

# PATENT SPECIFICATION

(11) 1 566 643

1 566 643

- (21) Application No. 24036/77 (22) Filed 8 June 1977  
(31) Convention Application No. 51/069116  
(32) Filed 9 June 1976  
(31) Convention Application No. 51/072657  
(32) Filed 19 June 1976 in  
(33) Japan (JP)  
(44) Complete Specification published 8 May 1980  
(51) INT CL<sup>3</sup> C23F 7/00 F24J 3/02  
(52) Index at acceptance  
C7U 4G1 4P 7A  
F4U 60



## (54) PROCESS FOR PRODUCING SOLAR COLLECTORS

(71) We, TOYO ALUMINIUM KABUSHIKI KAISHA, a Japanese Company, of No. 25-1, 4-chome, Minamikyutarmachi, Higashi-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a process for manufacturing solar collectors of aluminium or its alloys, and, more particularly, to a process in which aluminium or its alloy as substrate is dipped in a hot aqueous solution containing a silicate to form on the substrate a black coating with an excellent spectral selectivity.

In recent years, many studies have been made on solar collectors. Among them are copper sheets with copper oxide coating, copper or steel sheets with nickel-black or chromium-black thereon, and so on.

Aluminium is considered to be a very suitable material as a substrate for solar collectors because of its high thermal conductivity and low cost. However, no commercially acceptable aluminium solar collector with a good selective surface layer has been produced. Insofar as we are aware of, only a few methods have been proposed to give a spectral selectivity to the surface of aluminium or its alloy. The following two processes, for example, have been proposed:

(1) A process comprising the steps of anodizing aluminium to form a porous oxide film on its surface and then treating in an electrolyte containing metallic salts to deposit metals or metallic oxides in the pores in the oxide film. (Japanese Patent Laying-Open No. SHO 51-3333.)

(2) A process comprising the steps of subjecting aluminium to metallic cementation with copper and thickening and brightening treatments of the copper

layer through a conventional electroplating, and then dipping it in an alkaline solution containing a suitable oxidizing agent to form a selective coating on the plated surface. (Japanese Patent Laying-Open No. SHO 50-141531.)

However, these prior processes have the following short-comings: In the former process, the porous oxide film has to be at least 15 microns thick to form a selective surface by the deposition of metals or metallic oxides in the pores. The resultant selective surface shows a poor spectral selectivity because strong and broad absorption bands due to aluminium oxide appear in the infrared region, causing a large heat loss. The latter process involves two steps, that is, the formation of copper layer on the substrate and that of a selective absorption coating on the copper layer. Further, these steps produce waste liquid which has to be disposed of. This complicates the process and increases the manufacturing cost.

The present invention provides a simplified process for manufacturing solar collectors of aluminium or its alloys having an excellent spectral selectivity.

The present invention provides a process for the manufacture of a solar collector which comprises subjecting the cleaned surface of an article formed of aluminium or of an aluminium alloy containing at least one of the elements iron, copper, titanium, nickel, silver and gold to the action of a hot, aqueous alkaline solution containing 5—100 mg/l (in term of SiO<sub>2</sub>) of a water-soluble silicate and at least one kind of ions selected from zinc, magnesium, calcium, strontium or beryllium.

The aluminium used in the process according to this invention has a purity of preferably 97% or higher, more preferably, 99.0% or higher. The aluminium or aluminium alloy used may be in the form of a sheet, foil or any other configuration.

The silicates used in the process

50

55

60

65

70

75

80

85

90

according to the present invention are water soluble and are preferably selected from sodium orthosilicate ( $\text{Na}_4\text{SiO}_4$ ), sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ), potassium metasilicate ( $\text{K}_2\text{SiO}_3$ ), potassium tetrasilicate ( $\text{K}_2\text{Si}_4\text{O}_9 \cdot \text{H}_2\text{O}$ ) and water glass.

The concentration of the water-soluble silicate is from 5 to 100 mg (in terms of  $\text{SiO}_2$ ) per liter of water. A concentration of silicate below the lower limit would only give uncolored coatings on the substrate. On the contrary, a concentration of silicate greater than the upper limit will cause corrosive attack on the substrate and produce thereon a rugged surface with a poor spectral selectivity.

The pH of the silicate solution should preferably be 7.5—11.0 (more preferably 8.0—10.5). The temperature thereof is preferably 80°C or higher. At a temperature below 80°C, a good selective coating would not be formed even if the substrate is dipped in the solution for a long time.

It was further found that the presence of ions of zinc, magnesium, calcium, strontium or beryllium to the silicate solution promotes the blackening of the substrate surface, thus improving its spectral selectivity. Even if a deep black coating cannot be obtained in a solution containing silicate alone, the addition of one or more of such metallic ions brings satisfactory results without the necessity of changing the other treating conditions.

