

PAINT COATED METAL SHEETS

This is a continuation of application No. 07/141,955, filed Jan. 11, 1988, which was abandoned, which in turn is a continuation of Ser. No. 07/120,776, filed 11/16/87, which in turn is a continuation of Ser. No. 06/856,160 filed 4/25/86, all abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to paint coated metal sheets comprising applying a paint film on a metal sheet, said paint film having a surface layer with a thickness of 1-5000 Å containing fluorine atoms as a perfluoroalkyl group such as methyl fluoride, ethyl fluoride and so on introduced therein by a plasma treatment.

2. Description of the Related Art

Up to now, paint coated metal sheets have been widely used in various applications including buildings, automobiles, electric appliances and so on, and the main qualities required in these fields of application are to maintain a beautiful surface appearance and to assure good corrosion resistance.

As most of the paint coated metal sheets are subjected to mechanical working after the paint coating, the primary requirements of the paint film on the metal sheet are good adhesion, and good workability, particularly press formability, and the secondary requirements are good corrosion resistance, permanent color and brightness, stain resistance, and so on depending on the final applications of the products. In addition to the above requirements, it is also essential for the paint coated metal sheets that the paint film on the substrate will not be damaged during the mechanical working, especially press forming.

Once damaged, the paint film can no more function as barrier against corrosion, and the corrosion is caused and expands from where the substrate is exposed due to the damage of the paint film, thus markedly shortening the service life of the buildings, automobiles, electric appliances and so on, in which the paint coated metal sheets are used.

Of the paint coated metal sheets, the so-called "pre-coated thin metal sheet" in particular, which is nowadays used in roofings, automobiles and electric appliances, is subjected to severe working, especially press forming, and must show a relatively good elongation property of the paint film on the metal sheet. However, paint films which satisfy the required elongation property are generally soft so that they are easily damaged and poor in the strain resistance. This incompatibility has long been a problem.

In recent years, as proposed in "Practical Surface Technics" (Jitsumu Hyomen Gijutsu), Vol 30, page 358, 1983, studies have been made on production of paint coated steel sheets having excellent paint film properties by application of the so-called "three-coat system by roll-coating" according to which an undercoating for improving the adhesion with the metal substrate, an intermediate coating for improving the workability and a top coating for assuring the surface hardness are applied on the metal substrate. This three-coat system, however, has a problem that it is technically difficult to maintain the top coat layer to a thickness less than 3 microns so that the hardness of the top coat layer deteriorates the good workability of the intermediate paint coat layer, hence it is very difficult to satisfactorily

balance the incompatibility between the surface hardness and the workability which are originally sought for. This is a vital defect of the roll coating method.

Also, Japanese Laid-Open Patent Application No. Sho 59-169851 discloses "a pre-coated steel sheet pre-coated with polyvinyl chloride dispersion paint", according to which an ultraviolet ray curing type clear paint is applied on the polyvinyl chloride dispersion paint applied on the steel substrate and is cured by ultraviolet rays in order to prevent damages of the paint film during the forming of the pre-coat sheet. According to this prior art, the thickness of the ultraviolet ray curing type clear paint is as thick as 200 μ and this method has been limitedly applied to the polyvinyl chloride dispersion paint pre-coated steel sheets.

Further, it is known to fluorinate the surface of polymers by a plasma treatment. For example, according to the report by M. Anand et al. (Polymer, 361, Vol. 22, 1981), the surface of low-density polyethylene is fluorinated by using a mixture gas of carbon tetrafluoride, or fluorine and helium. The fluorination of the surface of polymer in this case is only for the purpose of rendering the polymer surface hydrophobic by introducing fluorine atoms into the surface layer of polyethylene. Therefore, this prior art is completely different from the present invention with respect to the technical object as described hereinbelow.

Also, it is known in the field of optical lenses and filters to apply a fluorine coating for the purpose of reducing the refractive power or preventing the reflection, and in the field of blood backs it is known to apply the same for the purpose of preventing the dissolution of plasticizers from the back material of polyvinyl chloride resin.

SUMMARY OF THE INVENTION

Therefore, the present invention is to provide paint coated metal sheets, which are remarkably improved in the hardness of paint film, or in the susceptibility to damages, while maintaining excellent workability, adhesion and corrosion resistance which are inherently possessed of by the paint film by fluorinating the surface layer of the paint films such as acryl and polyester paint films applied on metal substrates.

The conventionally known fluorination of the surface of resin articles is completely different from the fluorination of the surface of paint coated metal sheets with respect to the object and results of the plasma treatment despite the similarity in the chemical reaction on the surface of organic substances. For example, in the case of pre-coated steel sheets, in order to satisfy the requirement of workability, soft and expandable resins are normally used for the paint coating, but this type of resins are easily damaged and has a very poor stain resistance.

The inventiveness of the present invention is based on the discovery that when the pre-coated metal sheets having the above defects are subjected to the surface fluorination by a plasma treatment, they are converted into new pre-coated metal sheets which are highly resistive against the damages and stain and yet enjoy the inherent high workability.

The above technical advantages obtained by the surface fluorination by a plasma treatment can be remarkable and significant only when the surface fluorination is applied to the pre-coated metal sheets, particularly, steel sheets coated with paint. This is completely differ-