

# SURFACE-COATED STEEL SHEET WITH GOOD HEAT RESISTANCE AND RELEASABILITY

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention:

The present invention relates to a surface-coated steel sheet which exhibits good heat resistance and good releasability at elevated temperatures as well as good resistance to transfer and good surface smoothness. Being superior in heat resistance and releasability, the surface-coated steel sheet finds use in the production of printed circuit boards as a release sheet to prevent the platen from sticking to copper foil on the printed circuit board during hot pressing or to prevent layers of copper foil from sticking to each other when more than one printed circuit board are hot-pressed at one time. In addition, when used as a release sheet, it prevents the pattern of inner circuits of printed circuit board from being transferred to it and also prevents its surface irregularities from being transferred to copper coil. And, it is flat, stiff, and durable for repeated use. Moreover, it finds use in various applications as a highly oil-repellent steel sheet.

### 2. Description of the Related Art:

A copper-clad laminate is known as the substrate of printed circuit boards. It is produced from prepreg and copper foil (placed one over the other) by pressing with heating. (Prepreg is an intermediate product obtained by

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impregnating a base, such as paper and glass cloth, with a thermosetting resin.) A laminate with copper foil on both sides is produced by pressing copper foil, prepreg, inner layer circuit, prepreg, and copper foil (arranged in the order mentioned) between two platens of a press. In pressing operation, it is common practice to insert a member (called release sheet) between the platen and the copper foil so as to prevent the surface irregularities of the platen from being transferred to the copper foil and to prevent the platen from sticking to the copper foil. There is an instance where the release sheet has its both sides coated with a releasing material so that it avoids the sticking of prepreg powder, which is generated at the time of lamination, or molten prepreg resin (hereinafter referred to as "releasability").

The release sheet (coated with a releasing material) is required to have the following characteristic properties.

- (1) Good releasability that lasts through repeated operations.
- (2) Good heat resistance (or ability to withstand hot pressing).
- (3) Good transfer resistance (or ability to prevent the pattern of the inner circuits from being transferred to the release sheet and ability to prevent the surface irregularities from being transferred to the copper foil of the product).
- (4) Good flatness and stiffness and ability to press down the laminate uniformly.

The above-mentioned requirements are met by the following materials, which still have their respective disadvantages.

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- (1) Stainless steel (SUS) sheet used alone (without a releasing material). The problem in this case is that the expensive SUS leads to a high production cost and the stainless steel sheet loses its flatness after repeated use unless it is polished uniformly. (It needs polishing and cleaning before use.)
- (2) Stainless steel (SUS) sheet used in combination with release paper or film as a releasing material. The problem in this case is that SUS is expensive and release paper or film cannot be used repeatedly. The stainless steel sheet needs polishing and cleaning before it is used again.
- (3) Aluminum sheet used alone without a releasing material. The problem in this case is that aluminum sheet is expensive and yet unusable repeatedly.
- (4) Aluminum sheet or foil used in combination with resin coating as a releasing material. The problem in this case is a high material cost. Aluminum foil is subject to wrinkling (and hence becomes poor in flatness) even though it can be used repeatedly.
- (5) Interlayer used in combination with release paper or film as a releasing material. The problem in this case is a high material cost. Release film cannot be used again, and it is liable to wrinkling, losing its flatness.

Conventional technologies involve problems as mentioned above. That is, film, paper, or foil used for release purpose lacks flatness, and hence it cannot be applied to the production of copper-clad laminate that needs a good external



appearance. In addition, it is thin and hard to handle, and it cannot be recycled. (It is originally designed as a disposable item.) On the other hand, a mirror-finished stainless steel sheet is superior in surface flatness; however, it needs polishing and cleaning before it is used again. This leads to an increased production cost.

#### OBJECT AND SUMMARY OF THE INVENTION

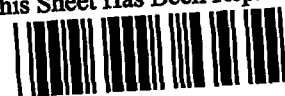
The present invention was completed to address the above-mentioned problems. It is an object of the present invention to provide a surface-coated steel sheet which is reusable and is superior in all of the characteristic properties such as transfer resistance, surface smoothness, heat resistance, and releasability.

The present invention covers a plated or unplated steel sheet with a resin coating film containing any one of epoxy resin, phenolic resin, polyimide resin, polyamideimide resin, ketone resin, wholly aromatic polyester resin, unsaturated polyester resin and silicone resin as the major constituent, said resin coating being characterized by its contact angle not smaller than  $15^\circ$  with gear oil (having a viscosity grade of ISO VG460) placed thereon which is measured when the steel sheet has a surface temperature of  $180^\circ\text{C}$ . The present invention requires that the resin coating have good oil repellency (in terms of contact angle as specified above) so that it exhibits good releasability at elevated temperatures.

According to the present invention, the resin coating film should have a pencil hardness of 2H or above (as provided

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in JIS K5400), so that it ensures the smoothness of copper foil after pressing.

According to the present invention, the resin coating film should have a surface roughness (Ra) not larger than 0.5  $\mu\text{m}$  (in terms of arithmetic average measured according to JIS B0601). Otherwise, its surface irregularities are transferred to copper foil, which prevents the formation of accurate printed circuit boards.

According to the present invention, the resin coating film should preferably contain a silicone resin and/or fluororesin (as a release agent) and a surface-roughening agent. They contribute to releasability and protect the copper foil from staining.

