

DESCRIPTION

5        A HEAT RESISTANT ADHESIVE INSULATIVE COATING, AND  
         AN ELECTRICAL STEEL SHEET WITH SUCH COATING,  
         A MAGNETIC CORE USING SUCH ELECTRICAL STEEL SHEET, AND  
         A METHOD OF PRODUCTION OF THE SAME

TECHNICAL FIELD

10        The present invention relates to a heat resistant  
         adhesive coating composition enabling adhesion by  
         stacking, pressing and heating (in the present invention,  
         unless otherwise described, "heating" means heating at  
         temperatures between room temperature and 300°C) and  
15        further keeping the adhesiveness after annealing such as  
         stress relief annealing (in the present invention, unless  
         otherwise described, "annealing" means heating at  
         temperatures above 300°C), and a surface coated electrical  
         steel sheet.

BACKGROUND ART

20        Electrical steel sheet is used mainly as magnetic  
         core for motors, transformers and the like. Generally,  
         the electrical steel sheet is coated on its surface with  
         an insulative coating. The sheet is successively punched  
         into predetermined shapes, stacked and connected together  
25        by welding, by the method known as "interlocking" wherein  
         recessed and projecting parts are fitted together, or by  
         other methods to form a magnetic core.

30        Thus laminated magnetic core is either used in as-  
         punched condition in electrical equipment or annealed at  
         a temperature of about 700°C to 800°C, then assembled into  
         electrical equipment. The latter annealing is called  
         "stress relief annealing" and is applied to magnetic  
         cores used for applications of electrical equipment  
         required for a high electrical efficiency, for the  
35        purpose of relieving the stress introduced to steel sheet  
         at the time of punching or cutting, thermal strain at the

end faces due to welding, plastic deformation strain of the interlocked parts and the like so as to improve the electrical properties of the magnetic core.

5       The method of welding or interlocking to connect the stacked electrical steel sheets has the problem of short-circuit at the edges of the laminations and lowering of the surface resistivity or the problem of deterioration of the electrical properties due to crookedness in processing. As a method for avoiding the defects due to  
10       welding or interlocking, a technique has been proposed of insulative coating which exhibits adhesion by hot pressing precoated on an electrical steel sheet, punching or cutting the sheet, stacking and hot pressing the laminations.

15       For example, Japanese Patent No. 2613725 proposes a method of manufacturing electrical steel sheet precoated on its surface with a mixed solution mainly comprised of an acryl-modified epoxy resin emulsion containing a latent curing agent followed by incomplete curing of the  
20       coating. Japanese Patent Publication (A) No. 2002-260910 discloses an electrical steel sheet with an insulative coating precoated with an adhesive resin including a foam agent. The techniques of Japanese Patent Publication (B) No. 55-9815 and Japanese Patent Publication (A) No. 2-  
25       208034 have also been proposed. These so-called adhesive coating techniques can alleviate the problems caused with interlocking or welding, but since these techniques use only organic compositions to coat the surfaces of the steel sheets, most of the compositions break down at a  
30       temperature of 300°C or more if stress relief annealing is applied, deteriorating adhesive strength. For this reason, there was the problem that electrical steel sheet with adhesive coatings can be used for magnetic cores not subjected to stress relief annealing, and cannot be used  
35       for magnetic cores subjected to stress relief annealing for the purpose of reducing core loss.

On the other hand, a method may be considered

wherein an electrical steel sheet are processed to predetermined shapes with punching or so, stress relief annealed, and connected with an adhesive for adhesion, but this would require application of an adhesive on each  
5 small punched out piece, so the workability would be poor.

Further, Japanese Patent Publication (B) No. 42-24519, Japanese Patent Publication (A) No. 58-128715, and Japanese Patent Publication (B) No. 47-47499 disclose  
10 coatings containing no resin compositions called "inorganic coatings". The coating of Japanese Patent Publication (B) No. 42-24519 does not have the function of adhering steel sheets with each other, so interlocking or welding or other fastening methods has to be used to  
15 obtain a magnetic core. The coatings disclosed in Japanese Patent Publication (A) No. 58-128715 and Japanese Patent Publication (B) No. 47-47499 are inorganic coatings comprised of only low melting point glasses, resulted in the coatings hard and abrading dies  
20 and therefore have the problem of a large amount of powder.

#### DISCLOSURE OF THE INVENTION

The present invention provides a heat resistant adhesive insulative coating with improved heat  
25 resistivity which maintains adhesiveness and insulative ability even after stress relief annealing, an electrical steel sheet with such coating, a magnetic core using such electrical steel sheet, and a method of production of the same.

30 To solve this problem, the present invention uses the following means:

(1) A heat resistant adhesive insulative coating including a resin with a softening point of room temperature to 300°C and a low melting point inorganic  
35 composition with a softening point of not more than 1000°C.

(2) A heat resistant adhesive insulative coating as

set forth in (1), characterized in that a 250°C adhesive strength is 10 kg/cm<sup>2</sup> or more and a 750°C adhesive strength is 1 kg/cm<sup>2</sup> or more.

5 (3) A heat resistant adhesive insulative coating as set forth in (1), characterized in that a coefficient of linear heat expansion at 30°C to 300°C is  $10 \times 10^{-7} (^{\circ}\text{C}^{-1})$  to  $150 \times 10^{-7} (^{\circ}\text{C}^{-1})$ .

10 (4) A heat resistant adhesive insulative coating as set forth in (4), characterized in that the low melting point inorganic composition is a low melting point glass frit, water glass, or these in which colloidal silica is further mixed.

