FORM 1

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

624701

APPLICATION FOR A STANDARD PATENT

I\We,

USINOR SACILOR
(a Societe Anonyme)

of 4, PLACE DE LA PYRAMIDE
LA DEFENSE 9
92800 - PUTEAUX
FRANCE

hereby apply for the grant of a standard patent for an invention entitled:

PROCESS FOR COLOURING THE SURFACE OF METALLIC MATERIALS AND PRODUCTS OBTAINED BY ITS USE.

which is described in the accompanying complete specification

Details of basic application(s):

Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
89.05430	FR	18 APR 89
89.08085	FR	15 JUN 89

My/our address for service is care of GRIFFITH HACK & CO., Patent Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria, Australia.

DATED this 12th day of April 1990

USINOR SACILOR
GRIFFITH HACK & CO.

TO: The Commissioner of Patents.

DMO:AL P12428

B

APPLICATION BY ASSIGNEE OF INVENTOR

AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

No. 53202/90

NAME OF APPLICANT

In support of an application/made by:

USINOR SACILOR (Societe Anonyme)

TITLE

for a patent for an invention entitled: Process for colouring the surface of metallic materials and products obtained by its use.

FULL NAME AND ADDRESS OF SIGNATORY

I, Roger VENTAVOLI

of 2, route d'Uckange - 57290 FAMECK (France)

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this declaration on its behalf.

FULL NAME AND ADDRESS OF INVENTOR(S)

2. The name and address of each actual inventor of the invention is as follows:

Pierre DE GELIS

4 Ter, rue Bonnemain - 78104 SAINT GERMAIN

France

SEE NOTES OVER

3. The facts upon which the applicant is entitled to make this application are as follows: IRSID would be entitled to have assigned to it a patent granted to the said inventors in respect of the said invention and the applicant is the assignee of the said IRSID.

DELETE PARAGRAPHS 3 AND 4 FOR NON CONVENTION APPLICATION

4. The basic application(s) as defined by Section 141 of the Act was (were) made as follows:

Country	France	on	April 18, 1989
in the name(s)	IRSID		
and in	France	on	June 15, 1989
in the name(s)	IRSID		

PLACE AND DATE OF SIGNING

5. The basic application(s) referred to in the preceding paragraph was (were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

Declared at Maizieres-les-METZ

this 25th day of April 1990

Signed Roger VENTAVOLI

Position Manager of Industrial Property Dpt

USINOR SACILOR
4, Place de la Pyramide
La Défense 9
92800 - PUTEAUX (France)

GRIFFITH HACK & CO

PATENT AND TRADE MARK ATTORNEYS

MELBOURNE · SYDNEY · PERTH

(12) PATENT ABRIDGMENT (11) Document No. AU-B-53202/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 624701

(54) Title
PROCESS FOR COLOURING THE SURFACE OF METALLIC MATERIALS AND PRODUCTS OBTAINED BY ITS USE

International Patent Classification(s)
(51)[5] C23C 008/36

(21) Application No. : 53202/90 (22) Application Date : 12.04.90

(30) Priority Data

(31) Number	(32) Date	(33) Country
89 05430	18.04.89	FR FRANCE
89 08085	15.06.89	FR FRANCE

(43) Publication Date : 25.10.90

(44) Publication Date of Accepted Application : 18.06.92

(71) Applicant(s)
USINOR SACILOR (A SOCIETE ANONYME)

(72) Inventor(s)
PIERRE DE GELIS

(74) Attorney or Agent
GRIFFITH HACK & CO , GPO Box 1285K, MELBOURNE VIC 3001

(56) Prior Art Documents
AU 587744 13722/88 C23C 14/34 C03C 17/06 17/36
AU 591038 13721/88 C23C 14/34 C03C 17/06 17/36
AU 598113 13093/88 C23C 14/08 H01L 39/24 C03C 17/245