According to the present invention, the resin coating film should preferably be formed in an amount of 0.5-8.0 g/m<sup>2</sup>.

According to the present invention, the plated or unplated steel sheet should preferably have a yield point no lower than 200 N/mm<sup>2</sup> and/or a tensile strength no lower than 300 N/mm<sup>2</sup>.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention covers a plated or unplated steel sheet with a resin coating film formed thereon. A steel sheet is preferable to an aluminum sheet when used as a release sheet; the latter transmits heat from the press platen to the laminate efficiently because of its high thermal conductivity but moves relative to the copper foil of the laminate during pressing because of its larger coefficient of expansion than

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that of copper foil. By contrast, a steel sheet has an adequate thermal conductivity as well as a coefficient of thermal expansion of  $12.5 \times 10^{-6}$  which is close to that of copper foil ( $17 \times 10^{-6}$ ). Therefore, it does not move relative to copper foil during pressing.

The base on which the resin coating film is made may be a stainless steel sheet (having good corrosion resistance) or an ordinary steel sheet with or without plating of single metal or alloy. Plating method is not specifically restricted. A zinc-plated or zinc alloy-plated steel sheet is desirable. Plating may be followed by chromating prior to resin coating; chromate film improves the adhesion of a resin coating film and produces the rust preventing effect.

According to the present invention, the steel sheet with a resin coating film requires that the resin coating film possess oil repellency at high temperatures. This requirement is based on the present inventor's finding that oil repellency at high temperatures greatly affects releasability at high temperatures. The desired oil repellency is established easily by measuring the contact angle of the resin coating under specific conditions.

Measurements of the contact angle of the resin coating is carried out by placing on the resin coating film a drop of gear oil having a viscosity grade of ISO VG460. The gear oil is restricted in viscosity to affect the contact angle measured. An example of the gear oil meeting this requirement is "Daphne Super Gear Oil 460" available from Idemitsu Kousan.



It has a kinematic viscosity of 459.9 mm<sup>2</sup>/s at 40°C and 30.85 mm<sup>2</sup>/s at 100°C, a flash point of 274°C, a density of 0.9028 (at 15°C), and a total acid number of 0.38 mgKOH/g. Measurements of the contact angle should be carried out at 180°C or under the condition that the surface temperature of the coated steel sheet is 180°C. A drop of the gear oil is placed on the surface of the resin coating film and the contact angle is measured by using a contact angle meter (such as Model CD-DT-A available from Kyowa Kaimen Kagaku Co., Ltd.).

The present invention requires that the gear oil give a contact angle not smaller than 15°; otherwise, the resin coating film lacks oil repellency and is poor in releasability.

According to the present invention, the resin coating film should preferably have a pencil hardness not lower than 2H (measured as specified in JIS K5400); otherwise, the resin coating film is liable to scratches which may be transferred to the copper foil.

According to the present invention, the resin coating film should preferably have an arithmetic average surface roughness (Ra) not larger than 0.5 μm (measured as specified in JIS B0601). The resin coating film has its surface irregularities, if it has any, transferred to the copper foil; this is a hindrance to accurate printed circuits.

The resin coating film is composed mainly of an organic resin. Since the surface-coated steel sheet of the present invention is used as a releasing aid for hot pressing at high temperatures, the organic resin should be one which has good



heat resistance and good releasability (as judged from the contact angle of the gear oil mentioned above). It includes, for example, epoxy resin, phenolic resin, polyimide resin, polyamideimide, polyether ketone (ketone resin), unsaturated polyester resin and wholly aromatic polyester. These resins may be incorporated with any known crosslinking agent so as to improve the resin coating film in hardness. Crosslinking between polymer chains contributes to the formation of dense film.

In addition, these resins may be incorporated with a release agent (such as silicone resin and fluororesin) so that the resin coating has improved releasability. The release agent lowers the surface energy of the resin coating, thereby enhancing oil repellency. The amount of the release agent should be 0.5-10 wt% of the resin coating. With an amount less than specified about, the release agent does not produce its effect. With an excess amount, the release agent will migrate to the copper foil, aggravating ink receptivity at the time of circuit printing.

For improved releasability, the resin coating should preferably be incorporated with a surface roughening agent which imparts minute surface irregularities to the resin coating film. An excessively roughened surface (with Ra larger than 0.5  $\mu\text{m}$ ) is not desirable, but a moderate roughened surface contributes to releasability. The surface roughening agent includes any particulate inorganic materials such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ .

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The resin coating should be formed such that it weighs 0.5-8.0 g/m<sup>2</sup>. With a basis weight less than 0.5 g/m<sup>2</sup>, the resin coating will not entirely cover the surface irregularities on the steel sheet and hence the resulting coated steel sheet causes them to be transferred to the copper foil. In addition, the coated steel sheet with thin coating is poor in releasability and corrosion resistance. The resin coating with an adequate basis weight does not permit the irregularities (15-80 μm) of the inner circuits (under the copper foil and prepreg) to be transferred to it through them. With a basis weight more than 8.0 g/m<sup>2</sup>, the resin coating permits the irregularities of the inner circuits to be transferred to it, and hence the coated steel sheet cannot be reused for release.