15 (5) A heat resistant adhesive insulative coating as set forth in (4), characterized in that low melting point inorganic composition has an average particle size of 20  $\mu\text{m}$  or less.

20 (6) A heat resistant adhesive insulative coating as set forth in (4), characterized in that a mixing ratio of the resin to the low melting point inorganic composition is, by mass percent, 20% to 500%.

(7) A heat resistant adhesive insulative coating as set forth in (4), characterized in that the low melting point inorganic composition is an  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ -based low melting point glass (R is an alkali metal).

25 (8) A heat resistant adhesive insulative coating as set forth in (4), characterized in that said water glass is sodium silicate.

30 (9) A heat resistant adhesive insulative coating as set forth in (1), characterized in that said resin includes one or more types of resin selected from an epoxy resin, acrylic resin, phenol resin, incompletely cured resin mainly comprised of an acryl-modified epoxy resin emulsion containing a latent curing agent, or a siloxane polymer.

35 (10) An electrical steel sheet with a heat resistant adhesive insulative coating comprised of steel sheet

having on at least one surface a coating as set forth in (1).

5 (11) An electrical steel sheet with a heat resistant adhesive insulative coating as set forth in (10), characterized in that the heat resistant adhesive insulative coating has a thickness of 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

(12) A magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating as set forth in (10).

10 (13) A method of production of a magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating comprising stacking and pressing electrical steel sheets as set forth in (10) to form an electrical steel sheet laminations, then annealing these  
15 at a temperature between 600 and 900°C to obtain a laminated magnetic core.

(14) A method of production of a magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating as set forth in (13), further  
20 comprising, at least in the step of pressing, connecting them by heating to adhere or connecting them by interlocking or fixtures or both of these.

) The insulative coating of the electrical steel sheet of the present invention is a composite to develop two  
25 types of adhesive ability. As the specific means for this, the coating includes a resin with a softening point of room temperature to 300°C and a low melting point inorganic composition having a softening point evaluated by differential thermal analysis method of 1000°C or less.  
30 The coating resin softens at hot pressing to function to adhere the magnetic core to connect together, while the low melting point inorganic composition functions to keep the adhesion of the magnetic core at stress relief annealing.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a general differential

thermal analysis curve of glass.

FIG. 2 is a schematic view of a ladder siloxane polymer.

#### BEST MODE FOR WORKING THE INVENTION

5 To relief strain from steel sheet, an annealing temperature of about 700°C to 800°C is generally required. Under this annealing temperature, organic composition ends up breaking down and cannot maintain its structure, thus the adhesiveness cannot be maintained. The inventors  
10 thought that inorganic compounds would be able to maintain their structures and could develop adhesion between laminations even at a high temperatures of 700°C to 800°C and studied various types of inorganic compounds. As a result, they have found that a group of low melting  
15 point inorganic compositions called "low melting point glass frit", and water glass, colloidal silica, and other low melting point inorganic compositions develop good adhesion of steel sheets at the annealing temperature around 750°C. However, since these low melting point  
20 inorganic compositions alone do not develop adhesion before completion of annealing, they cannot hold the magnetic core together. Therefore, the inventors have found that by combining a resin with these, a magnetic core adhesively connected before and after stress relief  
25 annealing can be obtained.

First, the low melting point inorganic compositions will be explained below. The inventors have found that the factor governing the quality of the adhesion at the temperature around stress relief annealing is the  
30 softening point of the low melting point inorganic composition.

The experiments for the present invention will be described in detail from the following description.

35 The present inventors confirmed the importance of above-mentioned softening point using samples under the following conditions and evaluating their adhesive

strength. A number of non-oriented electrical steel sheets with thicknesses of 0.5 mm without insulative coatings are prepared and coated using roll coaters with mixtures of low melting point inorganic compositions constituted by low melting point glass frit having average particle sizes of 5  $\mu\text{m}$  and various softening point, and resins constituted by epoxy resin:acrylic resin:phenol resin = 15:3:3 (mass%) in 20 mass% solid content aqueous emulsions. The ratio of resins to glass frits was adjusted to 100% in terms of solid content, i.e. the same mass. The amount of coating was 8 g/m<sup>2</sup> per side. The sheets were dried at 160°C. Test pieces were cut out from the samples and adhesive strengths at 250°C and 750°C were evaluated.

Here, the "softening point" is the temperature of bending point observed fourth after the start of measurement on a measurement curve of the differential thermal analysis method shown in FIG. 1 or the temperature of JIS-R3103-1 "Glass Softening Point Test Method" (ISO 7884-6: 1987, ASTM C338), whichever is lower, but when evaluation by both of these methods is difficult, another softening point may also be used instead.

The "250°C adhesive strength" is the strength between the two sample pieces of 10 cm (rolling direction length) x 3 cm (length perpendicular to the rolling direction) overlapped in shorter sides by 1 cm over an area of 3 cm<sup>2</sup>, adhered under a pressure of 10 kg/ 3 cm<sup>2</sup> at 250°C for 60 seconds. The strength was obtained by the measurements of a spring balance (kg) at the time of separation when the sample pieces were pulled off at room temperature in the rolling direction, divided by the area of 3 cm<sup>2</sup>. Note that in the present invention, the pressure and adhesive strength are indicated as measurements of a spring balance (kg) divided by area, kg/cm<sup>2</sup> which corresponds to  $9.8 \times 10^4$  Pa.

5      The "750°C adhesive strength" is the strength obtained by the measurements when the sample pieces are further heated without pressing at 750°C for 2 hours and pulled off at room temperature in the rolling direction, divided by the area of 3 cm<sup>2</sup>. The results of the tests are shown in Table 1.

