethylene tetrafluoride film of about 0.2 mm. in thickness was formed on the chromium plating layer.

Using "Tension," a tension tester manufactured by Toyo Measuring Instrument Company, Ltd., the binding strength of the film was measured at a tension speed of 20 mm./min. while delaminating said film partially. The results of the tension test are shown in the table below in comparison with the binding strength of a polyethylene tetrafluoride film which was formed in the same manner as described above, except that the surface of the soft steel plate had previously been roughened by sand blast method and the polyethylene tetrafluoride film was formed directly thereon. The binding strengths shown in the table are all an average of 5 specimens.

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>Primer</th>
<th>Binding Strength, kg-cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand blast treatment</td>
<td>Not used</td>
<td>0.60</td>
</tr>
<tr>
<td>Do.</td>
<td>Used</td>
<td>0.8-1.5</td>
</tr>
<tr>
<td>Present Invention (no sand blast treatment)</td>
<td>Not used</td>
<td>2.0-2.8</td>
</tr>
</tbody>
</table>

From the above table, it will be seen that the binding strength of the fluorine-containing polymer film formed on the surface of the chromiun plating surface through the intermediary of the chromium plating layer according to the present invention is unexpectedly great and thus the present invention is useful.

EXAMPLE 2

Using a plating bath of the same composition and a soft steel plate previously treated in the same manner as in Example 1, the chromium plating operation was carried out for 2 hours at a bath temperature of 60° C. and a current density of 60 a./dm². Then, the chromium plating thus formed was subjected to electrolytic etching for 8 minutes under the same conditions by reversing the polarities of electrodes, and thereafter the surface of the chromium plating layer was further plated with chromium for 2 hours in the same plating bath at 40° C. at a current density of 25 a./dm². Upon etching the surface of the resultant chromium plating layer electrolytically for 15 minutes under the same conditions by reversing the polarities of electrodes, a grayish chromium plating surface was obtained. A microscopic observation of the cross section revealed that a number of pits having depths of 16 to 17 μ had been formed in the plating layer.

The chromium plating surface thus obtained was coated with a polyethylene tetrafluoride film in the same manner as in Example 1 and the binding strength of said film was measured in the same manner as in Example 1. As a result, it was found that the binding strength was 2.6 kg./cm. or higher. A binding strength higher than 3.0 kg./cm. could not be measured because the specimen was cut at a point where the binding strength between the film and the metal showed said value.

EXAMPLE 3

The surface of a soft steel plate was roughened by the sand blast method in such a manner that the average height of the projections formed is about 25 μ. After subjecting the roughened surface to the pre-treatment which follows the electrolytic degreasing in Example 1, a chromium plating was formed thereon for 3 hours in a chromium plating bath of the same composition as in Example 1 at a temperature of 40° C. and a current density of 25 a./dm². Thereafter, the resultant chromium plating layer was electrolytically etched for 15 minutes under the same conditions by reversing the polarities of electrodes. The plating surface thus obtained was gray in color and a microscopic observation revealed that pits, cracks or crevices having depths of 8 to 28 μ had been formed in said plating layer.

A polyethylene tetrafluoride film was coated on the chromium plating surface in the same manner as in Example 1 and the binding strength was measured in the same manner as in Example 1. It was found that the binding strength was 2.5 kg./cm. or higher. The specimen was cut at a point where the binding strength between the film and the metal was 3.0 kg./cm.

EXAMPLE 4

Using a plating bath of the same composition as in Example 1, a soft steel plate which had previously been subjected to the same pre-treatments as in Example 1 was subjected to electrolytic etching for 2 seconds in said bath by reversing the polarities of electrodes. Then, the etched surface was further plated with chromium in the same bath at a temperature of 55° C. and a current density of
20 a./dm.² for 30 minutes. Successively thereafter, the chromium plating was continued for 2 hours at a current density of 40 a./dm.² and a light gray plating surface was obtained. A section of the chromium plating layer was observed through a microscope and it was found that a number of substantially semispherical projections had been formed on the surface of said plating layer, whose heights were not greater than about 42µ. Then, the plating surface was electrolytically etched for 8 minutes under the same conditions by reversing the polarities of electrodes and a grayish white surface was obtained. Through a microscope, it was found that a number of pits, cracks or crevices had been formed in the projections, whose depths were from 3 to 35µ.

