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(54) **Method of metal surface treatment.**

(57) A method of treatment of a metal surface in which there can be metal oxides on the surface which includes applying to the surface a solution formulated to be substantially non-reactive with the oxide allowing this to perfuse through the oxide but to be substantially reactive with the underlying metal and to also include metals to act as a buffer to localise action on the underlying metal and further provide a pacivating coat the method including the further step of then coating such appropriate surface. The solution may contain a weak acid in substantial concentration (e.g. 57,3 % phosphoric acid and 36,7 % water) and significant quantities of a buffering and inhibiting type compound (e.g. 5,4 % urea) as well as soluble metal salts (e.g. 0,08% copper sulphate, 0.08% cobalt sulphate, 0,08% chromium sulphate, 0,08% nickel sulphate, 0,08% manganese sulphate and 0,08% zinc sulphate).

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This invention relates to a method of a metal surface treatment.

Considerable problems have hitherto been experienced in effecting coating of some materials including paints and some metals on metal surfaces.

As illustrative, but not limiting, enormous difficulty is experienced in attempting to coat what is termed hard chrome onto a metal surface of another type for instance, steel, and while it is capable of being achieved, in practice, it requires a number of steps in an electroplating process which require both time and expertise in effecting.

In another application, it is known that it is very difficult to have a paint based upon a resin, adhere to a zinc coated steel surface where this has been newly prepared.

Perhaps because the paint whether this is based on an acrylic resin or some differing resin material requires a mechanical interlocking bond or not, it is conventionally

accepted that such paint should not be applied to a surface such as newly prepared zinc coated steel until the coat has weathered, which may take some months or in some cases, years.

In another instance, it is conventionally acknowledged that it is most difficult to effect the coating either of another metal or a protective coating on an aluminium surface.

It is now believed that this is because of the characteristic of the well acknowledged oxide formed on the surface of the aluminium metal.

The above three illustrations indicate difficulties that have been experienced thus far and are real problems in the art in relation to the coating of metal surfaces.

This invention is concerned with the treatment of metal surfaces including ferrous and non-ferrous metals and alloys which assist in the subsequent bonding of surface coatings and which incidentally assist in reducing vulnerability of the surface to subsequent further oxidisation.

The invention involving the method uses a solution which is applied to the metal surface and which is so compounded that it will provide a beneficial coating effect in relation to metal surfaces which will provide a base upon which subsequent coating can be more effective than has hitherto been the case, and in some instances enables a coating that has hitherto not been able to be as effectively or economically enabled to be secured to the surface of the said metal.

I have hitherto described a solution especially in relation to a preferred arrangement which I found was suitable for application to corroded metal surfaces.

This invention relates to firstly a broadening of the general discovery of that first invention and the discovery of its wider applicability to enable coating to be achieved subsequently which has hitherto not been realized.

Conventionally, treatment of a metal surface has been based on the concept of removing the oxidised surface which almost inevitably exists on the surface whether the metal appears to be bright clean or badly corroded.

Treatment therefore has taken two main approaches that is, either to apply to the surface a material which can substantially attack and thereby dissolve and remove the metal oxides as well as the metal underlying the oxides on the basis that this will remove any seat of corrosion or secondarily it relies upon the expectation of most of the metal oxide to be physically removed and then to cover the surface with a generally impermeable membrane which will therefore seal the surface from access of water or other corrosion inducing materials.

From experiments conducted thus far, neither of the two conventional processes appear to provide significant improvement and in a number of cases, according to experiments conducted would appear to, at least in the long term, worsen the vulnerability of the material to attack.

Typically, if steel is pickled by immersion in hydrochloric acid, besides the fact that the surface can

be irregularly corroded by the hydrochloric acid, the hydrochloric acid in itself must subsequently be neutralized or removed by quenching and this in itself leaves agents which can induce further oxidisation.

While an acid such as phosphoric acid can be used for pickling, it is seldom used for scale removal because it is an expensive acid and slow in operation.

However, some steel plates are often initially de-scaled in sulphuric acid, and then, after rinsing, immersed in a 2% phosphoric acid containing very small quantities of iron and at a high temperature, such as 80-90°C. for several minutes.