(57) Claim

1. Process for colouring the surface of a solid and opaque metallic material by virtue of the establishment of light interferences by creating at the surface of the said material a film of metallic oxides of controlled thickness, characterized in that the metallic material is subjected to a surface treatment using low-temperature plasma in an atmosphere under a pressure from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

8. Metallic product coloured at the surface by virtue of the establishment of light interferences by a film of metallic oxides, characterized in that the said film is formed by exposing the material to be coloured to a low-temperature plasma in an atmosphere under a pressure from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the

.../2

elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

AUSTRALIA 624701

PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant:
USINOR SACILOR

Address of Applicant: 4, PLACE DE LA PYRAMIDE
LA DEFENSE 9
92800 - PUTEAUX
FRANCE

Actual Inventor:

Address for Service: GRIFFITH HACK & CO.,
601 St. Kilda Road,
Melbourne, Victoria 3004,
Australia.

Complete Specification for the invention entitled:
PROCESS FOR COLOURING THE SURFACE OF METALLIC MATERIALS AND PRODUCTS OBTAINED BY ITS USE.

The following statement is a full description of this invention including the best method of performing it known to me:-

GRB 876

PROCESS FOR COLOURING THE SURFACE OF METALLIC MATERIALS AND PRODUCTS OBTAINED BY ITS USE

The present invention relates to a process for colouring the surface of metallic materials by forming a film of oxides. It applies advantageously to the colouring of flat products such as sheets of steel, especially of stainless steel.

The surface colouring of metallic materials, especially sheets or plates of stainless steel, finds its chief applications in the field of building. Components which are thus coloured are employed for roofing or wall cladding of buildings. A colouring of this kind is also applied to components of internal decoration, to sets of taps, cocks and fittings, to various household articles, and the like.

It is known that this colouring can be obtained by virtue of the formation of a film of oxides on the surface of the material and to the establishment of light interference phenomena. The colour observed for a given material is a function of the thickness of the deposited film.

Traditionally employed methods of colouring stainless steels consist in creating this film of oxides by chemical reaction by immersing the material to be coloured in an oxidizing solution such as a bath containing nitrate, chromate or permanganate ions (Patent US-A-4,692,191). Electrochemical methods can also be employed to produce this surface oxidation.

However, the use of such oxidizing baths requires stringent precautions to guarantee the safety of the operators and to prevent environmental pollution. Furthermore, these baths attack the metal and do not always make it possible to preserve the initial surface quality of the material.

The objective of the invention is to propose a rapid and nonpolluting method of colouring metallic materials, especially a sheet of stainless steel, which

additionally allows the material to be coloured to preserve its initial appearance, such as a shiny or satin appearance.

The present invention provides process for colouring the surface of a solid and opaque metallic material by virtue of the establishment of light interferences by creating at the surface of the said material a film of metallic oxides of controlled thickness, characterized in that the metallic material is subjected to a surface treatment using low-temperature plasma in an atmosphere under a pressure from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

The invention also provides metallic product coloured at the surface by virtue of the establishment of light interferences by a film of metallic oxides, characterized in that the said film is formed by exposing the material to be coloured to a low-temperature plasma in an atmosphere under a pressure from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

In a preferred embodiment the plasma is produced by electroluminescent discharge between an anode and a cathode, the cathode consisting of the source material and it being possible for the anode to consist of the material to be coloured.

The atmosphere preferably consists of a 2-80% by volume mixture of oxygen and nitrogen.

the term source material refers to an article forming a bed of atoms intended to form, in oxidized form, the deposit on the material to be coloured.

As will be understood, the process consists in placing the material in an enclosure containing an oxidizing plasma. This plasma tears atoms away from the surface of the source material. These atoms combine with the oxygen of the plasma and are deposited onto the surface of the material to be coloured. As a result of light interference phenomena, the surface of this material takes up a colour which is a function of the thickness of the film of oxides thus formed and therefore of the duration of the treatment.