Table 1

| Condi-<br>tion<br>no. | Composition (mass%)           |                  |     |                                |     |     |                  |                                |                               |     |     | Softening<br>point | Adhesive strength:<br>kg/cm <sup>2</sup> |             |
|-----------------------|-------------------------------|------------------|-----|--------------------------------|-----|-----|------------------|--------------------------------|-------------------------------|-----|-----|--------------------|------------------------------------------|-------------|
|                       | B <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | ZnO | Al <sub>2</sub> O <sub>3</sub> | BaO | MgO | K <sub>2</sub> O | Bi <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | SnO | PbO |                    | 250°C                                    | 750°C       |
| 1                     | 50                            | -                | -   | -                              | -   | -   | -                | -                              | -                             | -   | 50  | 300°C              | 30                                       | 3           |
| 2                     | -                             | -                | -   | -                              | -   | -   | -                | -                              | 50                            | 50  | -   | 350°C              | 40                                       | 5           |
| 3                     | 15                            | 5                | -   | -                              | -   | -   | -                | 80                             | -                             | -   | -   | 400°C              | 30                                       | 8           |
| 4                     | 25                            | 15               | 15  | 5                              | 30  | 10  | -                | -                              | -                             | -   | -   | 525°C              | 20                                       | 7           |
| 5                     | 20                            | 20               | -   | 5                              | 55  | -   | -                | -                              | -                             | -   | -   | 675°C              | 30                                       | 6           |
| 6                     | 20                            | 70               | -   | -                              | -   | -   | 10               | -                              | -                             | -   | -   | 760°C              | 40                                       | 7           |
| 7                     | 50                            | -                | 10  | 15                             | 15  | 10  | -                | -                              | -                             | -   | -   | 880°C              | 20                                       | 3           |
| 8                     | -                             | 50               | -   | 35                             | -   | 15  | -                | -                              | -                             | -   | -   | 1000°C             | 10                                       | 1           |
| 9                     | -                             | 45               | -   | 40                             | -   | 15  | -                | -                              | -                             | -   | -   | 1050°C             | 10                                       | No adhesion |

From Table 1, it has been learned that under condition nos. 1 to 8 using glass frit with a softening point of 1000°C or less, the 250°C adhesive strength is 10 kg/cm<sup>2</sup> or more and the 750°C adhesive strength is 1 kg/cm<sup>2</sup> both of them being good. On the other hand, under condition no. 9 using glass frit with a softening point of 1050°C, while the 250°C adhesive strength is as good as 10 kg/cm<sup>2</sup>, the 750°C adhesive strength is too weak to measure because the coated surface easily peeled off.

From the results described above, it has been learned that when using glass frit with a softening point of 1000°C or less, the 250°C adhesive strength is 10 kg/cm<sup>2</sup> or more and the 750°C adhesive strength is 1 kg/cm<sup>2</sup> both properties being good.

Regarding the reason why the 750°C adhesive strength depends on the softening point of the low melting point inorganic composition, the inventors considered the following mechanism. At the time of pressing and heating near 250°C, the resin softens and melts. In the case of coating both sides, the coating interface disappears and adhesion between coatings is achieved. However, the low melting point inorganic composition having higher temperature stability undergoes almost no reaction at the time. Next, when heating at 750°C, this time the low melting point inorganic composition softens and, depending on the type of the low melting point inorganic composition, melts, whereby the low melting point inorganic compositions contacting each other adhesive. As a result, the facing coatings are laminated and the adhesion between the steel sheets becomes complete. Therefore, the low melting point inorganic composition softening or melting at the stage of heating near 750°C is important.

Since low melting point inorganic composition with a high softening point such as condition no. 9 of Table 1

does not soften or melt at around 750°C, sufficient contact area cannot be obtained between them even if they contact each other so that insufficient bond is formed between them. As a result, the enough adhesive strength cannot be obtained.

On the other hand, since low melting point inorganic compositions with low softening point such as condition nos. 1 to 8 of Table 1, softens at around 750°C, a certain contact area can be obtained between them if they contact each other so that sufficient bond is formed between them. As a result, enough adhesive strength can be obtained.

The reason why a certain extent of 750°C adhesive strength is obtained even in the low melting point inorganic compositions with softening points of 880°C or 1000°C which are higher than the heating temperature, 750°C, has not been elucidated, but present inventors think that softening like reaction occurs at around 750°C even in those compositions which thereby integrates the coating and adheres the steel sheets.

The 250°C adhesive strength is set to 10 kg/cm<sup>2</sup> or more to enable handling of the core without separation after the step of temporary adhesion at the low temperature until the core is completely adhered at higher temperature. Further, the 750°C adhesive strength is set to 1 kg/cm<sup>2</sup> or more to enable preventing separation of the core after assembly into electrical equipment.

For the low melting point inorganic composition of the present invention, for example, low melting point glass frit, water glass, and a mixture of these with colloidal silica may be used.

When the low melting point inorganic composition is an inorganic powder, the particle size is also important. If the particle size is too large, the coating surface forms with coarse projections inhibiting contact between the coatings. To realize sufficient contact in the

coatings or between powders, the particle sizes of the low melting point inorganic ingredient used are preferably 20  $\mu\text{m}$  or less, more preferably, 4  $\mu\text{m}$  or less, and particularly 3  $\mu\text{m}$  or less.

