# United States Patent [19]

**Matsudaira et al.**

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[54] **PRECOATED METAL SHEETS AND MANUFACTURE THEREOF**


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[51] **Int. Cl.** ..... **B32b 15/04**

[58] **Field of Search** ..... 161/213, 214, 216; 117/6, 117/75



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[57] **ABSTRACT**

A precoated metal sheet for producing a metal working product which comprises a base metal sheet, a coating film of a thermosetting resin which is formed on the base metal sheet and cured to semi-hardened state having a tackiness of from 2.0 to 40 g/cm width at a temperature of 25° C and at a relative humidity of 75% and a polyolefin sheet adhered to the above semi-hardened coating film; and a method for manufacturing the precoated metal sheet.


**2 Claims, 2 Drawing Figures**

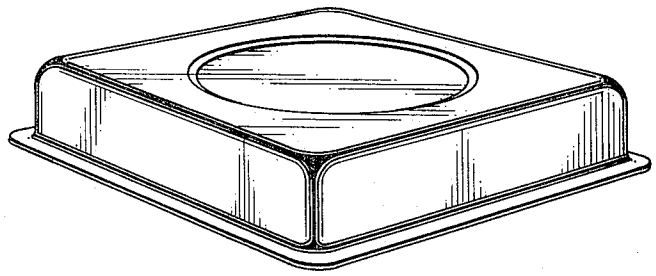
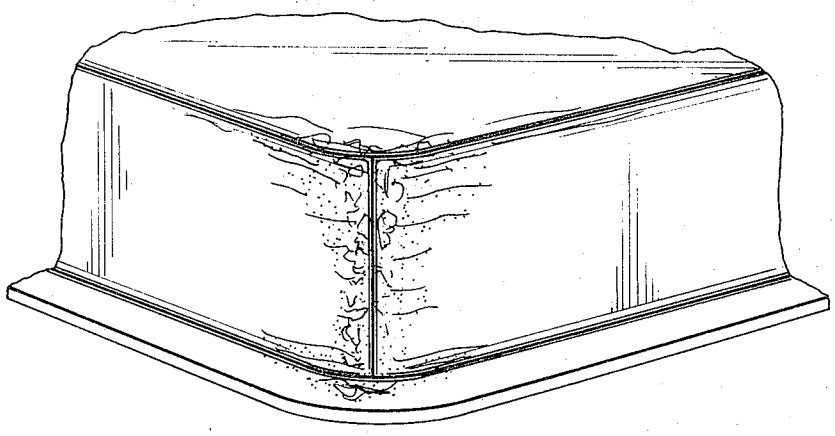


FIG 1

FIG 2



# PRECOATED METAL SHEETS AND MANUFACTURE THEREOF

This invention relates to a precoated metal sheet and manufacture thereof, more particularly to a precoated metal sheet for producing shaped articles by metal working with a coating film formed thereon.

It has long been practiced to shape an uncoated metal sheet in a suitable form and then apply a coating composition to the resulting shaped product. Because of the necessity to coat the shaped metal working products individually, this method is unfit for mass production, fails to give products of a uniform quality and renders the resulting products costly. On the other hand, so-called "precoating process" has been developed in which a coating composition is previously applied to a metal sheet material with or without conducting pretreatment or conversion coating, and the metal sheet material thus precoated is then shaped after hardening the coating film. In recent years, great interest has been aroused in this process because of the advantages of improved efficiency in metal working, high amenability to mass production, reduction in production cost, uniform quality of the products, etc. However, when the precoated metal sheet is shaped according to this process, cracking or peeling is liable to take place in the coating film, so that great difficulties are encountered in shaping.

An object of the invention is to provide a precoated metal sheet from which shaped metal working products can easily be obtained free from cracking or peeling of the coating film.

Another object of the invention is to provide a precoated metal sheet for producing the shaped metal working products having hard coatings which are excellent in physical and chemical properties such as hardness, abrasion resistance, scratch resistance, strain resistance, chemical resistance, etc.

Another object of the invention is to provide a precoated metal sheet for producing shaped metal working products, which is free from blocking phenomenon even when placed in layers or rolled up.