According to the present invention, the surface-coated steel sheet may be produced by coating a plated or unplated steel sheet with the resin coating film by any known method (such as dipping, roll coating, knife coating, and spraying), followed by heating to solidify the coated film.

Steel sheets (with or without plating) having controlled tensile properties and surface roughness will produce good effects in preventing transfer and providing smooth surface.

In order to prevent the transfer of the pattern of inner circuits during hot pressing, it is necessary to use a steel sheet with a high tensile strength (greater than 300 N/mm<sup>2</sup>, preferably 400 N/mm<sup>2</sup>) and a high hardness. The upper limit of tensile strength does not exist from the standpoint of preventing transfer. However, a practical upper limit is 1700

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N/mm<sup>2</sup> in view of the fact that an excessively high tensile strength makes it difficult to provide satisfactory flatness during rolling.

According to the present invention, it is recommended to use a plated on unplated steel sheet with a yield point of 200 N/mm<sup>2</sup> and above so as to prevent the transfer of the pattern of inner circuits during hot pressing. In other words, the prevention of transfer may be achieved by controlling either or both of tensile strength and yield point.

Yield point is concerned with not only the prevention of transfer but also the improvement in surface smoothness. Hence, it contributes to the external appearance of the surface coated steel sheet. In addition, the steel sheet (as a release sheet) should have an adequate stiffness so that it uniformly presses laminated substrates during hot pressing. According to the present invention, the steel sheet should have a yield point higher than 200 N/mm<sup>2</sup> (preferably 300 N/mm<sup>2</sup>) so that it meets requirements for transfer prevention and external appearance. Otherwise, the resulting copper-clad laminate would have an apparent irregular surface due to prepreg. Yield point has no upper limit from the standpoint of transfer prevention and external appearance. However, it should preferably be lower than 1500 N/mm<sup>2</sup> because steel sheets with an excessively high yield point are too hard to be rolled flat as desired.

In order that the surface irregularities of the release sheet are not transferred to the copper foil during hot

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pressing, the steel sheet should have a smooth surface in terms of surface roughness (Ra) smaller than  $0.30\text{ }\mu\text{m}$ , preferably smaller than  $0.2\text{ }\mu\text{m}$ . Any steel sheet with a rougher surface than specified above causes its surface irregularities to be apparently transferred to the surface of copper-clad laminates. No lower limits of Ra exist from the standpoint of preventing transfer; however, Ra should preferably be greater than  $0.05\text{ }\mu\text{m}$  because a steel sheet with an extremely small Ra shows its scratches noticeably.

The surface-coated steel sheet of the present invention is useful as a release medium in the production of copper-clad laminates. It will replace conventional mirror-finished stainless steel sheet and release film, and it is capable of repeated use. In its use for pressing, it is placed between a platen and a copper foil covering prepreg and inner circuits or it is placed between two laminates with their copper foils facing each other.

The invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope thereof. The examples may be modified without departing from the spirit and scope of the invention.

#### Example 1

Samples were prepared from a chromated steel sheet ( $20\text{ g/m}^2$  of Cr) with electroplated zinc ( $20\text{ g/m}^2$  of Zn),  $0.8\text{ mm}$  in thickness. The resin coating film of each sample has the composition, contact angle, pencil hardness, and arithmetic average roughness (Ra) as shown in Table 1. Incidentally, the

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base of the resin coating in Table 1 is identified by A (epoxy resin), B (polyimide resin), C (phenolic resin), D (ketone resin), and E (silicone resin). The release agent is silicone resin (a) or fluororesin (b), and it is used in an amount of 0-15 wt% of the resin coating. The surface roughening agent is  $Al_2O_3$  (①),  $SiO_2$  (②), or  $MgO$  (③), and it is used in an amount of 0-20 wt% of the resin coating film. The weight of the resin coating film varies from 0.25 to 15 g/m<sup>2</sup>. The resin coating film is incorporated with an isocyanate crosslinking agent according to need in order to control oil repellency, pencil hardness, and Ra.

#### Test methods:

The samples were measured for characteristic properties by the following test methods.

##### (1) Contact angle

A drop of gear oil ("Daphne Super Gear Oil 460", available from Idemitsu Kousan) is placed on the surface coated steel sheet with a surface temperature of 180°C, and the contact angle is measured by using a contact angle meter (Model CD-DT-A available from Kyowa Kaimen Kagaku Co., Ltd.).

##### (2) Surface roughness

Surface roughness is calculated in terms of arithmetic surface roughness (Ra) by measuring according to JIS B0601 with a surface-configuration meter ("Surfcom 554A" available from Tokyo Seimitsu Co., Ltd.).

##### (3) Pencil hardness

Measured according to the method provided in JIS K5400.



The result is shown in terms of the hardness of the pencil that gives scratches to the coating film.

#### (4) Releasability

Two layers of prepreg powder, with a copper foil (35  $\mu\text{m}$  thick) interposed between them, were held between two release sheets, and the assembly was pressed between the upper and lower platens of a hot press under a pressure of 30  $\text{kgf/cm}^2$  at 180°C for 60 min. After cooling to room temperature, the release sheets were removed from the laminate of prepreg and copper foil. The release sheets were visually examined for the amount of prepreg powder present on its surface and rated according to the following criteria. Incidentally, the prepreg powder was prepared by impregnating glass cloth with epoxy resin, drying, semicuring, and crushing into small pieces (2-5 mm).