This provides an iron phosphate coating which is considered useful for afterwards coating with paint.

The difficulty with simply coating the material with a material that forms in effect an impermeable membrane is the difficulty that it is almost impossible to ensure that there is not a humid atmosphere between the membrane and the metal surface provided either by the drying of the setting membrane or by entrapped air providing from time to time condensed water or perhaps more commonly, the breakdown in the surface at one or more places, and the subsequent ingestion between the commonly rather loosely adhered membranes and the metal surface, thus allowing water not only to be pulled into the interface but to be kept there because of the membrane and in fact therefore promote corrosion.

The first discovery of this invention is that it is of significant value to apply to the metal surface which will inevitably have oxide thereon upon any exposure to air, a material which is formulated so that

rather than attack the metal oxide, it will have no or minimal reactivity with respect to the metal oxide and hence much more readily than with other materials perfuse through the oxide without substantially affecting this or blocking this porous character of the oxide by the reaction products such as a gas or other materials.

The material however is selected or formulated so that when it reaches the base of the oxide, it is reactive with respect to the metal providing the surface from which the oxide is formed or perhaps in other words is substantially more reactive with respect to the metal base than the oxides so that by applying such material to the surface of a corroded material, the material will perfuse without significant reaction through the pores of the oxide and then attack the metal at the base releasing or lifting off the oxides.

The next discovery of this invention relates to the problem of limiting the corrosion and providing a further base upon which subsequent coating can be effective.

By including in the formulation, materials with significant concentrations having large molecular weights, it has been found that this material can confine the acid attack or the base attack so that firstly the rate of reaction is limited so that the release of gas is at a limited rate but at the same time, the reaction products are held within the vicinity of the area of reaction so that by including metal iron in the solution, especially those at a higher position in the electromotive series, then with the acid or base attack occurring, the reaction products will be taken into the solution with the result displacement potential of these other metals and these

are very likely to form a strong attachment bond with the then accessible metal bonds forming the base or insofar that there are complex molecules in the solution, there is a high likelihood of forming complex association bonds at or around the site of the reaction.

The characteristics of the solution then provide also in effect, protection from oxidation of the metal being exposed by the acid or base attack.

By then treating the thus prepared surface in such a way as to induce further coating either by metal buildup or by reason of organic or inorganic coating materials and in such a way as to be able to accept within the coating method the presence of the said solution or in another way neutralising this, one can then obtain a coating on metals in such a way and with materials that have not hitherto been able to be so combined, or so economically combined.

The invention can in one form then be said to reside in a method of treatment of a metal surface including the steps of preparing the surface and then building up a protective coating on the metal surface so prepared, the preparation of the surface including the step of applying to the surface a solution formulated or selected so as to be substantially non-reactive with any oxide of the metal surface, adapted to perfuse through any oxides on the surface of the metals insofar that these are porous without thereby being blocked by reaction products, and then adapted to react with the underlying metal providing the metal surface, and then to cover such underlying metal so as to allow ion exchange between metal ions such as those of higher electromotive series with respect to the metal of the surface and those in the formulation of the solution and the metal of the surface

but to substantially resist access to the metals or gas so as to significantly retard any formation of oxides of the metal forming the surface, and then applying compatible coating materials either by way of electro-deposition or otherwise onto the thus prepared surface.

It is to be emphasized that the results of the preparation appear to produce a surface which does not appear to have previously been provided and its compatibility to subsequent coating either by way of electro-deposition or to coating by applying a painting solution or otherwise is also a significant discovery in that the prepared surface appears to provide significant molecular bonding so that there is a better grip and therefore a potential for applying metals by way of electro-deposition that could not previously be applied with effective grip hitherto, and similarly with painting solutions, provided these are compatible with the solution that will to a certain extent be left on the surface, then there can also be a significant increase in bonding attachment.

The process therefore appears to have the joint advantage that it will not only not depend upon having to physically remove rust or to provide a first attack of a very strong acid with subsequent necessary treatments but of course with a single application being available and with the necessity of removal not being any longer present, a number of materials can be treated in situ and of course within a short period of time can be immediately coated without significant disadvantage by reason of underlying great rust or other oxide potential.