Another object of the invention is to provide a method for producing a precoated metal sheet having the above excellent characteristics.

These and other objects and advantages of the invention will be apparent from the following description.

The precoated metal sheet of the invention comprises a base metal sheet, a coating film of a thermosetting resin which is formed on the base metal sheet and cured to semi-hardened state having a tackiness of from 2.0 to 40 g/cm width at a temperature of 25°C and at a relative humidity of 75%, and a polyolefin sheet adhered to the above semi-hardened coating film.

Throughout the specification and claims tackiness is determined by the following method:

A combination of a balance and constant speed peeling device is used as a tester. A precoated metal sheet having semi-hardened state coating film is adhered to protective polyolefin sheet and pressed at a pressure of 0.2 kg/cm$^2$ with a rubber roll having a hardness of 70 determined according to JIS K 6301 5.1 (1). The precoated metal sheet with a protective polyolefin sheet adhered thereto is left to stand at room temperature for 24 hours and cut into a piece 25 mm wide by about 20 cm long. The protective sheet is peeled off about 1 to 2 cm long from the upper end of the specimen, which



is attached vertically to the end of the balance. The peeled upper end of the film is clamped with a clip, and the film is then peeled vertically at 180° at a rate of 75 mm/min. The peeling load reading on the balance provides a tackiness value. The measurement was conducted at a temperature of 25°C at a relative humidity of 75%. The greater the value, the more difficult it is to peel the film off.

The base metal sheets to be used according to this invention are a wide variety of metal sheets which have heretofore been used, such as mild steel sheet, aluminum sheet, chromium-plated steel sheet, zinc-plated steel sheet, etc. Employable as the compositions for forming the semi-hardened coating film are those containing as a binder a thermosetting resin, such as for example, (1) thermosetting acrylic resin containing hydroxyl group in the molecule and having an acid value of 5 to 20 and hydroxyl value of 10 to 70, 100 parts by weight of this resin being used with 20 to 60 parts by weight of melamineformaldehyde resin and/or not more than 20 parts by weight of bisphenol A-epichlorohydrine type epoxy resin having an epoxy equivalent of 300 to 800; (2) alkyd-melamine resin comprising 100 parts by weight of alkyd resin modified with non-drying oil and/or non-drying oil fatty acid and having an oil length of 10 to 30 and 20 to 60 parts by weight of melamineformaldehyde resin; (3) bisphenol A-epichlorohydrine type epoxy resin having an epoxy equivalent of 800 to 4,000, 100 parts by weight of this resin being used with 20 to 60 parts by weight of butyl-etherified phenol-formaldehyde resin or with 20 to 60 parts by weight of butyl-etherified urea-formaldehyde resin; and (4) oil free polyester-melamine resin comprising 100 parts by weight of oil free polyester having an acid value of 5 to 20 and hydroxyl equivalent of 400 to 1,300 and 20 to 60 parts by weight of melamine-formaldehyde resin modified with an aliphatic monoalcohol having from 1 to 4 carbon atoms. Such coating composition usually comprises 100 parts by weight of the thermosetting resin binder, not more than 120 parts by weight of extender pigment, not more than 100 parts by weight of coloring pigment and, if desired, not more than 20 parts by weight of plasticizer. Solvents are added to the composition in such an amount that the resultant composition have a viscosity of 30 to 200 sec., preferably 100 to 120 sec. (at 25°C, Ford cup No. 4). The solvents to be used may be any of a wide variety of those usually employable as solvent. Particularly preferable are mixed solvents comprising aromatic hydrocarbons and cyclohexanone, ethyleneglycol monobutyl ether, butanol, β-ethoxy-ethyl acetate, or like polar solvent added thereto. The plasticizers to be used are volatile plasticizers such as dimethylphthalate, diethylphthalate, triethyleneglycol monoethyl ether, diethyleneglycol monobutyl ether, etc. Solvents having a boiling point of more than 200°C also serve as plasticizer.