Good : none

Fair : slightly

Poor : less than 10%

Bad : more than 10%

#### (5) Repeated releasability

The above-mentioned procedure was repeated using the same release sheet until prepreg powder began to stick to the release sheet. The number of procedures repeated was regarded as the ability of the release sheet to be used repeatedly.

#### (6) Resistance of transfer

Layers of copper foil (35  $\mu\text{m}$  thick), prepreg powder, inner circuits, copper foil (35  $\mu\text{m}$  thick), and prepreg powder

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(arranged in the order mentioned) were held between two release sheets, and the assembly was pressed between the upper and lower platens of a hot press under a pressure of 40 kgf/cm<sup>2</sup> at 180°C for 60 min. After cooling to room temperature, the release sheets were removed from the laminate. The release sheets were visually examined to see if the irregularities of the inner circuits were transferred to the surface of the release sheet and were rated according to the following criteria.

Good : no transfer

Fair : slight transfer

Poor : less than 10% of transfer area

Bad : more than 10% of transfer area

(7) Staining of copper foil

The same procedure as (6) was repeated, and the resulting laminate was dipped in ethanol and then examined for the wetting state of its surface. Wetting is an indication of staining. The release sheet was rated according to the following criteria.

Good : wetting area 100%

Fair : wetting area 99-100%

Poor : wetting area 95-99%

Bad : wetting area less than 95%

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Table 1

| Sample No. | Coating weight (g/m <sup>2</sup> ) | Kind of base resin | Release agent |      | Roughening agent |     | Contact angle (°) | Pencil hardness | Ra  |
|------------|------------------------------------|--------------------|---------------|------|------------------|-----|-------------------|-----------------|-----|
|            |                                    |                    | Kind          | wt%  | Kind             | wt% |                   |                 |     |
| 1          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 2H              | 0.3 |
| 2          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 3H              | 0.3 |
| 3          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 4H              | 0.3 |
| 4          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 6H              | 0.3 |
| 5          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 9H              | 0.3 |
| 6          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.5 |
| 7          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.4 |
| 8          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.3 |
| 9          | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.1 |
| 10         | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 6H              | 0.3 |
| 11         | 3                                  | B                  | a             | 3    | ①                | 5   | 18                | 6H              | 0.3 |
| 12         | 3                                  | C                  | a             | 3    | ①                | 5   | 18                | 5H              | 0.3 |
| 13         | 3                                  | D                  | a             | 3    | ①                | 5   | 18                | 6H              | 0.3 |
| 14         | 3                                  | E                  | a             | 3    | ①                | 5   | 18                | 4H              | 0.3 |
| 15         | 3                                  | A                  | b             | 1    | ①                | 5   | 16                | 5H              | 0.3 |
| 16         | 3                                  | A                  | b             | 5    | ①                | 5   | 20                | 5H              | 0.3 |
| 17         | 3                                  | A                  | b             | 10   | ①                | 5   | 22                | 5H              | 0.3 |
| 18         | 3                                  | A                  | a             | 0.5  | ①                | 5   | 15                | 5H              | 0.3 |
| 19         | 3                                  | A                  | a             | 2    | ①                | 5   | 20                | 5H              | 0.3 |
| 20         | 3                                  | A                  | a             | 5    | ①                | 5   | 22                | 5H              | 0.3 |
| 21         | 3                                  | A                  | a             | 7    | ①                | 5   | 23                | 5H              | 0.3 |
| 22         | 3                                  | A                  | a             | 10   | ①                | 5   | 24                | 5H              | 0.3 |
| 23         | 3                                  | A                  | a             | 3    | ①                | 1   | 15                | 5H              | 0.3 |
| 24         | 3                                  | A                  | a             | 3    | ①                | 2   | 18                | 5H              | 0.3 |
| 25         | 3                                  | A                  | a             | 3    | ①                | 15  | 20                | 3H              | 0.3 |
| 26         | 3                                  | A                  | a             | 3    | ②                | 5   | 20                | 4H              | 0.3 |
| 27         | 3                                  | A                  | a             | 3    | ③                | 5   | 20                | 6H              | 0.3 |
| 28         | 0.5                                | A                  | a             | 3    | ①                | 5   | 20                | 9H              | 0.3 |
| 29         | 1                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.5 |
| 30         | 3                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.4 |
| 31         | 6                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.3 |
| 32         | 8                                  | A                  | a             | 3    | ①                | 5   | 20                | 5H              | 0.1 |
| 33         | 3                                  | A                  | a             | 3    | ①                | 5   | 10                | 5H              | 0.3 |
| 34         | 3                                  | A                  | a             | 3    | ①                | 5   | 5                 | 5H              | 0.3 |
| 35         | 3                                  | A                  | b             | 0.25 | ①                | 5   | 10                | 5H              | 0.3 |
| 36         | 3                                  | A                  | a             | 0    | ①                | 5   | 4                 | 5H              | 0.3 |
| 37         | 3                                  | A                  | a             | 0.25 | ①                | 5   | 12                | 5H              | 0.3 |