The surface of the chromium plating layer thus formed was coated with a polyethylene tetrafluoride film in the same manner as in Example 1.

Using "Tension," a tension tester manufactured by Toyo Measuring Instrument Company, Ltd., the binding strength of the film was measured at a tension speed of 20 mm./min. while delaminating said film partially. The results of the tension test are shown in the table below in comparison with the binding strength of a polyethylene tetrafluoride film which was formed in the same manner as described above, except that the surface of the soft steel plate had previously been roughened by sand blast method and the polyethylene tetrafluoride film was formed directly thereon. The binding strengths shown in the table are all an average of 5 specimens.

<table>
<thead>
<tr>
<th>Metal surface treatment</th>
<th>Primer</th>
<th>Binding strength, kg./dm.²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand blast treatment</td>
<td>Not used</td>
<td>0.02</td>
</tr>
<tr>
<td>Present invention</td>
<td>Used</td>
<td>0.8±1.5</td>
</tr>
</tbody>
</table>

At the point of cutting.

A binding strength greater than 3.0 kg./cm.² of the film which had been formed through the intermediary of the chromium plating according to the present invention, could not be measured because the specimen was cut at a point where the binding strength between the film and the metal showed said value.

From the above table, it will be seen that the binding strength of the fluorine-containing polymer film formed according to the present invention is unexpectedly great and thus the present invention is useful.

Although the field of application of the present invention is unlimited, the present invention is particularly advantageously used for the application of fluorine-containing polymer to the surfaces of various rollers, bearings, spinning machine parts, pistons and cylinders in pneumatic and hydraulic machinery. When polyethylene tetrafluoride is applied, for example, on the surface of a bearing, etc., the frictional resistance of the surface thereof can be prevented from becoming excessively large even when the polyethylene tetrafluoride film had been worn out to some extent, owing to the lubricity of the polyethylene tetrafluoride present in the pits, cracks or crevices in the chromium plated layer and the hard surface of said chromium plated layer. In addition, the releasing property of the metal surface with respect to other articles can be maintained highly satisfactorily. By employing the coating methods according to the present invention, it is possible to obtain a binding property and wear resisting property or lubricating property which are far more superior to those of the conventional coated films, depending upon the purpose of use of the coated film. Further, the methods of the present invention can be used in a wide range of application.

What is claimed is:

1. A method of coating a metal surface with a fluorine-containing polymer comprising electrolytically forming a frosted chromium plated layer on the metal surface whereby projections are formed on the surface of said chromium plated layer, electrolytically etching the surface of said chromium plated layer by reversing polarities of the electrodes to form a number of pits, cracks or crevices in said surface, coating a dispersion of fluorine-containing polymer on the resultant surface and sintering said polymer to form a continuous film of said polymer on said surface, thereby anchoring said film to said surface by portions of said polymer filling said pits, cracks or crevices.

2. A method of coating a metal surface with a fluorine-containing polymer comprising electrolytically forming a first chromium plated layer on the metal surface, electrolytically etching the surface of said chromium plated layer by reversing the polarities of the electrodes to form a number of pits, cracks or crevices therein, superposing a second chromium plated layer over said first chromium plated at a bath temperature lower than the bath temperature for forming the first chromium plated layer, electrolytically etching the surface of the second chromium layer by reversing the polarities of the electrodes to form a number of further pits, cracks or crevices therein, coating a dispersion of a fluorine-containing polymer on the resultant surface and sintering said polymer to form a continuous film of said polymer on said surface, thereby anchoring said film to said surface by portions of said polymer filling said pits, cracks or crevices.

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