5       Next, the inventors studied the mixing ratio between the low melting point inorganic composition and resin.

10       The inventors prepared a number of non-oriented electrical steel sheets having thicknesses of 0.35 mm with insulative coatings mainly comprised of magnesium chromate. These were coated using roll coaters with a mixture containing a low melting point inorganic composition constituted by low melting point glass frit having an average particle size of 3  $\mu\text{m}$  and a softening point of 550°C ( $\text{B}_2\text{O}_3=30\%$ ,  $\text{SiO}_2=20\%$ ,  $\text{BaO}=30\%$ ,  $\text{Na}_2\text{O}=10\%$ ,  $\text{ZnO}=10\%$ ), and an aqueous emulsion of resin composition of 20 mass% solid content constituted by epoxy resin:acrylic resin:phenol resin =20:5:3 (mass%). At this time, the mixing ratio of the resin to the glass frit was variously changed. The amount of coating was 5 g/m<sup>2</sup> per side. The sheets were dried at a temperature of 150°C. Test pieces were cut out from the samples. The 250°C and 750°C adhesive strength were then evaluated. The results of the tests are shown in Table 2.

Table 2

| Condition no. | Resin/glass frit mixing ratio (mass%) | Adhesive strength: kg/cm <sup>2</sup> |       |
|---------------|---------------------------------------|---------------------------------------|-------|
|               |                                       | 250°C                                 | 750°C |
| 1             | 10                                    | 5                                     | 0.5   |
| 2             | 20                                    | 10                                    | 2     |
| 3             | 50                                    | 20                                    | 5     |
| 4             | 100                                   | 40                                    | 6     |
| 5             | 300                                   | 50                                    | 4     |
| 6             | 500                                   | 40                                    | 1     |
| 7             | 700                                   | 40                                    | 0.5   |

As shown in Table 2, condition nos. 2 to 6, i.e. a resin/glass frit mixing ratios of 20% to 500%, had excellent adhesion strength both at 250°C of 10 kg/cm<sup>2</sup> or more and at 750°C of 1 kg/cm<sup>2</sup>. On the other hand, condition no. 1 with the ratio of 10% had less adhesive strengths of 5 kg/cm<sup>2</sup> at 250°C and 0.5 kg/cm<sup>2</sup> at 750°C. Condition no. 7 with a resin/glass frit mixing ratio of 700% had good adhesive strength of 40 kg/cm<sup>2</sup> at 250°C but bad adhesive strength of 0.5 kg/cm<sup>2</sup> at 750°C. These results show that, both the 250°C and 750°C adhesive strength are good when the mixing ratios of resin/glass frit are 20% to 500%.

Regarding the reason why the adhesive strength is dependent on the ratio of resin to low melting point inorganic composition, the inventors have an understanding of the following mechanism. The resin shares a function of adhesion when heated at 250°C, while the low melting point inorganic composition share a function of adhesion when heated at 750°C. Considering the development of the function of each composition at each heating temperature, the mechanism of dependence of adhesive strength on the ratio of both composition can be deduced. That is the consideration of the state of surface occupancy of the organic resin when heated at 250°C while that of the low melting point inorganic composition when heated at 750°C.

When the ratio of resin to low melting point inorganic composition is small, for example, like in

condition no. 1 of Table 2, the majority of the surface are covered by the inorganic composition, resulting in almost no resin appeared on the surface of the coating. If such coatings are superposed, pressed, and heated at 250°C, the resin cannot sufficiently function as binder between the coatings because of insufficient contact area between them resulting in small 250°C adhesive strength such as 5 kg/cm<sup>2</sup> in no. 1. In such condition, insufficient contact and adhesion between low melting point inorganic compositions are obtained even if such coatings are heated at 750°C whereby the low melting point inorganic composition softens and melts. As a result, 750°C adhesive strength also becomes small such as 0.5 kg/cm<sup>2</sup> in the case of condition no. 1. Due to above mentioned mechanism, if the ratio of resin to low melting point inorganic composition is too small, the adhesive strength at both 250°C and 750°C are low.

On the other hand, if the mixing ratio of resin to low melting point inorganic composition is large, while the coating surface has enough resin to perform sufficient adhesive function resulting in good 250°C adhesive strength obtained such as 40 kg/cm<sup>2</sup> as shown in condition 7, the low melting point inorganic composition is not sufficiently present on the coating surface resulting in small 750°C adhesive strength such as 0.5 kg/cm<sup>2</sup> in the case of condition no. 7.

Coefficients of linear heat expansion of the low melting point inorganic composition from 30°C to 300°C in the range of  $10 \times 10^{-7}$  to  $150 \times 10^{-7}$  (°C<sup>-1</sup>) prevent variations in electrical properties of magnetic cores.

The inventors prepared magnetic cores made of steel sheets with coatings under the following conditions and the magnetic properties are evaluated. A number of non-oriented electrical steel sheets with thicknesses of 0.5 mm without any insulative coatings on their surfaces are prepared. They are coated with mixtures of low melting

point glass frit having an average particle size of 5  $\mu\text{m}$  and various heat expansion coefficients as low melting point inorganic compositions, and a resin aqueous emulsions of 20 mass% solid content constituted by epoxy resin:acrylic resin:phenol resin =10:4:5 (mass%) using roll coaters. The mixing ratios of resin to the glass frit was adjusted to 200% in solids content. The amount of coating was 10  $\text{g}/\text{m}^2$  per side and the sheets was dried at a sheet temperature of 150°C.

10 From these samples, ring shaped samples having inside diameters of 10.16 cm (4 inch) and outside diameters of 12.7 cm (5 inch) were prepared. Twenty of these were stacked, pressed at 10  $\text{kg}/\text{cm}^2$  and heated at 250°C for 4 hours to prepare magnetic cores laminated with  
15 adhesive coating. The magnetic cores were annealed without pressing at 750°C for 2 hours and core losses were evaluated at 50 Hz with a magnetic flux density of 1.5 Tesla. The results are shown in Table 3.