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|----|----|---|---|----|---|-----|----|----|-----|
| 38 | 3  | A | a | 3  | ① | 5   | 20 | H  | 0.3 |
| 39 | 3  | A | a | 3  | ① | 5   | 20 | F  | 0.3 |
| 40 | 3  | A | a | 3  | ① | 5   | 20 | B  | 0.3 |
| 41 | 3  | A | a | 3  | ① | 5   | 20 | 5H | 0.6 |
| 42 | 3  | A | a | 3  | ① | 5   | 20 | 5H | 0.8 |
| 43 | 3  | A | b | 12 | ① | 5   | 23 | 5H | 0.3 |
| 44 | 3  | A | a | 12 | ① | 5   | 20 | 5H | 0.3 |
| 45 | 3  | A | a | 15 | ① | 5   | 22 | 5H | 0.3 |
| 46 | 3  | A | a | 3  | ① | 0   | 20 | 5H | 0.3 |
| 47 | 3  | A | a | 3  | ① | 0.5 | 20 | 5H | 0.3 |
| 48 | 3  | A | a | 3  | ① | 0.8 | 20 | 5H | 0.3 |
| 49 | 3  | A | a | 3  | ① | 17  | 20 | 5H | 0.3 |
| 50 | 3  | A | a | 3  | ① | 20  | 20 | 2H | 0.3 |
| 51 | 10 | A | a | 3  | ① | 5   | 20 | 4H | 0.3 |
| 52 | 15 | A | a | 3  | ① | 5   | 20 | 6H | 0.3 |

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### Example 2

This example demonstrates how the performance of the release sheet depends on the contact angle, coating hardness, and arithmetic surface roughness (Ra). Table 2 shows the results of experiments with Samples Nos. 1-9, 33, 34, and 38-42. It is noted from the table that Samples Nos. 33-34, which have a contact angle of oil smaller than  $15^\circ$ , are poor in releasability, and that Samples Nos. 38-40, which have a low pencil hardness and Samples No. 41-42, which has a large Ra, are particularly poor in resistance to transfer.

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Table 2

| Sample No. | Contact angle (°) | Pencil hardness | Surface roughness | Releasability | Repeated releasability (cycles) | Resistance to transfer | Copper foil staining |
|------------|-------------------|-----------------|-------------------|---------------|---------------------------------|------------------------|----------------------|
| 1          | 20                | 2H              | 0.3               | fair          | fair                            | fair                   | good                 |
| 2          | 20                | 3H              | 0.3               | good          | good                            | fair                   | good                 |
| 3          | 20                | 4H              | 0.3               | good          | good                            | good                   | good                 |
| 4          | 20                | 6H              | 0.3               | good          | good                            | good                   | good                 |
| 5          | 20                | 9H              | 0.3               | good          | good                            | good                   | good                 |
| 6          | 20                | 5H              | 0.5               | fair          | fair                            | fair                   | good                 |
| 7          | 20                | 5H              | 0.4               | good          | fair                            | good                   | good                 |
| 8          | 20                | 5H              | 0.3               | good          | good                            | good                   | good                 |
| 9          | 20                | 5H              | 0.1               | good          | good                            | good                   | good                 |
| 33         | 10                | 5H              | 0.3               | bad           | bad                             | poor                   | poor                 |
| 34         | 5                 | 5H              | 0.3               | bad           | bad                             | poor                   | bad                  |
| 38         | 20                | H               | 0.3               | fair          | poor                            | bad                    | fair                 |
| 39         | 20                | F               | 0.3               | fair          | poor                            | bad                    | poor                 |
| 40         | 20                | B               | 0.3               | poor          | bad                             | bad                    | bad                  |
| 41         | 20                | 5H              | 0.6               | fair          | poor                            | bad                    | fair                 |
| 42         | 20                | 5H              | 0.8               | poor          | bad                             | bad                    | fair                 |

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Example 3

This example demonstrates how the performance of the release sheet depends on the basis weight of resin coating and the kind of base resin. Table 3 shows the results of experiments with Samples Nos. 10-14, 28-32, and 51-52. It is noted that the resin coating becomes poor in repeated releasability and resistance to transfer according as the basis weight of resin coating increases. All of the base resins A to E used were satisfactory.

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Table 3

| Sample No. | Coating weight (g/m <sup>2</sup> ) | Kind of base resin | Releasability | Repeated releasability (cycles) | Resistance to transfer | Copper foil staining |
|------------|------------------------------------|--------------------|---------------|---------------------------------|------------------------|----------------------|
| 28         | 0.5                                | A                  | fair          | fair                            | fair                   | good                 |
| 29         | 1                                  | A                  | good          | good                            | good                   | good                 |
| 30         | 3                                  | A                  | good          | good                            | good                   | good                 |
| 31         | 6                                  | A                  | good          | good                            | good                   | good                 |
| 32         | 8                                  | A                  | good          | fair                            | fair                   | good                 |
| 10         | 3                                  | A                  | good          | good                            | fair                   | good                 |
| 11         | 3                                  | B                  | good          | good                            | good                   | good                 |
| 12         | 3                                  | C                  | good          | good                            | good                   | good                 |
| 13         | 3                                  | D                  | good          | good                            | good                   | good                 |
| 14         | 3                                  | E                  | good          | fair                            | fair                   | fair                 |
| 51         | 10                                 | A                  | poor          | bad                             | bad                    | fair                 |
| 52         | 15                                 | A                  | poor          | bad                             | bad                    | poor                 |

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Example 4

This example demonstrates the effect of the kind and amount of the release agent. The results are shown in Table 4. It is noted that Samples Nos. 35, 36 are poor in releasability and resistance to transfer, and Samples Nos. 43, 44, and 45, which contain an excess amount of release agent, are poor in resistance to copper foil resistance. Both of the release agents a and b were satisfactory.