The concept then is to formulate the solution and treat the surface so that in fact quite contrary to what has been the conventional concept, the oxide of the

metal is not attacked and it is the concept that one should arrange the formulation that there is most decidedly preferrential attack to the base metal so that access to the base metal is not impeded by any reaction with the oxides this of course assuming as has been discovered by experiment that all of the oxides of metal forming on the surface in a corrosion type situation appear to be porous and of course that the formulation is suitable for the selected metal and the oxide in question. There is also an assumption that the formulation will wet the oxides and if this is not generally possible, additional material such as appropriate surfactants may be necessary to assist such wetting and therefore perfusion of the formulation through the oxides.

An understanding of the action is perhaps better achieved by reference to a preferred formulation which also happens to be useful for a number of metals with their oxides on their surface.

The preferred formulation also perhaps surprisingly, has materials which individually provide a single function or a multiplicity of functions but it is well understood that such functions can be provided by two or more materials acting in concert.

The reference to the preferred formulation then is not to be taken as necessarily limiting the applicability of the method to such formulation although the components of the formulation have provided significant advantages but clearly many other formulations, once the underlying concept of the method has been realized, can be devised to provide the same function and significant advantages.

According to the preferred solution then, this includes a acid and preferably also phosphoric acid H_3PO_4

produced from commercial acid of 82% H_3PO_4 known as syrupy phosphoric acid. Because orthophosphoric acid is a triprotic acid, it forms three series of salts corresponding to three stages of ionisation. The primary phosphates are more soluable in water than tertiary phosphates.

The solution also contains a significant proportion of urea. Typically a mixture of 82% orthophosphoric acid, mixed with an aqueous solution of urea in the proportions - one part by weight of urea, to two parts by weight of the phosphoric acid solution - produces a crystalline addition product which is strongly acid and which is soluable in water. In the solution preferred in the embodiment, there is an excess of phosphoric acid over that which is required to produce this addition product.

The preferred solution also contains significant amounts of the sulphates of copper, nickel, chromium,manganese, cobalt, and in some cases zinc. These can have several functions, one of which is to act as an activator in assisting the attacking or underlying metal providing the metal surface and they also of course provide for sequential deposition of the metal on the surface and subsequent passivating of the surface.

The depositions also include phosphates which are of course formed when this preferred solution is formed which grow on the phosphate ion primary layer.

Typically then, when the preferred solution is applied to a metal surface such as iron, the metals in the solution, for example copper, being cathodic to the dissolving iron, increase the rate of solution of iron by depositing on the iron and forming local cells with it. Thus a large number of centres for crystal growth

are produced which result in rapid formation of phosphate coating.

In a preferred instance then, a copper film is formed in relation to a still surface with the copper film being uniformly adherent when the preferred solution is applied by wiping, or if the surface temperature of the steel is raised to about 80°C. For the later building up of the coat, the steel sheet is then immersed after draining in either nickel sulphate or chromium sulphate for several minutes so that nickel or chromium phosphate is deposited on the iron phosphate underlayer and finally there becomes a layer of pure nickel or chromium phosphate.

The term phosphate is given as a simple terminology reference but of course, especially with the urea present, there would be a mixed phosphate with the crystalline addition product of urea and orthophosphoric acid. An absorption barrier is accordingly formed in the unrusted areas of the specimen by the urea phosphoric acid complex and there is of course a lower reaction rate than that of the solution absorbed into the rust.

In the metal oxide, autophoretic or electrophoretic separation of the excess phosphoric from the completed reaction appears to occur, accelerating attack on the underlying iron compared with the unoxidized areas providing a reservoir of acid.

The action of the urea therefore can be likened to an inhibitor, but it also has additional characteristics which are of significant advantage in the method.

A first of these is that it assists in wetting of oxidized metal surfaces and it has a characteristic perhaps termed an ability to creep over surfaces which has been suggested as being caused by an ability to crystallize and recrystallize at its edges, thereby achieving this creeping feature.