In coating a metal sheet material with a coating composition according to this invention, the metal sheet material is usually subjected to degreasing or acid pickling for pretreatment, which, however, need not be conducted depending on the surface condition of the metal sheet material. Furthermore, the material is usually provided with conversion coating, which may be omitted in some cases. The metal sheet which has been subjected to pretreatment or conversion coating as desired is then coated by conventional means, for exam-

ple by using roll coater or curtain flow coater. The coating composition to form a semi-hardened top coat film is applied to a thickness of about 5 to 50 microns when dried. The baking conditions, which may vary depending on the kind of the coating compositions used, are usually a temperature of 70° to 190°C and a baking time of about 30 to 90 seconds so as to produce a semi-hardened coating film having a thickness of 2.0 to 40 g/cm width, preferably 5 to 20 g/cm width. A polyolefin sheet is then applied over the coating film which has been semi-hardened by baking. If the tackiness of the coating film is less than 2.0 g/cm width, the polyolefin sheet is liable to peel off from the coating film. On the other hand, if it is more than 40 g/cm width, the polyolefin sheet will be torn when peeled off from the shaped metal product obtained by shaping the present metal sheet. The polyolefin sheets to be used for this purpose are, for example, those of polyethylene, polypropylene and the like. Preferably, the sheet is usually about 0.02 to 0.2 mm in thickness. The polyolefin sheet can be applied to achieve the desired results by placing the sheet over the semi-hardened coating film. Since the coating film is in the specific semi-hardened state, the polyolefin sheet can be adhered to the semihardened coating film without using any adhesive or tackifying agent, to such extent that it will not be peeled off while transported or shaped. After shaping of the precoated material, the polyolefin sheet can be peeled off satisfactorily without damaging the coating film. Thus we have found a novel fact that the semi-hardened coating film permits a polyolefin sheet to be adhered thereto without using any adhesive or tackifying agent and that the sheet can be peeled off ideally without damaging the coating film.

The precoated metal sheet of this invention can be shaped by any desired working process. The polyolefin sheet is then peeled off the semi-hardened coating film, and the coating film is thereafter baked for complete hardening. The coating film on the precoated metal sheet of this invention, being in semi-hardened state, is free from cracking or peeling even when the metal sheet is shaped. In addition, the polyolefin film on the semi-hardened coating film protects the coating film from damage during shaping. The product of this invention has another advantage of being free, for example, from damage when it is transported after shaping and before the semi-hardened coating film is completely baked for finishing, since the plastic film protects the semi-hardened coating film. The metal working product thus obtained has a coating which is excellent in hardness, abrasion resistance, stain resistance, and chemical resistance and is free from any cracking or peeling as well as from all the drawbacks of the conventional precoating process, assuring full utilization of its advantages.

In the present invention various modifications can be conducted without departing from the spirit and scope thereof. For example, primer can be applied to the metal sheet prior to the application of the composition for forming semi-hardened coating film in order to improve adhesion property and corrosion resistance. The primer may be a wide variety of those conventionally used. For example, coating compositions of the epoxy resin or vinyl resin type are chiefly used. The composition of the epoxy resin type, for instance, comprises 60 to 100 parts by weight of epoxy resin, not more than 40 parts by weight of melamine, urea or phenolic resin, not more than 50 parts by weight of extender pigment, not more than 50 parts by weight of rust-proofing pigment and a suitable amount of solvent. The coating composition of the vinyl type comprises 60 to 100 parts by weight of vinyl chloride-vinyl acetate copolymer resin, not more than 40 parts by weight of epoxy resin, not more than 40 parts by weight of phenolic resin, not more than 50 parts by weight of extender pigment, not more than 50 parts by weight of rust-proofing pigment, and a suitable amount of solvent. The primer is applied to such a thickness as to form an approximately 0.5 to 10 micron thick coating when dried and the coating is baked at a temperature of 150° to 250°C for 20 to 60 seconds, whereby it is completely baked and hardened. If baking for hardening is insufficient, the coating will have poor adhesion to the metal sheet, hence the need for complete baking and hardening.

For a better understanding of the invention examples are given below, in which the parts and percentages are all by weight. The photographs referred to in examples are as follows:

FIG. 1 is a photograph showing the surface of can obtained in Example 1; and

FIG. 2 is a photograph showing the surface of can obtained in Comparison Example 1.

