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(71) Applicant: LUCAS INDUSTRIES public limited company
Great King Street
Birmingham, B19 2XF(GB)

(72) Inventor: Dawes, Cyril
17 Clarry Drive Four Oaks
Sutton Coldfield West Midlands(GB)

(72) Inventor: Smith, John David
25 Raddington Drive
Solihull West Midlands(GB)

(74) Representative: Pearce, Anthony Richmond et al,
Marks & Clerk Alpha Tower Suffolk Street Queensway
Birmingham B1 1TT(GB)

(54) Coated metal substrate and method of coating a metal substrate.

(57) A non-alloy steel is treated to provide a good keying surface for a solid polymeric or wax coating by heat treatment at 550 to 720 deg C for up to 4 hours in an atmosphere of, eg ammonia and endothermic or exothermic gas, followed by cooling to produce an epsilon iron nitride surface layer. The solid coating adheres tenaciously to the surface layer to give excellent salt spray resistance.

EP 0 074 211 A1

COMPLETE DOCUMENT

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This invention relates to a coated metal substrate and to a method of coating a metal substrate and is particularly concerned with steel substrates and to a corrosion resistant coating provided thereon.

It is well known that most steels are prone to environmental attack and become badly corroded in a relatively short period of time, particularly when exposed to a moist environment containing salt. In order to reduce the corrosion of steel, it is also well known to coat the steel with a corrosion resistant coating such as paint composition containing a polymer. However, if such a paint composition is applied directly to the surface of the steel substrate, an effective adhesion between the paint composition and the steel is not usually obtained. In particular, even when the steel substrate has been chemically cleaned before application of the paint composition thereto, the paint peels away from the surface of the substrate relatively easily, particularly when subjected to changes in ambient temperature and humidity. Once the paint composition peels away from the steel substrate, the latter is immediately prone to corrosion through oxidation.

In order to improve the adhesion between the steel substrate and the paint composition, it is known to effect pretreatment of the steel substrate by a process known as phosphating. In a typical phosphating treatment, the steel substrate is first cleaned for 2 to 5 minutes using an alkaline cleaner maintained at 50 to 70 degrees C, then the cleaner is removed by rinsing the cleaned substrate in two successive rinsing operations with water at ambient temperature, each operation being of a duration of half to one minute. Then, the cleaned and rinsed steel substrate is sprayed with a zinc phosphate solution maintained at 40 to 70 degrees C, the spraying operation taking about one and a half minutes. Alternatively, the steel substrate can be immersed in a zinc phosphate solution for about 5 minutes. Following this, the substrate is rinsed with water at ambient temperature and again rinsed with water at ambient temperature which is often de-ionized. As an alternative to this second rinse, the substrate may be subjected to a chromate rinse. A further rinse with deionised water at ambient temperature may be effected and will be effected if the above mentioned chromate rinse has been performed. Finally, the component is dried in an oven and is then ready for painting with a paint composition.

With this conventional phosphate pretreatment process, there are a number of disadvantages. The phosphating solution requires close chemical control to maintain consistent results. Control of effluent from the treatment plant is essential since excessive pollution of the site drainage system with zinc ions is not permitted. Additionally, it is likely that legislation will be enacted in the near future to restrict the phosphate ion concentration in site effluent discharge. High levels of plant maintenance are also required to maintain consistent results. The number of clean water rinsing operations required in the process makes it vulnerable to rising water costs. The process requires a high capital investment. The phosphating process is usually sited in a flow line arrangment organised for specific products and this greatly reduces or often eliminates any flexibility of product throughput. Lastly, the phosphating process is sensitive to the cleaniness of the components to be processed therefore requires close control at the cleaning stage.

An object of the present invention is to provide a coated steel substrate and a method of coating a steel substrate in which the above disadvantages can be obviated or mitigated and in which the corrosion resistance of the coated substrate can be materially improved.