It is known to subject the surface of metallic materials to a surface treatment using plasma in an atmosphere consisting of a rare gas such as argon. In a

treatment of this kind the surface of the negatively polarized material is bombarded by the plasma ions, which causes the surface atoms of the material to be torn away.

In a prior patent application (FR-88/05,091, publication no 2630133) in the name of the Applicant, a method is disclosed for improving the corrosion resistance of metallic materials, in which the material to be treated is placed as a cathode in a plasma obtained by electroluminescent discharge, and therefore in an atmosphere at low pressure (below 1000 Pa). The plasma thus formed is of the type commonly referred to as "cold" or "low temperature" plasma, in contrast to the thermonuclear fusion plasmas called "hot" plasmas. Its degree of ionization is low (10^{-7} to 10^{-3}). The electrical energy is transferred to the electrons which are relatively few in number, but highly energetic (1 to 10 eV). They thus excite the gas to be heated, whose temperature can range from 20 to approximately 700°C, and produce excited species in a large number.

The inventor has found that, in the case where the atmosphere contains an oxidizing gas, even at a low concentration, a film of metallic oxides formed from metal atoms originating from the cathode is found on the anode. This film colours the surface of the material by virtue of the establishment of light interferences, a result which is similar to that obtained by the chemical and electrochemical methods usually employed for colouring metallic materials. In addition, the operation does not affect the initial surface appearance of the material, such as a shiny or satin appearance, in contrast to the previous methods, which involve a surface attack on the material.

To obtain this deposition of oxides in a controlled manner, one operating method is as follows. The metallic material, for example a plate of stainless steel, which it is desired to colour at the surface is placed in an enclosure. The latter contains a gas containing oxygen atoms and capable of being ionized by an electroluminescent discharge established between a

cathode and an anode which face each other. The anode consists of the material to be coloured itself and the cathode is in contact with the gaseous atmosphere of the process enclosure.

The cathode consists of a metal plate, made of a material such as a ferritic or austenitic stainless steel, a chromed stainless steel, titanium, aluminium or the like. As a general rule the nature of the cathode material determines the nature of the oxides which are deposited on the component to be coloured. With a ferritic stainless steel the deposit consists of iron and chromium oxides. With an austenitic stainless steel the deposit also contains nickel oxides. With a chrome steel the deposit consists essentially of chromium oxides. With pure titanium or aluminium, the deposit consists of titanium or aluminium oxides. The choice of the nature of the oxides deposited onto the component to be coloured depends on the characteristics sought after for the deposit, such as its adhesiveness or its corrosion resistance.

The atmosphere in the process enclosure is a rarified atmosphere, with a pressure of less than 1000 Pa. As already indicated, it contains at least, and even only in the form of traces, a gas exhibiting an oxidizing power and readily ionizable, and therefore chosen, for example, from oxygen, ozone, air, carbon dioxide, nitrogen oxides and water vapour. Mixtures between one or more of these gases and a neutral gas, such as argon, can also be employed. In practice, it will be possible to employ reconstituted air, that is to say a mixture containing 80 % by volume of nitrogen and 20 % by volume of oxygen. The use of natural air simplifies the problem of producing a low pressure in the enclosure.

The colour which appears at the surface of the anode material is a function of the thickness of the deposit of oxides. This thickness is of the order of a few hundred angstroms and itself depends:

- on the voltage maintained between anode and cathode to support the discharge, and which can range

from 200 to 5000 V

- on the current density in the anode, which can range from 1 to 100 mA/cm^2
- on the time during which the deposition is carried out, which can range up to 60 minutes
- on the distance between the anode and the cathode, which can range from 1 mm to several centimetres, and preferably from 1 to 50 mm.

It is easy to determine experimentally what colour is obtained for given process conditions. The uniformity of the colour depends on the surface quality of the material to be coloured, on the uniformity of its temperature and on good adjustment of parallelism between the material and the cathode. On the other hand, the colour does not depend on the chemical composition of the deposit.