Table 3

| Condi-<br>tion<br>no. | Composition (mass%)           |                  |     |                                |     |     |                  |                                |                               |     |     | Coefficient of<br>linear heat<br>expansion<br>(°C <sup>-1</sup> ) | Core<br>loss<br>(W/kg) |
|-----------------------|-------------------------------|------------------|-----|--------------------------------|-----|-----|------------------|--------------------------------|-------------------------------|-----|-----|-------------------------------------------------------------------|------------------------|
|                       | B <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | ZnO | Al <sub>2</sub> O <sub>3</sub> | BaO | MgO | K <sub>2</sub> O | Bi <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>5</sub> | SnO | PbO |                                                                   |                        |
| 1                     | 45                            | 30               | -   | -                              | -   | -   | 25               | -                              | -                             | -   | -   | 160 x 10 <sup>-7</sup>                                            | 3.27                   |
| 2                     | -                             | -                | -   | -                              | -   | -   | -                | -                              | 45                            | 55  | -   | 150 x 10 <sup>-7</sup>                                            | 3.08                   |
| 3                     | -                             | -                | 20  | -                              | -   | -   | -                | -                              | 40                            | 40  | -   | 135 x 10 <sup>-7</sup>                                            | 3.03                   |
| 4                     | 10                            | 5                | -   | -                              | -   | -   | -                | 85                             | -                             | -   | -   | 105 x 10 <sup>-7</sup>                                            | 3.05                   |
| 5                     | 20                            | 15               | -   | 5                              | 60  | -   | -                | -                              | -                             | -   | -   | 90 x 10 <sup>-7</sup>                                             | 3.07                   |
| 6                     | 45                            | -                | 15  | 10                             | 20  | 10  | -                | -                              | -                             | -   | -   | 80 x 10 <sup>-7</sup>                                             | 3.02                   |
| 7                     | 55                            | -                | -   | -                              | -   | -   | -                | -                              | -                             | -   | 45  | 55 x 10 <sup>-7</sup>                                             | 3.06                   |
| 8                     | 25                            | 65               | -   | -                              | -   | -   | 10               | -                              | -                             | -   | -   | 30 x 10 <sup>-7</sup>                                             | 3.04                   |
| 9                     | -                             | 45               | -   | 40                             | -   | 15  | -                | -                              | -                             | -   | -   | 10 x 10 <sup>-7</sup>                                             | 3.09                   |
| 10                    | -                             | 100              | -   | -                              | -   | -   | -                | -                              | -                             | -   | -   | 5 x 10 <sup>-7</sup>                                              | 3.26                   |

As shown in Table 3, under condition nos. 2 to 9 using low melting point inorganic composition having a coefficient of linear heat expansion from 30°C to 300°C in the of  $10 \times 10^{-7} (^{\circ}\text{C}^{-1})$  to  $150 \times 10^{-7} (^{\circ}\text{C}^{-1})$ , the core losses  
5 of magnetic cores after annealing are good smaller than 3.1 (W/kg). On the other hand, under condition no. 1 using glass frit having a coefficient of linear heat expansion of  $160 \times 10^{-7} (^{\circ}\text{C}^{-1})$ , the core loss value was as large as 3.27 (W/kg) and under condition no. 10 using  
10 glass frit having a coefficient of linear heat expansion of  $5 \times 10^{-7} (^{\circ}\text{C}^{-1})$ , the core loss was also as large 3.26 (W/kg). These results show that when the low melting point inorganic composition has a coefficient of linear heat expansion from 30°C to 300°C in the range of  $10 \times 10^{-7}$   
15  $(^{\circ}\text{C}^{-1})$  to  $150 \times 10^{-7} (^{\circ}\text{C}^{-1})$ , the core loss of magnetic core after annealing is good.

Regarding the reason why the core loss of magnetic core after annealing is dependent on the coefficient of linear heat expansion of the low melting point inorganic  
20 composition, the inventors have an understanding of the following mechanism. The pressing and hot adhesion at 250°C cause the resin in the coating to soften and melt, the interface of the coatings disappears if the sheet is coated on both sides and they are bonded with each other  
25 remaining the inorganic composition in almost no reaction. When the sheets are heated at 750°C, the low melting point inorganic composition softens and melts depending on the type of them and the contacting low melting point inorganic compositions bond with each  
30 other. As a result, the facing coatings are adhered together and the steel sheets are completely bonded together followed by the core losses evaluated after cooling to room temperature. An important consideration here is the stress developed in the magnetic core when  
35 all the surfaces of the steel sheets are adhered at a high temperature of 750°C and are cooled down to room

temperature.

In general, the magnetic properties of magnetic core deteriorate if the core has stress. Here, the relationship between the coefficient of heat expansion of a substance and stress will be explained. When the materials with high and low coefficients of heat expansion are adhered at a high temperature and then cooled down to room temperature, tensile stress is formed in the material with high coefficient and compressive stress is formed in the material with small coefficient. Electrical steel sheet, both grain-oriented and non-oriented, has a coefficient of linear heat expansion of about  $100 \times 10^{-7} (^{\circ}\text{C}^{-1})$ . On the other hand, the low melting point inorganic compositions used for the experiment have the coefficients of  $5 \times 10^{-7} (^{\circ}\text{C}^{-1})$  to  $160 \times 10^{-7} (^{\circ}\text{C}^{-1})$ . Therefore, when inorganic powder having the coefficient smaller than the steel sheet are used, a tensile stress are formed in the steel of the magnetic core, while when inorganic powder having a coefficient of heat expansion larger than the steel sheet is used, a compressive stress are formed in the steel of the magnetic core.