According to one aspect of the present invention,there is provided a coated steel substrate comprising a non-alloy steel which has been treated so as to have an epsilon iron nitride surface layer, and a solid organic protective coating on said surface layer.

The applicants have found that an epsilon iron nitride surface on a steel substrate provides an ideal keying surface for a solid organic coating.

According to another aspect of the present invention, there is provided a method of coating a steel substrate comprising the steps of effecting a heat treatment operation on a non-alloy steel substrate so as to produce an epsilon iron nitride surface layer thereon, and applying a coating layer to said surface layer so as to provide a solid organic protective coating thereon.

The non-alloy steel is preferably one which contains up to 0.5 wt% carbon.

The solid organic protective coating takes the form of an organic polymer coating composition. However, it is within the scope of the present invention to provide a protective coating in the form of a solid wax film which may be applied in solution by the use of a suitable solvent.

Preferably, the epsilon iron nitride surface layer is formed by heat treating the steel substrate at a temperature of 550 to 720 degrees C for up to 4 hours in an atmosphere of ammonia, ammonia and endothermic gas, ammonia and exothermic gas or ammonia and nitrogen, with the optional inclusion of at least one of carbon dioxide, carbon monoxide, air and methane, followed by cooling. The terms "exothermic gas" and "endothermic gas" are well understood in the art. Carbon dioxide, carbon monoxide, air and exothermic gas are oxidizing gases. Carbon dioxide, methane and endothermic gas are carburizing gases. Most preferably, the cooling step is effected by allowing the treated steel substrate to cool under a protective (ie. non-oxidizing) atmosphere. However, it is within the scope of the present invention to effect the cooling step by quenching in oil. If an oil quench cooling is employed, then it is necessary to degrease the steel substrate to remove the oil and preheat to a temperature of,eg 200 deg C,to remove moisture from the micropores in the substrate, before applying the organic coating.

The invention is applicable to any steel substrates which are required to be rendered corrosion resistant, for example steel sheets, tubes rods or other articles of manufacture produced by, for example, rolling, pressing, forging or extruding.

The organic coating may be applied be means of a wet process, for example one employing a solvent to disperse f the organic coating, but may alternatively be effected by powder coating. With powder coating, the whole process can be dry so that there is no problem of solvent or other liquid removal and disposal.

In addition to increasing the adhesion between the steel substrate and the organic coating, the epsilon iron nitride layer produced as described above imparts other advantageous properties to the substrate. In particular, it is found that increased strength in components made from thin strip or sheet can be obtained. The epsilon iron nitride layer is very hard (approximately 1100HB) and has anti-seizure properties which can be exploited in certain applications merely by masking the required areas during the application of the organic coating. The processing costs are lower than for phosphating and a further reduction may be obtained when only corrosion resistance is required by the use of higher temperatures and shorter times within the above ranges.

It is preferred to effect the heat treatment operation so that the epsilon iron nitride surface layer has a thickness of about 25 microns. Thicknesses greater than about 25 microns can lead to spalling or cracking of the surface layer. Typically, such a layer thickness of about 25 microns can be obtained by heat treatment at 660 deg C for 45 minutes. Such a layer thickness may also be produced by heat treatment at 570 deg C for 3 hours or at 610 deg C for 90 minutes. However, heat treatment temperatures and times may be employed to produce layer thicknesses of less than 25 microns, eg down to 15 microns. For example, heat treatment at 570 deg C for 2 hours can be employed to produce a layer thickness of 16-20 microns.

The advantageous effects of the invention will become apparent from the following test:-

A number of test plates of non-alloy steel having a carbon content of 0.10% were subjected to a phosphate pretreatment or a pretreatment according to the present invention and were then coated with one of three organic coating systems. The resultant samples were subjected to a salt-spray test in accordance with ASTM Standard B117-64 in which 5 plus or minus 1 parts by weight of sodium chloride are dissolved in 95 parts by weight of distilled water, the pH of the solution being adjusted so that, when atomised at 95 degrees F, the collected solution will have a pH in the range of 6.5 to 7.2 and the temperature in the exposure zone of the salt-spray chamber is maintained at 95 plus 2 minus 3 degrees F.