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Table 4

| Sample No. | Release agent |      | Releas-<br>ability | Repeated<br>releasability<br>(cycles) | Resistance<br>to transfer | Copper foil<br>staining |
|------------|---------------|------|--------------------|---------------------------------------|---------------------------|-------------------------|
|            | Kind          | wt%  |                    |                                       |                           |                         |
| 18         | a             | 0.5  | fair               | fair                                  | fair                      | good                    |
| 19         | a             | 2    | good               | good                                  | good                      | good                    |
| 20         | a             | 5    | good               | good                                  | good                      | good                    |
| 21         | a             | 7    | good               | good                                  | good                      | good                    |
| 22         | a             | 10   | good               | fair                                  | fair                      | fair                    |
| 15         | b             | 1    | good               | good                                  | fair                      | good                    |
| 16         | b             | 5    | good               | good                                  | good                      | good                    |
| 17         | b             | 10   | good               | good                                  | good                      | good                    |
| 36         | a             | 0    | bad                | bad                                   | bad                       | bad                     |
| 37         | a             | 0.25 | bad                | bad                                   | bad                       | poor                    |
| 35         | b             | 0.25 | bad                | bad                                   | bad                       | poor                    |
| 44         | a             | 12   | fair               | poor                                  | poor                      | bad                     |
| 45         | a             | 15   | fair               | poor                                  | poor                      | bad                     |
| 43         | b             | 12   | poor               | bad                                   | bad                       | bad                     |

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#### Example 5

This example demonstrates the effect of the kind and amount of the surface roughening agent. The results are shown in Table 5. It is noted that Samples Nos. 46-48, which have a low content of surface roughening agent, are poor in repeated releasability and resistance to transfer, and that all the samples tend to become poor in overall performance according as the amount of surface roughening agent increases. All of the surface roughening agents ①, ②, and ③ were satisfactory.

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Table 5

| Sample No. | Roughening agent |     | Releas-ability | Repeated releasability (cycles) | Resistance to transfer | Copper foil staining |
|------------|------------------|-----|----------------|---------------------------------|------------------------|----------------------|
|            | Kind             | wt% |                |                                 |                        |                      |
| 23         | ①                | 1   | fair           | Fair                            | fair                   | good                 |
| 24         | ①                | 2   | good           | Good                            | good                   | good                 |
| 25         | ①                | 15  | good           | Good                            | fair                   | good                 |
| 26         | ②                | 5   | good           | Good                            | good                   | good                 |
| 27         | ③                | 5   | good           | Good                            | good                   | good                 |
| 46         | ①                | 0   | poor           | bad                             | bad                    | fair                 |
| 47         | ①                | 0.5 | poor           | bad                             | bad                    | poor                 |
| 48         | ①                | 0.8 | fair           | bad                             | bad                    | poor                 |
| 49         | ①                | 17  | fair           | poor                            | poor                   | poor                 |
| 50         | ①                | 20  | poor           | bad                             | bad                    | bad                  |

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#### Example 6

In this example, the release sheet was prepared from steel sheets of various kinds (0.8 mm thick) which had been cold-rolled, annealed, and temper-rolled. The steel sheets were given adequate tensile strength and yield point by selecting the steel kind and the annealing method. The release sheet was given an adequate surface roughness ( $R_a$ ) by the rolls (for cold rolling and temper rolling) with varied surface roughness.

The temper-rolled steel sheet underwent electric zinc plating (with 20 g/m<sup>2</sup> of Zn) and subsequently chromating (with 20 mg/m<sup>2</sup> of Cr).

The plated-chromated steel sheet was coated with a resin solution containing 100 parts by weight of epoxy resin and 5 parts by weight (as solids) of silicone resin. Upon baking, the resin solution turned into a resin coating film, 3  $\mu$ m thick, which functions as a release coating. The hardness of the resin coating film was adjusted by changing the amount of melamine resin (capable of crosslinking with the epoxy resin) and the baking temperature.

The thus obtained release sheets were tested according to the following test methods. Incidentally, all the samples tested in this Example were found to have a contact angle larger than 15° by the same test for contact angle as used in Example 1 mentioned above.

#### (1) Tensile properties

The samples are tested for tensile strength and yield

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point according to JIS Z2241 (Tensile test method for metallic materials) using a specimen No. 5 specified in JIS Z2201.

Those specimens which have no definite yield point are regarded as having a yield point equivalent to a proof stress at 0.2% permanent set.

(2) Surface roughness

Surface roughness is calculated in terms of arithmetic surface roughness (Ra) by measuring according to JIS B0601 with a surface-configuration meter ("Surfcom 554A" available from Tokyo Seimitsu Co., Ltd.).

(3) Pencil hardness

Measured (in the same way as in Example 1) according to the method provided in JIS K5400. The result is shown in terms of the hardness of the pencil that gives scratches to the coating film.