## EXAMPLE 1

An aluminum sheet of 0.5 mm in thickness was degreased and its surface was subjected to conversion coating with "Bonderite 722" (Trade mark, product of Nippon Parkerizing Co., Ltd., Japan). "Bonderite 722" is mixture comprising phosphoric acid, chromic acid and sodium fluoride as principal ingredients. The sheet was then coated by a roll coater with an epoxy type coating composition given in Table 1 below as a primer and then with a thermosetting acrylic coating composition given in Table 1 below for a top coat, respectively followed by baking. The primer was fully hardened by baking, whereas the top coat was baked to semi-hardened state of a tackiness of 20 g/cm width. A 17 micron thick polyethylene film was then applied over the resulting coating, and the product was shaped into a square can by stamping. The polyethylene sheet was thereafter peeled off, with the result that the coating surface was found to be free from any cracking and peeling. The shaped article obtained was baked at a temperature of 200°C for 10 minutes to effect complete hardening. The surface of the resulting product, as the photograph of FIG. 1 shows, is free from any cracking or peeling. Further the coating obtained had the properties listed in Table 2.

## COMPARISON EXAMPLE 1

The same aluminum sheet was coated with exactly the same primer and top coat forming composition and baked in the same manner as in Example 1, except that the top coat was also completely baked and hardened. The resulting product was then shaped into a square can by stamping, with the result that, as shown in the photograph of FIG. 2, marked cracking and apparent peeling were observed. The properties of its coating are set forth in Table 2 below.

## COMPARISON EXAMPLE 2

A shaped article was prepared by conducting the same treatment as in Example 1 and using the same primer as in Example 1, except that a coating composi-

tion presently used for precoated metal was applied to form a top coat, the coating composition comprising 160 parts of a 50% xylol solution of acrylic copolymer(copolymer of styrene, n-butyl acrylate, hydroxyethyl methacrylate and acrylic acid in a weight ratio of 30 : 70 : 15 : 2), 40 parts of "U-van 20 SA" (Trade mark, butylated melamine resin, product of Mitsui Toatsu Co., Ltd., Japan), 80 parts of titanium oxide, 35 parts of "Solvesso 100" (Trade mark, mixed solvent of the aromatic hydrocarbons, product of ESSO Standard Oil Co., U.S.A.), and 30 parts of β-ethoxy-ethyl acetate. The coating obtained had the properties shown in Table 2 below.

## EXAMPLE 2

A zinc-plated iron sheet, 0.3 mm in thickness, was degreased, with its surface thereafter subjected to conversion coating with "Bonderite 3300" (Trade mark, product of Nippon Parkerizing Co., Ltd., Japan). "Bonderite 3300" is principally zinc phosphate. The sheet was coated by a curtain flow coater with a vinyl type coating composition given in Table 1 below as a primer and with a thermosetting aminoalkyd type coating composition given in Table 1 below as a top coat forming composition, followed by the same treatments as in Example 1, except that the polyolefin film adhered was a 20 micron thick polypropylene film. The semi-hardened top coat had a tackiness of 16 g/cm width. The resulting coating had the properties listed in Table 2 below.

## EXAMPLE 3

"Can-Super" (Trade mark, 0.24 mm in thickness, chromium-plated steel sheet, product of Shin Nihon Seitetsu Co. Ltd., Japan) was coated with an acrylic coating composition by a roll coater and set to semi-hardened state having a tackiness of 28 g/cm width in the same manner as in Example 1. The sheet thus treated was then shaped in to a cylindrical cup by a press. The film adhered was a polyethylene sheet, 17 microns in thickness. The composition of the coating material is shown in Table 1 below, and coating conditions and properties of the coating as determined by testing are given in Table 2 below.

The coating had very excellent properties as in Example 1.