In this experiment, it is considered that a large compressive force is formed in the magnetic core of condition no. 1 having the highest coefficient, while a large tensile stress is formed in the magnetic core of condition no. 10 having the smallest coefficient. Since the coefficients of linear heat expansion are in these two conditions have largest differences from that of steel sheet, the largest stresses are seems to be formed in the cores tested. On the other hand, although the coefficients are different from that of the steel sheet in condition nos. 2 to 9, since the differences are small, tensile stress or compressive stress formed in the magnetic cores were small if any resulting little effect on the core losses.

The low melting point inorganic composition of the present invention contributes to the development of the

adhesion after stress relief annealing and is preferably a low melting point glass having a softening point of not more than the normal stress relief annealing temperature of 750°C. Since low melting point glass softens and melts during stress relief annealing and hardens upon cooling, two sheets using the glass can be adhered after stress relief annealing. Following compositions may be used as the low melting point glass,  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$  (R shows an alkali metal here),  $\text{P}_2\text{O}_5\text{-R}_2\text{O}$  (R shows an alkali metal)-based composition,  $\text{SiO}_2\text{-PbO-B}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3\text{-Bi}_2\text{O}_3$ ,  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO}$ ,  $\text{SnO-P}_2\text{O}_5$ ,  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZrO}_2$  and the like. In particular, an  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$  is preferable because it is lead-free and has a high adhesive strength after stress relief annealing.

The low melting point inorganic composition may be in liquid like water glass. In the water glass, sodium silicate is particularly preferable. The advantage of using water glass is to easily obtain flat coated surface free from unevenness due to particles since no powder particles are included in water glass. In particular, a high adhesive strength after stress relief annealing of 1.0 MPa or more is obtained when using sodium silicate. Further, when using potassium silicate, an adhesive strength of a high 4.0 to 7.0 MPa is obtained before stress relief annealing.

The low melting point inorganic composition of the present invention used may be the above-mentioned inorganic compositions further mixed with colloidal silica. By mixing colloidal silica etc., it is possible to adjust the viscosity at stress relief annealing when the inorganic composition softens. Further, remaining colloidal silica without softening during the stress relief annealing functions as an supporting elements in the coating and raises the strength of adhesive coating after stress relief annealing.

The resin able to be used in the present invention may be not only a heat curable resin such as a phenol resin or epoxy resin which undergoes a curing reaction

when adhesion of steel sheets by pressing and heating, but also a thermoplastic resin such as an acrylic resin or methacrylic resin which does not undergo a curing reaction even if heated may also be used. Either a  
5 thermoplastic or heat curable resin may be used, but a resin having a adhesiveness is preferable.

The resin of the present invention softens at temperatures from room temperature to 300°C. Considering blocking etc., preferable resins are those which soften  
10 to an extent expressing fluidity at no less than 50°C, 80°C, 100°C, or more preferably 120°C but not more than 300°C. Softening "to an extent expressing fluidity" means a viscosity of about  $1 \times 10^8$  dPa·s or less. As the mechanism by which a cured resin on the surface of a  
15 steel sheet softens due to heating at 300°C or less, the case where the resin is a thermoplastic and the temperature expressing thermoplasticity is 120°C to 300°C may be possible.

Further, as the mechanism by which a heat curable  
20 resin softens, the case of heating to a temperature higher than the glass transition temperature so as to soften the resin to a rubbery state or fluid state of the resin may be possible. Especially, in the case of a resin cured at a temperature as low as 200°C or less for a short  
25 time of about tens of seconds or less, the heating sometimes causes a glass transition although cross-linking reaction which forms a three-dimensional skeleton also occurs. When such resin is heated to a higher temperature, the cross-linking reaction again prevails  
30 and the resin is cured.

The acryl-modified epoxy resin emulsion containing a latent curing agent used as the resin in the present invention is an emulsion obtained by mixing a latent  
35 curing agent with an epoxy resin reacted with an acrylic resin to cover the mixture of the epoxy resin and latent curing agent. The "epoxy resin" referred to here

indicates a resin having two or more epoxy groups in the monomer including the following types: bisphenol A, bisphenol F, bisphenol AD, naphthalene, phenol novolac, o-cresol novolac, glycidyl ester, alicyclic types and the like. As the latent curing agent, dicyandiamide, melamine, organic acid dihydrazide, aminoimide, kelamine, tertiary amine salts, imidazole salts, trifluoroboro amine salts, a microcapsule type curing agent, molecular sieve type curing agent and so on. The mixture of the above epoxy resin and epoxy resin curing agent is modified by an acrylic resin.

The word "modified" referred to here means causing an acrylic resin to be chemically-bond to the surface of the mixture of epoxy resin and epoxy resin curing agent. The acrylic resin used for this modification may include the followings or the combination of those polymerized or copolymerized: methacrylic acid, a methacrylic acid ester, acrylic acid, an acrylic acid ester, styrene, vinyl acetate and the like. The ratio of epoxy resin to latent epoxy resin curing agent in the mixture changes greatly depending on the type of the epoxy resin and the curing agent, but usually 0.05 to 2 parts by mass with respect to 1 part by mass of the epoxy resin is suitable. The mixture mainly comprised of the acryl-modified epoxy resin emulsion containing a latent curing agent has to be coated on the surface of the steel sheet in advance, and baked to an incompletely cured state. This state means a state free from sticking or blocking and still having an adhesive when pressed and heated after cutting and stacking. Usually, the incompletely cured state can be made by drying at a 100 to 300°C oven temperature for 10 to 90 seconds.