After removal from the salt-spray test, the performance of the samples was evaluated by measuring the degree of creep of corrosion from two diagonal lines scratched through the organic coating in the form of a cross. The creep was checked by applying 710 tape manufactured by the 3 M's Company over the diagonal lines and then removing it by pulling back rapidly at 180 degrees to the sample surface. Pass or failure judgements were made using a permissible creep value of 2 mm on either side of the diagonal lines. The results are illustrated in the Table below:-

TABLE

Organic Coating System Applied	Typical Hours to Failure on Salt-Spray Test: Phosphate Pretreatment	Typical Hours to Failure on Salt-Spray Test: Pretreatment of Invention
(A) Polymer coatings		
1. Single coat of an air-drying two-pack epoxy formulation	96	150
2. Stoving alkyd/melamine primer coat + stoving alkyd/melamine gloss top coat.	240	300
3. Single coat of a stoving epoxy/phenolic /urea formulation.	400	450
4. Cathodic electroplate (single coat)	400	400

5. Single epoxy or polyester powder coating	500+	500+
(B) Wax coating		
1. Hard wax coating	50	250

In the column headed "Pretreatment of Invention", the steel samples were pretreated by heating them for two hours at 570 deg C in the case of samples (A)1 to 3, (A)4 and (B)1 and for 45 minutes at 660 deg C in the case of sample (B)4, in an atmosphere of 50% ammonia and 50% endothermic gas followed by slow cooling under a protective atmosphere of the same composition. The resultant steel samples had an epsilon iron nitride surface layer of a thickness of 16-20 microns.

It will be seen from the above Table that pretreatment of the steel samples according to the present invention produces a substantial improvement in corrosion resistance under salt spray conditions. Accordingly, the present invention is considered to be particularly suitable for steel articles for under bonnet motor vehicle applications. It will be appreciated that salting of roads during the winter time makes it necessary for exposed parts of the vehicle which are formed of steel to be rendered resistant to salt spray corrosion as effectively as possible.

The invention will now be described in further detail in the following Examples,in which unless otherwise stated the percentages are by volume:-

Example 1

A yoke body for a small electric motor was manufactured from non-alloy steel according to British Standard BS 1449 CS3 (C content=0.10 wt%). The body was then nitrocarburised for 2 hours at 570 deg.C in an atmosphere of 50% ammonia and 50% endothermic gas mixture (40% nitrogen, 40% hydrogen and 20% carbon monoxide) followed by slow cooling under the protection of the same atmosphere, to produce an epsilon iron nitride surface layer having a thickness of 16-20 microns on the body.

After this, an epoxy/phenolic/urea polymer coating formulation sold by International Paints Ltd under the code No. 0830X3020 was applied to the nitrocarburised body and stoved to produce a polymer coating having a thickness of 12-15 microns.

The resultant yoke body had a salt-spray resistance of more than 400 hours as measured according to the above-described Salt-Spray Test.

Example 2

A body for an electrical horn was manufactured from non-alloy steel according to British Standard BS 1449 CS2 (C content= 0.08 wt%). The body was then nitrocarburised at 610 deg.C for one and a half hours under the atmosphere employed in Example 1, and was then oil quenched. The resultant body had an epsilon iron nitride layer of a thickness of 16-20 microns.

The body was then degreased by washing in an alkaline cleaner sold by the Diversey Co. Ltd under the Trade Mark DIVERSPRAY 62.