The thickness of oxides increases if:

- the process time increases
- the current density at the anode increases
- the voltage at the electrodes increases
- the distance between the electrodes decreases.

By way of example, the surface of a plate of stainless steel 70 x 120 mm in size, subjected, in an atmosphere containing 80 % of nitrogen and 20 % of oxygen by volume, to a current of 300 mA intensity (that is a current density of 3.6 mA/cm^2), with a voltage of 1200 V between electrodes and a distance to the cathode of 10 mm, assumes the following colours:

- with 2 to 4 minutes' treatment: yellow to pink yellow
- with 5 to 6 minutes' treatment: red-violet
- with 7 to 12 minutes' treatment: dark blue to pale blue
- with 18 minutes' treatment: yellow
- with 22 minutes' treatment: pink
- with 27 minutes' treatment: blue-green
- with 30 minutes' treatment: green
- with 60 minutes' treatment: pink

Patterns can be drawn on the material to be coloured by virtue of masks which make it possible to modify the times of exposure to the plasma of different areas of the sample, and thereby the thickness of oxides which covers them. Shaded tones can be obtained by arranging the cathode obliquely relative to the sample, so as to vary the distance between the electrodes continuously and therefore consequently the thickness of the deposit on the anode. Furthermore, if it is desired to obtain a uniform colouring of a nonplanar article, it is necessary to employ a cathode of the same shape and arranged parallel to the article to be coloured.

The invention is obviously not limited to the example just described. Thus, the material to be coloured can be merely placed facing the cathode source material, without being itself included in the circuit for producing the electroluminescent discharge. Similarly, the low-temperature plasma required can be produced by processes other than electroluminescent discharge. Excitation of the atmosphere using microwaves or radio frequency may be mentioned, for example. However, in all cases a voltage lower than that of the material to be coloured must be applied to the source material.

The coloured article is obviously not normally intended to subsequently undergo a surface treatment which would mask the colouring obtained. This is why the invention applies chiefly to stainless steels, in the case of which such treatments are not indispensable for good preservation of the article in a commonplace surrounding atmosphere.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for colouring the surface of a solid and opaque metallic material by virtue of the establishment of light interferences by creating at the surface of the said material a film of metallic oxides of controlled thickness, characterized in that the metallic material is subjected to a surface treatment using low-temperature plasma in an atmosphere under a pressure from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

2. Process according to claim 1, characterized in that the low-temperature plasma is produced by electroluminescent discharge between an anode and a cathode, the cathode consisting of the source material.

3. Process according to claim 2, characterized in that the anode consists of the material to be coloured.

4. Process according to one of claims 1 to 3, characterized in that the said gas is chosen from oxygen, ozone, air, nitrogen oxides, water vapour and mixtures thereof with a neutral gas.

5. Process according to claim 2 or 3, characterized in that it is operated at a voltage of 200 to 5000 V.

6. Process according to any one of claims 2, 3 or 5, characterized in that an anode current density of 1 to 100 mA/cm^2 is established.

7. Process according to any one of claims 1 to 6, characterized in that a distance of 1 to 50 mm is maintained between the source material and the material to be coloured.

8. Metallic product coloured at the surface by virtue of the establishment of light interferences by a film of metallic oxides, characterized in that the said film is formed by exposing the material to be coloured to a low-temperature plasma in an atmosphere under a pressure

from 0.1 to 1000 Pa, and containing at least one oxidizing gas and in contact with a source material containing the elements whose oxides it is intended to deposit on the material to be coloured, the said source material being negatively polarized relative to the material to be coloured.

9. Metallic product according to claim 8, characterized in that it consists of a plate or a sheet.

10. Metallic product according to claim 8 or 9, characterized in that it is made of stainless steel.

DATED THIS 14th DAY OF January 1992

USINOR SACILOR S.A.
By Its Patent Attorneys

GRIFFITH HACK & CO.
Fellows Institute of Patent
Attorneys of Australia

MPS