Table 1

| | | Example 1 | | Example 2 | | Example 3 | |
|---|---|---|---|---|---|---|---|
| 1. Primer | | | | | | | |
| | Resin | "Epikote 1007" (Epoxy resin, product of Shell Chemical Co., U.S.A.) | 80 parts | "Vinylite VMCH" (Vinyl resin, product of Union Carbide Corp., U.S.A.) | 90 parts | | |
| | | "Beckamine P-354" (Butylated urea resin, product of Dainihon Ink Chemical Co., Ltd., Japan) | 40 parts | "Epikote 828" (Epoxy resin, product of Shell Chemical Co., U.S.A.) | 10 parts | | |
| | Pigment | Zinc chromate | 20 parts | Titanium dioxide | 40 parts | | |
| | Solvent | "Solvesso 100" (Trade mark, defined in Comparison Example 2) | 65 parts | Xylol | 140 parts | | |
| | | β-ethoxyethyl acetate | 65 parts | Isophorone (Ketone solvent, product of Union Carbide Corp., U.S.A.) | 140 parts | | |
| | | Total | 270 parts | Total | 420 parts | | |
| 2. Top coat forming Comp. | | | | | | | |
| | Resin | 50% acrylic copolymer solution (Copolymer of styrene, ethylacrylate, hydroxylethyl metacrylate and acrylic acid in a weight ratio of 40 : 45 : 15 : 12, dissolved in a 8 : 2 weight ratio mixture of xylol and butanol) | 140 parts | "Cardura 30" (Trade mark, alkyd resin, product of Shell Chemical Co., U.S.A.) | 75 parts | "Duracron RE. 487" (Trade mark, acrylic resin, product of Mitsubishi Rayon Co., Ltd., Japan) | 160 parts |
| | | U-van 20 SA (Trade mark, defined in Comparison Example 2) | 60 parts | "U-van 20 SA" (Trade mark, defined in Comparison Example 2) | 80 parts | "Epikote 1001" (Trade mark, epoxy resin, product of American Cyanamid Co., U.S.A.) | 10 parts |
| | | | | | | "Cymel 300" (Trade mark, melamine resin, product of American Cyanamid Co., U.S.A.) | 10 parts |

Table 1 — Continued

| | | Example 1 | | Example 2 | | Example 3 | |
|---|---|---|---|---|---|---|---|
| Pigment | | Titanium dioxide | 80 parts | Titanium dioxide | 80 parts | Titanium dioxide | 80 parts |
| Plasticizer | | Dimethylphthalate | 15 parts | Triethylene glycol monoethyl ether | 30 parts | Diethylene glycol monobutyl ether | 30 parts |
| Solvent | | "Solvesso 100" (Trade mark, defined in Comparison Example 2) | 25 parts | "Solvesso 100" (Trade mark, defined in Comparison Example 2) | 55 parts | "Solvesso 100" (Trade mark, defined in Comparison Example 2) | 30 parts |
| | | β-ethoxyethyl acetate | 25 parts | Butanol | 10 parts | β-ethoxyethyl acetate | 25 parts |
| | | Total | 345 parts | Total | 330 parts | Total | 345 parts |

Table 2

| | | Example 1 | Comp. Ex. 1 | Comp. Ex. 2 | Example 2 | Example 3 |
|---|---|---|---|---|---|---|
| Coating and baking conditions | | | | | | |
| Primer coat | Baking temp. | 200°C | 200°C | 200°C | 150°C | — |
| | Baking time | 40 sec. | 40 sec. | 40 sec. | 30 sec. | — |
| | Dry coating thickness | 3 μ | 3 μ | 3 μ | 7 μ | — |
| Top coat for semi-hardening | Baking temp. | 100°C | 200°C | 250°C | 80°C | 180°C |
| | Baking time | 60 sec. | 10 min. | 60 sec. | 90 sec. | 40 sec. |
| | Dry coating thickness | 25 μ | 25 μ | 25 μ | 40 μ | 10 μ |
| Tackiness *1 | | 20 g/cm width | 0 | 0 | 16 g/cm width | 28 g/cm width |
| Top coat for complete hardening | Baking temp. | 200°C | — | — | 150°C | 250°C |
| | Baking time | 10 min. | — | — | 20 min. | 2 min. |
| Properties of coating | State of shaped portion (inspected with unaided eye) | No cracking and peeling in coating film | Coating film cracked and peeled markedly | Slight cracking in coating film | No cracking and peeling in coating film | No cracking and peeling in coating film |
| | Pencil hardness *2 | 3H | 3H | H | 3H | 3H |
| | Abrasion resistance *3 | 8.0 mg | 8.5 mg | 12.5 mg | 5.0 mg | 8.0 mg |
| | Stain resistance *4 | | | | | |
| | Spirit ink (red) | Good | Good | Stained markedly | Good | Good |
| | Spirit ink (black) | Good | Good | Stained markedly | Good | Good |
| | Lipstick (No. 614, product of Isehan Co., Japan) | Good | Good | Stained markedly | Good | Good |
| | Lipstick (No. 615, product of of Isehan Co., Japan) | Good | Good | Stained markedly | Good | Good |
| | Chemical resistance *5 | No change | No change | Softened | Good | No change |

