

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be better understood from the following descriptions of preferred embodiments, but should not be limited thereto.

#### EXAMPLE 1

A steel sheet (0.6×100×100 mm) was coated with a primer coat of epoxy resin in 5 μ thickness and a top coat of polyester in 20 μ thickness and baked, and its surface was fluorinated by using a gas plasma of carbon tetrafluoride under the conditions:

Gas flow rate	50 cm <sup>3</sup> (STP)/min.
Gas pressure	0.5 Torr
Discharge power	40 W
Discharge time	5 minutes

The paint film qualities of the resultant paint coated steel sheets as fluorinated were determined by the pencil hardness test (JIS K-5400, 6.14 for breaking and scratching), the 180° bending test and the stain test. As obvious from Table 1, the result shows that the hardness of the paint film is remarkably improved with no deterioration of workability by the surface fluorination with the use of the plasma treatment.

and the stain test. As shown in Table 1, the results of the tests reveal that the hardness and the resistance to stain are remarkably improved without sacrifice of the workability.

#### EXAMPLE 3

A primer coat of epoxy-type alkyd resin paint in 5 μ was applied on the surface of a zinc-nickel alloy galvanized steel sheet (0.8 mm in thickness, 100 mm in width and 100 mm in length; alloy coat of 20 g/m<sup>2</sup>) and baked, a top coat of urethan-type resin paint was applied in 20 μ thereon and baked again, and the surface of this colored galvanized steel sheet was fluorinated by using a gas plasma of 6% fluorine—94% helium under the following conditions:

Gas flow rate	40 cm <sup>3</sup> (STP)/min.
Gas pressure	0.5 Torr
Discharge power	50 W
Discharge time	1 minute

The paint film qualities of the resultant colored zinc-nickel alloy plated steel sheet were determined by the pencil hardness test (JIS K-5400, 6.14), the 180° bending test and the stain test.

As shown in Table 1, the results show that the hardness and the resistance to stain are remarkably improved without lowering the workability.

TABLE 1

Evaluation of Paint Film Qualities						
Gas	Pencil Hardness Test* <sup>1</sup>		Workability		Strain Resistance* <sup>2</sup>	
	Before Treatment	After Treatment	Before Treatment (20° C.)	After Treatment (20° C.)	Before Treatment	After Treatment
Example 1 CF <sub>4</sub>	2H/F	4H/2H	0T	0T	Δ/○	◎/◎
Example 2 C <sub>2</sub> F <sub>6</sub>	H/HB	3H/H	0T	0T	X/X	◎/◎
Example 3 6% Fe—94% He	3H/H	6H/3H	1T	1T	Δ/○	◎/◎

\*<sup>1</sup>The breaking in the pencil hardness test was done in accordance with JIS K-5400, 6.14

\*<sup>2</sup>Determined by marking with magic ink (red and black) and wiping off with ethanol after 24 hours.

#### EXAMPLE 2

A pre-coated steel sheet (0.6 mm in thickness, 100 mm in width 100 mm in length) was prepared by applying a primer coat of polyester in 5 μ thickness and a top coat of polyester in 20 μ thickness onto a galvanized steel sheet (20 g/m<sup>2</sup> of zinc coat) and baking the paint film. The surface of this pre-coated steel sheet was fluorinated by using a gas plasma of ethane hexafluoride under the following conditions:

Gas flow rate	3-10 cm <sup>3</sup> (STP)/min.
Gas pressure	0.035 Torr
Discharge power	300 W
Discharge time	5 seconds

The paint film qualities of the resultant paint coated galvanized steel sheet were determined by the pencil hardness test (JIS K-5400, 6.14), the 180° bending test

What is claimed is:

1. A paint coated metal sheet comprising a metal substrate and a paint film applied thereon, the uppermost surface part of said paint film containing fluorine atoms introduced thereto as perfluoroalkyl groups including methyl fluoride and ethyl fluoride said perfluoroalkyl groups being introduced into said surface up to a depth of 1-5000 Å by a plasma treatment, with the remaining part of said paint film being non-fluorinated by said plasma treatment.

2. A paint coated metal sheet according to claim 1, wherein said plasma treatment employs a gas plasma such as carbon tetrafluoride, ethane hexafluoride, perfluoropropane and a mixture of fluorine and helium.

3. A paint coated metal sheet according to claim 1, in which the metal substrate is a zinc plated steel sheet or a zinc alloy plated steel sheet.

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