(4) Resistance to transfer to copper foil

A copper foil and a layer of prepreg powder were held between two release sheets, and the assembly was pressed between the upper and lower platens of a hot press under a pressure of 40 kgf/cm<sup>2</sup> at 180°C for 60 min. After cooling to room temperature, the release sheets were removed from the laminate of prepreg and copper foil. The release sheets were visually examined to see if the surface irregularities of the release sheet were transferred to the surface of the copper foil. They were rated according to the following criteria. Incidentally, the prepreg was prepared from epoxy-impregnated glass cloth (0.1 mm thick) cured at 140-160°C for 60-90 min

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under a pressure of 20-50 kgf/cm<sup>2</sup>.

Criteria for resistance to transfer:

Good : no transfer to copper foil

Fair : slight transfer to copper foil

Poor : transfer to copper foil

Bad : remarkable transfer to copper foil

(5) Irregularities of prepreg

Samples are pressed in the same way as in (4) above and then visually examined for the number of irregularities due to prepreg in an area of 500 × 500 mm of copper foil. Samples are rated according to the following criteria.

Good : none

Fair : one or two

Poor : three to six

Bad : seven and above

(6) Repeated releasability

The same procedure as in (4) above is repeated using the same release sheet as used in (4) above until a state arises in which the release sheet does not peel easily from the copper-clad prepreg. The number of procedures repeated is regarded as the ability of the release sheet to be used repeatedly.

(7) Resistance to flaws

Samples are tested in the same way as in (6) above and then visually examined for surface flaws. The criteria for rating are given below.

Good : no surface flaws

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Fair : almost no surface flaws

Poor : some surface flaws

Bad : many surface flaws

(8) Resistance to transfer of inner circuits to release sheet

Layers of copper foil, prepreg, inner circuits, prepreg, and copper foil (arranged in the order mentioned) were held between two release sheets, and the assembly was pressed between the upper and lower platens of a hot press under a pressure of 40 kgf/cm<sup>2</sup> at 180°C for 60 min. After cooling to room temperature, the release sheets were removed from the laminate. The release sheets were visually examined to see if the irregularities of the inner circuits were transferred to the surface of the release sheet and were rated according to the following criteria. Incidentally, the inner circuits are formed on a 0.3mm-thick laminate with copper foil on both sides. The wiring of the circuits has a height of 25  $\mu$ m (equivalent to the thickness of the copper foil). The prepreg and copper foil are the same ones as used in (4) above.

Good : no transfer

Fair : slight transfer

Poor : apparent transfer

Bad : remarkable transfer

The results are shown in Table 6.

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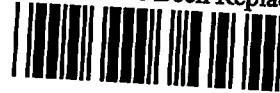
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Table 6

| Sample No. | Tensile properties (N/mm <sup>2</sup> ) |                  | Surface roughness Ra ( $\mu$ m) | Pencil hardness | Transfer of inner circuits | Irregularities of prepreg | Transfer to copper foil | Resistance to flaws |
|------------|-----------------------------------------|------------------|---------------------------------|-----------------|----------------------------|---------------------------|-------------------------|---------------------|
|            | Yield point                             | Tensile strength |                                 |                 |                            |                           |                         |                     |
| 53         | 240                                     | 388              | 0.26                            | 2H              | fair                       | fair                      | fair                    | fair                |
| 54         | 269                                     | 412              | 0.27                            | 2H              | fair                       | good                      | fair                    | fair                |
| 55         | 334                                     | 444              | 0.26                            | 2H              | good                       | good                      | fair                    | fair                |
| 56         | 241                                     | 276              | 0.27                            | 2H              | fair                       | fair                      | fair                    | fair                |
| 57         | 189                                     | 312              | 0.26                            | 2H              | fair                       | fair                      | fair                    | fair                |
| 58         | 725                                     | 755              | 0.25                            | 2H              | good                       | good                      | fair                    | fair                |
| 59         | 692                                     | 710              | 0.24                            | 2H              | good                       | good                      | fair                    | fair                |
| 60         | 1240                                    | 1400             | 0.25                            | 2H              | good                       | good                      | fair                    | fair                |
| 61         | 1480                                    | 1630             | 0.25                            | 2H              | good                       | good                      | fair                    | fair                |
| 62         | 248                                     | 378              | 0.19                            | 2H              | fair                       | fair                      | good                    | fair                |
| 63         | 250                                     | 387              | 0.12                            | 2H              | fair                       | fair                      | good                    | fair                |
| 64         | 254                                     | 380              | 0.06                            | 2H              | fair                       | fair                      | good                    | fair                |
| 65         | 260                                     | 384              | 0.27                            | 4H              | good                       | good                      | fair                    | good                |
| 66         | 261                                     | 376              | 0.27                            | 6H              | fair                       | fair                      | fair                    | good                |
| 67         | 257                                     | 371              | 0.26                            | H               | good                       | good                      | fair                    | poor                |
| 68         | 241                                     | 276              | 0.27                            | B               | fair                       | fair                      | fair                    | fair                |

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It is noted from Table 6 that Samples Nos. 53 to 68 are good in resistance to transfer and have a good appearance with few irregularities resulting from prepreg. The steel sheet of these samples has tensile properties (yield point and tensile strength) and Ra which meet the requirements of the present invention. In addition, these samples are improved in resistance to flaws owing to the resin coating film which has a pencil hardness within an adequate range. Incidentally, the resin coating film was capable of releasing repeatedly seven times.