Further, as the resin which softens upon heating, a siloxane polymer may be used. A siloxane polymer is a polymer having Si-O-Si inorganic bonds comprising the main skeleton. Si, like C, can directly chemically bond with organic groups or H such as with Si-CH<sub>3</sub>, Si-C<sub>6</sub>H<sub>5</sub>, and

Si-H, so it is possible to obtain a siloxane polymer with organic groups or H at the skeleton.

5 A structure where one of the four Si bond arms forms an Si-R (R shows an organic group or H here) bond and the other three form Si-O bonds is called a "T nucleus". A structure in the T nucleus where there are three bonds with Si through O, i.e.  $R-Si(-O-Si)_3$ , is called a "T3 nucleus". The type of Si nucleus can be evaluated by NMR. In addition to the T nucleus, there are a D nucleus and a Q nucleus as the Si nucleuses which form siloxane polymers. A D nucleus is a structure in which two of the four bond arms of Si form Si-R (R shows an organic group or H) bonds and the remaining two form Si-O bonds. A Q nucleus is a structure in which four of the found Si bond arms form Si-O bonds.

15 When the Si's of T3 nuclei repeatedly bond in accordance with a certain rule, a ladder like molecule is formed such as shown in FIG. 2.

20 A polymer comprised of a ladder like molecule becomes entangled in ladder shaped molecular chains upon coating and baking to give a hard surface state free from stickiness or blocking. The entangled molecular chains unravel at 100°C or more to exhibit fluidity. If in a range exhibiting fluidity, in addition to Si nuclei to which methyl groups are bonded, Si nuclei to which epoxy groups are bonded may also be contained.

25 The siloxane polymer of the present invention is obtained by hydrolysis in the presence of a hydrochloric acid catalyst using one or both of organotrialkoxysilane or organotrichlorosilane as a starting material. As the organotrialkoxysilane, triethoxysilane, trimethoxysilane, methyl trimethoxysilane, methyl triethoxysilane, ethyl trimethoxysilane, ethyl triethoxysilane, propyl trimethoxysilane, propyl triethoxysilane, isobutyl trimethoxysilane, isobutyl triethoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, methacryloxypropyl trimethoxysilane, methacryloxypropyl

triethoxysilane, glycidoxypopyl trimethoxysilane, glycidoxypopyl triethoxysilane, aminopropyl trimethoxysilane, aminopropyl triethoxysilane, etc. may be mentioned. As an organotrichlorosilane, methyl  
5 trichlorosilane, ethyl trichlorosilane, phenyl trichlorosilane, etc. may be mentioned.

One or both of an organotrialkoxysilane and organotrichlorosilane may be dispersed in an organic solvent and then hydrolyzed. As the solvent, methanol,  
10 ethanol, propanol, butanol, or other various types of alcohols, acetone, toluene, xylene, etc. may be used. The mass ratio of the organic solvent to the organoalkoxysilane at the time of hydrolysis is preferably 1:0.5 to 1:2.

15 The hydrolysis is performed by adding water in an amount of 0.1 to 1 part of molar ratio to the number of moles of all of the alkoxy groups in the starting material. As the catalyst for the hydrolysis, hydrochloric acid is added. When using an  
20 organotrichlorosilane as the starting material, addition of water causes hydrochloric acid to be produced as a byproduct, so the hydrolysis is performed in the presence of a hydrochloric acid catalyst even without doing anything special and hydrochloric acid may not need be  
25 added.

The hydrolyzed sol usually is concentrated or otherwise processed to promote the polycondensation reaction and results in the siloxane polymer. Performing the concentration for example using a rotary evaporator  
30 it is preferred to remove the organic solvent or byproduct alcohol etc. and to obtain a concentrate of a mass of about 15 to 60% of the mass of the solution before concentration from the viewpoint of expression of softening by heating. As a method other than  
35 concentration, KOH or another alkali may be added and refluxing performed under a nitrogen atmosphere etc. to promote the polycondensation reaction to obtain the

siloxane polymer. The obtained siloxane polymer is diluted by an organic solvent or water about 1.5 to 10 fold to obtain a coating solution. Normally, by baking at 100°C to 200°C for 15 to 120 seconds, an adhesive condition under pressure and heating is obtained.

Note that the resin or low melting point inorganic composition in the present invention sometimes, depending on the heating and annealing atmosphere or other conditions, does not show any melting, at least in appearance, and remains in the state of particles in the coating of the present invention. If the heating and annealing causes the development of the adhering function, the appearance does not provide any problem in the present invention.

Although the present invention can be applied to any electrical steel sheet such as grain-oriented electrical steel sheet, non-oriented electrical steel sheet, etc. manufactured by ordinal rolling and annealing process regardless of type, the effects are most exhibited when applied to non-oriented electrical steel sheet used for magnetic cores for motor.

In the usual process of manufacturing grain-oriented electrical steel sheet or non-oriented electrical steel sheet, the steel sheets are finish annealed, then a coating is applied on the steel sheet. In the case of grain-oriented electrical steel sheet, a phosphate based coating including silica is formed, while in the case of non-oriented electrical steel sheet, a chromate coating is formed. In the case of grain-oriented electrical steel sheet, there are methods forming a film mainly comprised of a forsteritic silicate during the finish annealing, a method of not allowing its formation, or a method removing the formed forsteritic film by pickling or other means. The present invention can be applied regardless of the presence of surface film.