The properties of coating were determined by the following test methods:

*1 Tackiness

The same as disclosed before.

*2 Pencil hardness

Determined according to JIS K 5400.6.14 (70).

*3 Abrasion resistance

Test was conducted on a Taber's Abraser, using a weight of 500 g and a CS-10 abrading wheel. The result was expressed in terms of the amount of coating worn away after 300 revolutions.

*4 Stain resistance

The coating was stained with spirit ink (red and black) and lipstick and then left to stand at room temperature for 24 hours. The surface of coating was wiped with absorbent cotton impregnated with ethanol. If the surface was found free from stain or color, the result was interpreted as good.

*5 Chemical resistance

A glass ring (about 25 mm in inner diameter and 30 mm in height) was placed on the coating in snug-fit contact therewith and completely sealed with vaseline or paraffin. A 5% aqueous solution of acetic acid was poured into the ring to approximately one half its height and the ring was covered with a glass plate. The specimen was retained in horizontal position and left to stand at room temperature for 6 hours. The ring was then removed from the specimen, which was thereafter dried in the indoor air for 1 hour. Subsequently, the state of the coating was inspected.

What we claim is:

**1.** A precoated metal sheet for producing a metal working product which comprises a base metal sheet, a coating film of a thermosetting resin which is formed on the base metal sheet and cured to semi-hardened state having a tackiness of from 2.0 to 40 g/cm width at a temperature of 25°C and at a relative humidity of 75% and a polyolefin sheet removably adhered to the above semi-hardened coating film; said base metal sheet being one species selected from the group consisting of mild sheet, aluminum sheet, chromium-plated steel sheet and zinc-plated steel sheet; said thermosetting resin being one species selected from the group consisting of

1. thermosetting acrylic resin containing hydroxyl group in the molecule and having an acid value of 5 to 20and hydroxyl value of 10 to 70, 100 parts by weight of this resin being used with 20 to 60 parts by weight of melamine-formaldehyde resin and/or not more than 20 parts by weight of bisphenol A — epichlorohydrine type epoxy resin having an epoxy equivalent of 300 to 800,
2. alkyd-melamine resin comprising 100 parts by weight of alkyd resin modified with non-drying oil and/or non-drying oil fatty acid and having an oil length of 10 to 30 and 20 to 60 parts by weight of melamine-formaldehyde resin,
3. bisphenol A—epichlorohydrine type epoxy resin having an epoxy equivalent of 800 to 4,000 100 parts by weight of this resin being used with 20 to 60 parts by weight of butyl-etherified phenol-formaldehyde resin or with 20 to 60 parts by weight of butyl-etherified urea-formaldehyde resin, and
4. oil free polyester-melamine resin comprising 100 parts by weight of oil free polyester having an acid value of 5 to 20 and hydroxyl equivalent of 400 to 1,300 and 20 to 60 parts by weight of melamine-formaldehyde resin modified with an aliphatic monoalcohol having from 1 to 4 carbon atoms.

**2.** A precoated metal sheet for producing a metal working product according to claim **1,** in which said polyolefin sheet is one species selected from the group consisting of polyethylene and polypropylene.

* * * * *