The concentration of these metallic ions should be preferably in the following ranges:

Zinc	3—30 mg/l
Magnesium	5—35 mg/l
Calcium	1—20 mg/l

Strontium	1—20 mg/l
Beryllium	1—20 mg/l

40

Deionized or distilled water is preferably used to prepare the silicate solution to minimize ill effect of other ions on the spectral selectivity of the coating formed. The specific resistance of the deionized and distilled water is preferably 1 MΩ or higher for the former and 0.1 MΩ or higher for the latter. However, the water used in the present invention is not limited to deionized or distilled water. It has been found that a brown or black coating with a good spectral selectivity can be formed by the use of water containing small amounts of iron, potassium and/or chromium ions. The maximum permissible concentrations are 1.0, 8.0 and 1.0 mg/l for iron, potassium and chromium ions, respectively.

45

50

55

Further, we have studied which aluminium alloys are suitable as the substrate used in the process according to the present invention. Twenty one aluminium alloys were prepared by adding 0.5 per cent by weight of each of the following alloying elements to 99.99 per cent pure aluminium. The alloying elements used were beryllium, boron, magnesium, silicon, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, silver, cadmium, tin, antimony, tantalum and gold.

60

65

70

These aluminium alloys and 99.99 per cent pure aluminium in the form of sheet were degreased and dipped for 30 minutes in a hot alkaline aqueous solution containing 25.0 mg/l (in terms of  $\text{SiO}_2$ ) of sodium orthosilicate. The change in color of the sheets was as shown in Table 1.

75

TABLE 1

80	Color of coating	Test sheets
	No change in color	99.99% pure aluminium Al-Mg, Al-Zn, Al-Cd, Al-Sn alloys
	Ashy brown	Al-Be, Al-Si, Al-Cr, Al-Mn, Al-Zr, Al-Mo, Al-Sb alloys
85	Dark brown	Al-B, Al-V, Al-Co, Al-Ta alloys
	Black	Al-Ti, Al-Fe, Al-Ni, Al-Cu, Al-Ag, Al-Au alloys

The experiment has revealed that aluminium alloys containing a small amount of Fe, Ni, Ti, Cu, Ag or Au are suitable as a substrate for the formation of black coating.

We, have also found that aluminium alloys containing one or more of these alloying elements can have a coating with excellent spectral selectivity if the amount thereof is within the following ranges:

Fe: 0.05—2.0% by weight
Cu: 0.05—4.0%
Ti: 0.05—1.0%
Ni: 0.03—1.0%
Ag: 0.05—1.0%
Au: 0.05—0.5%

100

For smaller amounts than the lower limits, the coating formed on any of the

alloys is pale brown and show a poor spectral selectivity. For larger amounts than the upper limits, the black coating formed is dirty and has a poor spectral selectivity because uncolored intermetallic compounds and corrosion pits remain.

The process according to the present invention has the following advantages:

- (1) It provides a selective absorption surface which can convert solar energy into thermal energy with high efficiency.
- (2) Its simplicity makes it practical at a reasonable cost.
- (3) Absence of harmful heavy metallic salts excludes any water pollution problem.

The present invention will be understood more readily by reference to the following experiments and examples. Unless otherwise stated, amounts are given in per cent by weight and the amount of silicate is given in terms of  $\text{SiO}_2$ .

#### Experiment 1

Using deionized water (of specific resistance greater than  $1 \text{ M}\Omega \text{ cm}$ ), aqueous solutions containing sodium orthosilicate in the amounts shown in Table 2 were prepared. These solutions were then adjusted to pH 9.5 (at  $30^\circ\text{C}$ ) by the addition of a few drops of dilute ammonia water or dilute sulfuric acid solution.

Aluminium sheets (AA-1100) about 0.5 mm thick were first immersed in a 10% caustic soda solution at  $60^\circ\text{C}$  for 1 minute so as to remove rolling oil and thin oxide film from the surface without spoiling its original surface brightness. A sheet was immersed in each of the silicate solutions at  $95^\circ\text{C}$  for 10 minutes. This treatment formed colored coatings on the sheets as set out in Table 2. The coatings exhibited spectral selectivity, the extent of which depended upon the column produced.

TABLE 2

Amount of sodium orthosilicate (in mg/l)	Extent of coloring
0	No change
5	Light brown
10	Brown
20	Dark Brown
30	Black
40	"
60	"
80	Dark brown
100	Ashy brown

#### Experiment 2

Aqueous solutions containing 3, 7 and 14 mg/l of potassium metasilicate, respectively, were prepared with deionized water and their

pH were adjusted in the same way as described in Experiment 1. Aluminium alloy sheets (AA-3003) degassed in the same way as described in Experiment 1 were dipped in each of these silicate solutions at  $80^\circ\text{C}$  for 10 minutes. Coatings having the colors reported in Table 3 were formed on their surface. The coatings exhibited spectral selectivity, the extent of which depended upon the colour produced.