A wax coating was then provided on the nitrocarburised body at a coating weight of 2 to 4 g per square metre by immersing the latter in a solvent-based dewatering rust-preventative wax sold by Castrol Oil Co Ltd. under the code V425. Such a wax composition is of a type which comprises a mixture of waxy aliphatic and branched chain hydrocarbons, calcium soaps of oxidized petrolatum and calcium resinate to produce a wax of the requisite hardness at room temperature. The wax was contained in a mixture of liquid petroleum hydrocarbons consisting of white spirits and C_9 and C_{10} aromatics. In the case of V425, the composition has a wax content of 15% by weight.

The resultant body had a salt-spray resistance of more than 150 hours as measured according to the above-described Salt-Spray Test.

The Applicants have have found that the epsilon iron nitride layer itself has an inherent resistance to corrosion by humidity and this property is particularly useful in cases where the organic coating becomes chipped in service or where it is desired to leave part of the surface of the epsilon iron nitride layer uncoated with the organic layer.

CLAIMS

1. A coated steel substrate comprising a non-alloy steel which has been treated so as to have an epsilon iron nitride surface layer, and a solid organic protective coating on sais surface layer.

2. A coated steel substrate as claimed in claim 1, wherein the solid protective coating is selected from an organic polymer coating and a wax.

3. A method of coating a steel substrate comprising the steps of effecting a heat treatment operation on a non-alloy steel substrate so as to produce an epsilon iron nitride surface layer thereon, and applying a coating layer to said surface layer so as to provide a solid organic protective coating thereon.

4. A method as claimed in claim 3, wherein said heat treatment step is effected by heating the steel substrate at a temperature of 550 to 720 deg C for up to 4 hours in an atmosphere of ammonia, ammonia and endothermic gas, ammonia and exothermic gas or ammonia and nitrogen, with the optional addition of at least one of carbon dioxide, carbon monoxide, air and methane.

5. A method as claimed in claim 4, wherein the cooling step is effected by allowing the heated substrate to cool under a non-oxidizing atmosphere.

6. A method as claimed in claim 4, wherein the cooling step is effected by quenching the heated substrate in oil, is employed, and then degreasing before applying the coating layer.

7. A method as claimed in claim 3, 4, 5 or 6, wherein the coating layer is applied by means of a wet process.

8. A method as claimed in claim 3,4,5 or 6, wherein the coating layer is applied by powder coating.

9. A method as claimed in claim 3 or 4, wherein the heat treatment operation is effected so as to produce a surface layer having a thickness of not more than about 25 microns.

10. A method as claimed in claim 9, wherein the heat treatment operation is effected so as to produce a thickness of about 15 to 25 microns.

11. A method as claimed in claim 9, wherein the heat treatment operation is effected so as to produce a thickness of about 25 microns.

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EUROPEAN SEARCH REPORT

0074211

Application number

EP 82 30 4451

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	GB-A-2 026 045 (HONDA) *The whole document*	1-4,9-10	C 23 C 11/14 B 05 D 3/10
X	GB-A-2 027 062 (HONDA) *Page 3, lines 90-125; page 4, lines 1-45*	1-4,9-10	
E	EP-A-0 053 521 (LUCAS INDUSTRIES) *The whole document*	1-3,7,8	
A	GB-A-1 299 308 (CESKOSLOVENSKA AKADEMIE VEB) *Claims 1-3,7*	1	**TECHNICAL FIELDS SEARCHED (Int. Cl. 3)**
A	PATENTS ABSTRACTS OF JAPAN, vol. 4, no. 155, 29th October 1980, page 136 C-29; & JP - A - 55 102 471 (HONDA GIKEN KOGYO K.K.) (05-08-1980) *Abstract*	1	C 23 C 11/00
A	PATENTS ABSTRACTS OF JAPAN, vol. 4, no. 155, 29th October 1980, page 134 C-29; & JP - A - 55 102 465 (HONDA GIKEN KOGYO K.K.) (05-08-1980) *Abstract*	1	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14-12-1982	DEVISME F.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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& : member of the same patent family, corresponding document