Another advantageous feature is the character of the combination of urea and phosphoric acid and also another feature is the fact that it provides especially in the higher concentrations at the metal face, this more viscous layer which significantly inhibits the action which firstly reduces the size of any gas bubble evolution which means that the action is much more uniform over the whole of the surface and the effect appears to be somewhat akin to a micro-etch rather than a macro-etch or significant pitting and it also appears to provide an association complex with the materials at the reacting face which is substantially insoluble subsequently but provides a good binder for subsequent coating. It is also useful because it will be compatible when used as a complex associating molecule with subsequent electroplating techniques.

Reference has been made to the applications to especially steel surfaces, but it is to be understood that it would appear that the concept applies to any metal surface.

As illistrative, aluminium alloy is very suitable for this treatment, and as with steel, an aluminium alloy should be appropriately degreased by application of

appropriate solvents which allow for removal of fatty compounds that are typically found on the surface of metals.

With relation to the preferred solution, an aluminium part, if heated to approximately 90°C and then immersed in the preferred solution for approximately 5 minutes, will have significantly corrosion products removed and there will be observed a minor etching.

With the preferred solution, a copper deposit will be noticed on the surface of the aluminium in a friable form. This can be simply removed by washing and scrubbing the surface leaving a clean aluminium surface but preferably in relation to this invention, the part can be immediately plated in copper, nickel or chromium plating baths, leaving the copper. The copper will be replaced in the action but it provides a good basis upon which the action can proceed.

A selection of the various compounds or materials forming the solution will depend upon many factors including effectiveness in relation to the material to be used, the costing, safety of usage and of course the long term effectiveness of the answer provided.

It is appreciated that there are many combinations of solutions that would be suitable and that at least in the wider concept of this invention, it is the discovery of the mechanism so that compounds can be effectively formulated and when applied, can be understood as to provide a useful basis for subsequent coating.

The preferred solution has significant advantages in sofar that with relatively safe materials from a

toxicity point of view and from a cost point of view, a solution which is relatively simple and economic can be widely used in relation to a large variety of metal surfaces.

It is to be emphasized however, that this is realized as being typical and not limited to the inventive concept at least in its wider concept.

Typically then, acids or bases with relatively weak dissociation constants may be used in a formulation either with or in replacement of phosphoric acid typically a dissociation constant of 7.5×10^{-3} or as in the case of ascetic acid 1.8×10^{-5} or in the case of formic acid 1.8×10^{-4} all could be suitable.

Typically, other acids that are considered useful provided the other formulation aspects are satisfactory, can include oxalic acid, carbonic acid, hydrogen selenide, hydrofluoric acid and so on.

Typically, bases can also be used including ammonia, dymethylamine, methylamine, trimethylamine and the like.

It is significant that as well as a weakly dissociated acid or base, there needs to be a significant concentration of a material which conventionally can be useful as an inhibitor.

It is to be emphasized that the action is not only an inhibitor in this application, but it is a name used to indicate the type of material suitable in this case.

Large molecules such as the polysaccharides or urea or substituted ureas, amides, thiourea and substituted

thioureas may also be suitable.

This of course is not to suggest a limitation to the scope but simply to indicate an illustrative example of type of molecule and the fact that a significant concentration will firstly assist to inhibit the acid action on the oxide of the metal, assisting hopefully in also perfusing through the oxide to the underlying metal and then assisting firstly in the limiting of the reaction base and access of oxide forming materials from externally and finally, being either compatible with or forming an association complex with the underlying metal in combination with other portions of the compound provided.

Finally, it is a necessary feature to assist in the later passivation that there be metal ions provided in the material and typically these are transitional elements sulphates.

Once again however, this is illustrative in that the sulphates are generally water soluable and we have been talking generally of aqueous solutions and also that these salts are more economic than others which are also water soluable.

Having now described in general terms aspects of the invention, the invention will be better understood with reference to examples which shall now be given, of the way the invention can be preferrably carried out.