TABLE 3

Amount of potassium metasilicate (in mg/l)	Extent of coloring
0	No change
3	Light brown
7	Black
14	"

#### Example 1

A solution containing 16.3 mg/l of sodium orthosilicate and 20.0 mg/l (in terms of Mg ion) of magnesium sulfate was prepared and adjusted to pH 9.5 in the same manner as described in Experiment 1, and then heated to boiling. A degreased aluminium sheet (AA-1100) was immersed in the solution for 10 minutes. A black coating was formed thereon and it showed good spectral selectivity.

#### Example 2

A solution containing 16.3 mg/l of sodium orthosilicate and 10.0 mg/l (in terms of Zn ion) of zinc sulfate was prepared and adjusted to pH 10.0 in the same manner as described in Experiment 1, and then heated to boiling. A degreased aluminium sheet (AA-1100) was dipped in the solution for 10 minutes. A black coating was formed thereon and it showed good spectral selectivity.

#### Example 3

A solution containing 16.3 mg/l of sodium orthosilicate, 10.0 mg/l (in terms of Mg ion) of magnesium sulfate and 5.0 mg/l (in terms of Zn ion) of zinc sulfate was prepared and adjusted to pH 9.5 in the same manner as described in Experiment 1 and then heated to boiling. A degreased aluminium sheet (AA-1100) was dipped therein for 10 minutes and a black coating was formed. It showed good spectral selectivity.

#### Example 4

A solution was prepared by adding 4.3 mg/l of sodium orthosilicate, 5.0 mg/l (in terms of Ca ion) of calcium sulfate and 10.0 mg/l (in terms of Be ion) of beryllium sulfate to city water containing 12 mg/l of  $\text{SiO}_2$ , 0.08 mg/l of Fe ion and 5.4 mg/l of K ion. It was

adjusted to pH 10.5 by adding a dilute sodium hydroxide solution and then heated to boiling. A degreased aluminium sheet (AA-1100) was immersed therein for 10 minutes. The black coating formed thereon was similar to those formed in solutions prepared with deionized water and showed good spectral selectivity.

#### Example 5

Using deionized water, a solution containing 6 mg/l of sodium orthosilicate and 12 mg/l (in terms of Zn ion) of zinc sulfate was prepared and adjusted to pH 9.5 by adding dilute ammonia solution. An aluminium sheet (AA-1100) was degreased by dipping in 1% caustic soda solution at 60°C for 1 minute, and then treated for 10 minutes in the silicate solution at 92—95°C. A black coating formed thereon and showed excellent spectral selectivity.

#### WHAT WE CLAIM IS:—

1. A process for the manufacture of a solar collector which comprises subjecting the cleaned surface of an article formed of aluminium or of an aluminium alloy containing at least one of the elements iron, copper, titanium, nickel, silver and gold to the action of a hot, aqueous alkaline solution containing 5—100 mg/l (in term of SiO<sub>2</sub>) of a water-soluble silicate and at least one kind of ions selected from zinc, magnesium, calcium, strontium or beryllium.

2. A process as claimed in claim 1 in which the pH of said silicate solution is 8.0 to 10.5.

3. A process as claimed in claim 1 or claim 2 in which said article is sodium

orthosilicate, sodium metasilicate, potassium metasilicate, potassium tetrasilicate or waterglass.

4. A process according to any of the preceding claims in which the concentration of zinc, magnesium, calcium, strontium or beryllium ions are respectively 3—30 mg/l, 5—35 mg/l, 1—20 mg/l, 1—20 mg/l and 1—20 mg/l.

5. A process according to any of the preceding claims in which said silicate solution is made up with deionized or distilled water.

6. A process according to any of the preceding claims in which the maximum permissible concentrations of iron, potassium and/or chromium ions in the water used for preparing said aqueous alkaline solution are 1.0 mg/l or less, 8.0 mg/l or less and 1.0 mg/l or less, respectively.

7. A process according to any of the preceding claims in which an aluminium alloy is used and the amount of alloying element is 0.05—2.00% by weight of iron, 0.05—4.0% by weight of copper, 0.05—1.0% by weight of titanium, 0.03—1.0% by weight of nickel, 0.5—1.0% by weight of silver or 0.05—0.5% by weight of gold.

8. A process for the manufacture of a solar collector according to claim 1 and substantially as hereinbefore described with reference to any of the Examples.

9. Solar collectors whenever produced by the process of any of the preceding claims.

BARON & WARREN,  
16, Kensington Square,  
London, W8 5HL  
Chartered Patent Agents.