[Effect of the invention] The surface-coated steel sheet of the present invention is composed of a steel sheet (with or without plating) and an oil-repellent resin coating formed on the surface thereof. Therefore, it is superior in heat resistance, releasability, surface hardness, and surface smoothness. It finds use as a release sheet for pressing a laminate such as printed circuit board. Owing to its good properties, it can be used repeatedly without special treatment unlike conventional mirror-finished stainless steel sheet or release-coated aluminum foil. Thus the present invention contributes to cost saving and material saving. In addition, the surface-coated steel sheet of the present invention will find use as an oil-repellent steel sheet in various field as well as release sheet.

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WHAT IS CLAIMED IS:

1. A surface-coated steel sheet composed of a plated or unplated steel sheet and a resin coating film formed thereon, said resin coating film containing as the major constituent any one of epoxy resin, phenolic resin, polyimide resin, polyamideimide resin, ketone resin, wholly aromatic polyester resin, unsaturated polyester resin, and silicone resin, characterized in that said resin coating film has a contact angle not smaller than  $15^\circ$  with gear oil (having a viscosity grade of ISO VG460) placed thereon which is measured when the steel sheet has a surface temperature of  $180^\circ\text{C}$ .

2. A surface-coated steel sheet as defined in Claim 1, wherein the resin coating film has a pencil hardness of 2H or above which is measured according to the test method provided in JIS K5400.

3. A surface-coated steel sheet as defined in Claim 1, wherein the resin coating film has an arithmetic average surface roughness (Ra) not larger than  $0.5\ \mu\text{m}$  which is measured according to JIS B0601.

4. A surface-coated steel sheet as defined in Claim 2, wherein the resin coating film has an arithmetic average surface roughness (Ra) not larger than  $0.5\ \mu\text{m}$  which is measured according to JIS B0601.

5. A surface-coated steel sheet as defined in Claim 1, wherein the resin coating film contains a silicone resin and/or fluororesin as a release agent.

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6. A surface-coated steel sheet as defined in Claim 2, wherein the resin coating film contains a silicone resin and/or fluororesin as a release agent.

7. A surface-coated steel sheet as defined in Claim 3, wherein the resin coating film contains a silicone resin and/or fluororesin as a release agent.

8. A surface-coated steel sheet as defined in Claim 4, wherein the resin coating film contains a silicone resin and/or fluororesin as a release agent.

9. A surface-coated steel sheet as defined in Claim 1, wherein the resin coating film contains a surface-roughening agent.

10. A surface-coated steel sheet as defined in Claim 2, wherein the resin coating film contains a surface-roughening agent.

11. A surface-coated steel sheet as defined in Claim 3, wherein the resin coating film contains a surface-roughening agent.

12. A surface-coated steel sheet as defined in Claim 4, wherein the resin coating film contains a surface-roughening agent.

13. A surface-coated steel sheet as defined in Claim 5, wherein the resin coating film contains a surface-roughening agent.

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14. A surface-coated steel sheet as defined in Claim 6, wherein the resin coating film contains a surface-roughening agent.

15. A surface-coated steel sheet as defined in Claim 7, wherein the resin coating film contains a surface-roughening agent.

16. A surface-coated steel sheet as defined in Claim 8, wherein the resin coating film contains a surface-roughening agent.

17. A surface-coated steel sheet as defined in any of Claims 1 to 16, wherein the resin coating film is formed in an amount of 0.5-8.0 g/m<sup>2</sup>.

18. A surface-coated steel sheet as defined in any of Claims 1 to 16, wherein the plated or unplated steel sheet has controlled tensile properties.

19. A surface-coated steel sheet as defined in Claim 17, wherein the plated or unplated steel sheet has controlled tensile properties.

20. A surface-coated steel sheet as defined in any of Claims 1 to 16, wherein the plated or unplated steel sheet has an arithmetic average surface roughness (Ra) not larger than 0.30  $\mu\text{m}$  which is measured according to JIS B0601.

21. A surface-coated steel sheet as defined in Claim 17, wherein the plated or unplated steel sheet has an arithmetic average surface roughness (Ra) not larger than 0.30  $\mu\text{m}$  which is measured according to JIS B0601.

22. A surface-coated steel sheet as defined in Claim 18,





wherein the plated or unplated steel sheet has a yield point no lower than 200 N/mm<sup>2</sup> and/or a tensile strength no lower than 300 N/mm<sup>2</sup>.

23. A surface-coated steel sheet as defined in Claim 19, wherein the plated or unplated steel sheet has a yield point no lower than 200 N/mm<sup>2</sup> and/or a tensile strength no lower than 300 N/mm<sup>2</sup>.

24. A surface-coated steel sheet as defined in Claim 20, wherein the plated or unplated steel sheet has a yield point no lower than 200 N/mm<sup>2</sup> and/or a tensile strength no lower than 300 N/mm<sup>2</sup>.

25. A surface-coated steel sheet as defined in Claim 21, wherein the plated or unplated steel sheet has a yield point no lower than 200 N/mm<sup>2</sup> and/or a tensile strength no lower than 300 N/mm<sup>2</sup>.

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