The composition and preparation of the solution used in the first application to the metal surface in one preferred form is as follows:

Four hundred grams dry urea (46%N 0.4 biuret) is dissolved in 1600 millilitres of hot water (85°C) and to this is added 200 millilitres of a sulphate solution, this being made by dissolving 40 grams of each of the following metal sulphates in 1140 millilitres of water - these sulphates being Copper Sulphate, Cobalt Sulphate, Chromium Sulphate, Nickel Sulphate, Manganese Sulphate and Zinc Sulphate - and to this mixture adding 3200 millilitres of phosphoric acid 82% technical grade.

This provides approximately 5 litres of the solution.

The above solution contains by weight then:

Urea	5.4%
Phosphoric Acid	57.3%
Water	36.7%
Copper Sulphate	0.08%
Cobalt Sulphate	0.08%
Chromium Sulphate	0.08%
Nickel Sulphate	0.08%
Manganese Sulphate	0.08%
Zinc Sulphate	0.08%

In the forthcoming examples this solution will be referred to as the solution of the preferred embodiment of the invention.

EXAMPLE 1

The metal article to be plated may first be cleaned to remove grease, oil, and loose solids by any of the common methods such as solvent cleaning, emulsion cleaning or alkaline cleaning. Where mill scale and rust are present, it is of course feasible to use weathering and wire brushing, acid pickling, grit blasting or flame cleaning. In the present invention it is found that new steel may be cleaned with solvent such as

perchlorethylene 80% and butanol 20% by weight, or methyl ethyl ketone, particularly if the initial temperature of the specimen is for example from 20°C - 100°C. Adequate cleaning may be given by immersing the specimen in the solution of the preferred embodiment of the invention at temperatures of 40°C - 100°C for times depending on the temperature but generally of the order of 10 seconds to 1 minute at 100°C. If the specimen is heated to 100°C - 140°C first and dipped in the solution of the preferred embodiment of the invention a cloud of fine bubbles emanates from the specimen and indicates that micro-etching has occurred and the surface is ready for further treatment.

The article may then be placed in the selected electroplating bath, for example a copper plating bath comprising:

Sodium cyanide NaCN	37 grams per litre
Copper cyanide CuCN	30 grams per litre
Rochelle salt $KNaC_4H_4O_6$ $4H_2O$	50 grams per litre
Sodium carbonate Na_2CO_3	38 grams per litre

Operating conditions:

50 - 70°C, 2-6 amps per dm^2, 2 - 6 volts, pH 12.2 - 12.8, current efficiency 50 - 60%, anodes copper rolled and annealed, steel vat, free cyanide 3 - 6 grams per litre.

Or the article may be placed in a selected electroplating bath for example a chromium plating bath comprising:

Chromic acid CrO_3	450 grams per litre
Sulphuric acid H_2SO_4	4.5 grams per litre

The solution should be boiled with citric acid 12.5 grams per litre, tartaric acid 18 grams per litre or oxalic acid 25 grams per litre to give some reduction. The operating conditions are, 40 - 50°C 12 - 20 amps per dm^2, current efficiency 12 - 15%, volts 4 - 5, 7% antimonial lead anodes, in a vat made of steel, lined with 7% antimonial lead.

EXAMPLE 2

Where the metal article to be heated is zinc or zinc based alloys such as used in diecastings, the application of the solution of the preferred embodiment of the invention may be carried out by brushing, spraying or immersion. As the solution rate for the zinc is much higher than that for steel, temperatures and times of immersion are reduced to prevent undue etching of the surface, for example at 40°C, 5 - 10 seconds may be adequate. The copper plating bath shown in example 1 is recommended for zinc and zinc based diecastings; the pH value should be controlled by adding sodium hydroxide if it is too low, tartaric acid if it is too high.

A chromium plating solution for direct plating on the zinc and zinc based diecastings is as follows:

Chromic acid CrO_3	331 grams per litre
Sulphuric acid H_2SO_4	0.6 grams per litre
Sodium hydroxide NaOH	48 grams per litre

Operating conditions:

15 - 21°C, current density 100 amps per dm^2, 6 - 12 volts.

EXAMPLE 3

When the metal article to be heated is aluminium or aluminium alloys, as in sheet or castings, the application of the solution of the preferred embodiment of present invention to the article is best achieved at temperatures in the range of $20^{o}C$ - $40^{0}C$ and the progress of treatment can be gauged by the appearance of a friable thin film of copper on the specimen. The specimen can then be transferred to a copper plating solution such as alkaline copper of composition:

Copper sulphate $CuSO_4\ 5H_2O$	15 grams per litre
Sodium oxalate $Na_2C_2O_4$	10 grams per litre
Triethanolamine $N(CH_2CH_2OH)_3$	22 grams per litre

Operating conditions:

$20^{o}C$, 0.3 - 0.6 amps per dm^2, copper anodes, vat: earthenware or polymer lined.

Or transferred direct to a chromium plating solution such as that in example 1.

Or transferred to an autocatalytic copper plating that is current-less bath such as that proposed by A.E. Cahill in U.S. Patent 2,874,072 (1959).

For example a solution could be:

Copper nitrate $Cu(NO_3)_2 3H_2O$	15 grams per litre
Sodium hydroxide NaOH	20 grams per litre
Formaldehyde HCHO	100 millilitres of a 36% solution
Sodium bicarbonate $NaHCO_3$	10 grams per litre
Sodium potassium tartrate $NaKC_4H_4O_6 4H_2O$	30 grams per litre
Water remainder to 1 litre	

Or transferred to a zincate solution containing 525 grams of sodium hydroxide and 100 grams of zinc oxide per litre and immersed for 1 - 3 minutes at 20°C, rinsed and copper plated in the previously mentioned copper baths, followed by plating with hard chromium from solution as in example 1.

EXAMPLE 4

Treatment of the metal articles with the solution of the preferred embodiment of the invention is followed by dipping in a concentrated solution of metal sulphate or phosphate at 40 - 100°C for 5 seconds - 1 minute at 100°C, which produces a metal phosphate coating such as chromium phosphate. A suitable solution is for example:

Chromium sulphate	280 grams
Water	600 millilitres
Orthophosphoric acid (82%)	600 millilitres

A further solution is for example:

Chromium phosphate	200 grams
Water	600 millilitres
Orthophosphoric acid (82%)	20 millilitres

EXAMPLE 5

In example 4, metal sulphates or phosphates are used such as cobalt, nickle, manganese, silver, gold, platinum and zinc.

EXAMPLE 6

This example involves the direct plating in a single solution of copper onto a metal in single stage process.

A suitable solution is as follows:

Orthosphosphoric acid (82%)	58%
Urea or thiourea	6%
Copper sulphate	10%

The copper sulphate may be replaced by nickel, cobalt, manganese, zinc, silver or gold, or by chromic acid to directly plate these metals onto a metal surface.

EXAMPLE 7

The solution of the preferred embodiment of the invention is used to prepare the surface of aluminium alloy castings for hard chrome plating from a normal plating solution of chromic acid 250 grams per litre, sulphuric acid 25 grams per litre and is operated at 300 amps per square foot at 4 - 8 volts.

These examples are by way of illustration only and are not intended to limit the invention.

CLAIMS

1. A method of treatment of a metal surface including the steps of preparing the surface and then building up a protective coating on the metal surface so prepared, the preparation of the surface including the step of applying to the surface a solution formulated or selected so as to be substantially non-reactive with any oxide of the metal surface, adapted to perfuse through any oxides on the surface of the metals insofar that these are porous without thereby being blocked by reaction products, and then adapted to react with the underlying metal providing the metal surface, and then to cover such underlying metal so as to allow ion exchange between metal ions such as those of higher electromotive series with respect to the metal of the surface and those in the formulation of the solution and

the metal of the surface but to substantially resist access to the metals or gasses so as to significantly retard any formation of oxides of the metal forming the surface, and then applying compatible coating materials either by way of electro-deposition or otherwise onto the thus prepared surface.

2. A method of metal surface treatment as in Claim 1 wherein said solution includes:

(1) a weak acid or weak base,

(2) an inhibitor, and

(3) salts of one or more transition metals

the acid or base having the characteristic that the acid or base will not substantially react with the oxides of the metal comprising the metal surface but will react with the unoxidised metal of the metal surface,

the inhibitor being selected to limit substantially the rate of reaction of the acid with the unoxidized metal, and to provide a buffering action of the acid in the said solution, and further to at least substantially limit gaseous effusion and hence limiting access of further solution to the metal surface, and

the concentration and types of the said acid or base, inhibitor and metal salts being further selected such that at least after an initial reaction with the base metal surface there is a bonding of the metal of the one or more of the metal salts in solution with the unoxidized metal surface as a complex.

3. A method of metal surface treatment as in Claim 2 wherein the weak acid is selected from a group comprising phosphoric acid, acetic acid, tartaric acid, citric acid, succinic acid, malaeic acid, tannic acid and formic acid.

4. The method of metal surface treatment as in Claim 2 wherein the weak base is selected from the group comprising ammonia, methylamine, dimethylamine and trimethylamine.

5. A method of metal surface treatment as in either of the preceding claims in which the inhibitor is selected from a group comprising urea and substituted ureas, amides, thiourea and substituted thioureas, and polysaccharides.

6. A method of metal surface treatment as in any one of Claims 2 to 6 wherein the metal salts are selected from a group comprising cobalt sulphate, copper sulphate, nickel sulphate, chromium sulphate, zinc sulphate, or manganese sulphate.

7. A method of metal surface treatment as in Claim 2 in which the acid is phosphoric acid and the inhibitor is urea and the proportions by weight are within the range of approximately 5 - 15% by weight of urea as compared to the weight of phosphoric acid.

8. A method of metal surface treatment as in any one of Claims 2 to 7 in which the concentration of metals salts is in the range of 0.5 - 1.5% by weight as compared to the weight of phosphoric acid.

9. A method of metal surface treatment as in any one of the preceding claims in which said compatible coating is applied by means of a chemical plating solution to thereby deposit a metal coat onto the thus prepared surface.

10. A method of metal surface treatment as in any one of the preceding claims in which said compatible coating solution is applied by means of an electro-plating solution and the method includes the further step of applying an electric current to thereby obtain the deposition of a metal coat onto the thus prepared surface.

11. A method of metal surface treatment as in any preceding claim in which said compatible coating is applied by means of a solution of polymeric resins and pigments in a solvent and said coating material is a paint.

12. The method of treatment of a metal surface which includes the steps of applying to the surface a solution including phosphoric acid, urea, and one or more soluble metal salts selected from the salts of the metals chromium, cobalt, copper, nickel, zinc and manganese and then applying, either with the said

solution or with a further solution, to the thus prepared surface, coating materials applied either by way of electro-deposition or otherwise onto the thus prepared surface.

13. The method of treatment of a metal surface as in Claim 12 in which the urea is present in a concentration of from 5 - 15%, by weight compared to the weight of phosphoric acid.

14. The method of treatment of a metal surface as in Claim 12 in which the concentration of phosphoric acid is the range of 40 - 75% by weight as compared to the weight of the solution.

15. The method of treatment of a metal surface as in any one of Claims 12, 13 or 14 in which the further application comprises the use of a chemical plating solution to thereby deposit a metal coat onto the thus prepared surface.

16. The method of treatment of a metal surface as in any one of Claims 12, 13 or 14 in which the further application comprises the use of an electroplating solution and further applying an electric current to thereby obtain the deposition of a metal coat onto the thus prepared surface.

17. The method of treatment of a metal surface as in any one of Claims 12, 13 or 14 in which the further

application comprises the use of solution of a polymeric resin and pigments in a solvent and said coating material is a paint.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 79104738.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - A - 2 252 327 (PMD CHEMICALS) + Page 15 + --	1,4,5
	DE - B - 2 108 294 (VEREINIGTE DEUTSCHE METALLWERKE) - Columns 1 and 3 + --	1,3,5
	FR - A - 2 262 099 (PFIZER) + Page 9 + --	1,3
	GB - A - 683 638 (ETHICON SUTURE LAB.INC.) + Pages 2 and 4 + --	1,3,5
	US - A - 1 954 743 (PETERSON) + Pages 1 and 2 + --	1,6
	US - A - 1 837 118 (ELDER) + Totality + ----	1,6

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 23 F 9/00
C 23 F 7/00

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 23 F
C 23 G

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	15-02-1980	SLAMA