The electrical steel sheet with a heat resistant adhesive insulative coating of the present invention is

obtained by coating electrical steel sheet with a coating solution including the heat resistant adhesive insulative coating composition using a roll coater, bar coater, flow coater, dip coater, spraying, or another method. The  
5 amount of coating is preferably 1 g/m<sup>2</sup> to 30 g/m<sup>2</sup>, more preferably 2 g/m<sup>2</sup> to 10 g/m<sup>2</sup>.

The heat resistant adhesive insulative coating composition is preferably comprised of a resin and a low melting point inorganic composition mixed together, but  
10 may also be applied in condition where the two components are mixed in blocks or in condition where the two are coated separately in two layers. Or it may be comprised of a matrix formed by an organic ingredient in which the low melting point inorganic composition is dispersed in a  
15 dot, stripe, or may be comprised of an inorganic matrix of siloxane bonds etc. in which an organic ingredient is dispersed in a dot or point form.

The coating thickness is preferably 0.5 μm to 20 μm per side. If the coating thickness is less than 0.5 μm,  
20 the entire surface of the steel sheet may not be sufficiently covered resulting in insufficient adhesive strength obtained, while if greater than 20 μm, the occupancy rate may sharply drop during pressing and heating. For this reason, a coating thickness of 0.5 μm  
25 to 20 μm is better.

The coating composition of the present invention is coated on the surface of the electrical steel sheet, then baked to cure it so that no sticking or blocking occurs. By baking at 50 to 200°C, an electrical steel sheet with a  
30 heat resistant adhesive insulative coating can be obtained. This step may be performed right before the parts of the magnetic core are punched out or the parts of the magnetic core are stacked, but coating in advance at the time of manufacturing of the steel sheet to obtain  
35 a so-called "pre-coated" electrical steel sheet is particularly preferable in the sense of streamlining the

process of production of magnetic cores. When stacking the pieces of steel sheet punched out from this steel sheet into the required shapes so as to form a connected laminations, the resin softens by heating to a  
5 temperature higher than the baking temperature.

When electrical steel sheet having the coating of the present invention on both surfaces are stacked and hot pressed, the resins softens and are merged with each other at the time of hot pressing, so the pieces of the  
10 electrical steel sheet can be adhered upon cooling.

When pieces of electrical steel sheet having the coating of the present invention on only one surface are stacked in the same orientation, the resin softened spreads evenly over the surfaces of the pieces of  
15 electrical steel sheet without the coating layer of the present invention, so the sheets can be adhered upon cooling. The hot pressing temperature is preferably not more than 300°C because higher hot pressing temperature is costly. The pressure of the hot pressing is preferably  
20 0.1 MPa to 50 MPa, preferably 1 MPa to 20 MPa. If the hot pressing pressure is too low, adhesion may be insufficient resulting in incomplete integration of the magnetic core. If the hot pressing pressure is too high, the adhesive layers may become fluid enough to seep out.

25 The electrical steel sheet of the present invention can be punched out to desired shapes, stacked, pressed and heated to obtain a laminated magnetic core. Even when the core is applied with stress relief annealing if required, the adhesion between the stacked steel sheets  
30 is maintained. The temperature of the stress relief annealing is usually 650°C to 850°C, and more often 700°C to 800°C.

Note that the coating of the present invention has adhesion even without stress relief annealing or other  
35 annealing, so can be utilized for magnetic cores not subjected to stress relief annealing as well. The coating

can be utilized as adhesive coating for stress relief annealed use and non-stress relief annealed use.

Further, when for stress relief annealed use, at the time of fastening by pressing and heating, fastening by interlocking or fixtures may also be combined.

Example 1

Aqueous suspensions each containing 20 mass% (on a mass basis of 100% total solids) resin comprised of acrylic resin:epoxy resin:phenol resin = 10:4:3 (mass%) mixed with glass frits having a softening point of 450°C and various particle sizes were prepared. The resin/glass frit mixing ratio in each solution containing the glass frit was adjusted to 200%. Each coating solution was coated on a finish annealed non-oriented electrical steel sheet having a thickness of 0.5 mm without insulative coating, using a roll coater to a coating amount of 6 g/m<sup>2</sup> per side. The sheet was dried at 150°C and cooled. The coating thickness per side was 10 µm. From each sample, test pieces of a length in the rolling direction of 10 cm and a length in the direction perpendicular to the rolling direction of 3 cm were cut out. Further, two such test pieces were overlaid to a length at the short sides of 1 cm and an overlap area of 3 cm<sup>2</sup>, pressed at 10 kg/cm<sup>2</sup>, heated to 250°C in that state, held there for 60 seconds, and cooled to prepare test pieces for the use of 250°C adhesive strength evaluation. Some of such test pieces were heated, without a load, to 750°C 2 hours and cooled to prepare test pieces for 750°C adhesive strength evaluation. The test pieces thus prepared were evaluated for adhesive strengths using a tensile tester. The results are shown in Table 4.

Table 4

| Condi-<br>tion<br>no. | Resin/glass frit<br>average particle<br>size: $\mu\text{m}$ | Adhesive strength: $\text{kg}/\text{cm}^2$ |                                    | Remarks   |
|-----------------------|-------------------------------------------------------------|--------------------------------------------|------------------------------------|-----------|
|                       |                                                             | 250°C                                      | 750°C                              |           |
| 1                     | 2                                                           | 40                                         | 7                                  | Example   |
| 2                     | 5                                                           | 35                                         | 8                                  | Example   |
| 3                     | 10                                                          | 40                                         | 6                                  | Example   |
| 4                     | 15                                                          | 30                                         | 4                                  | Example   |
| 5                     | 20                                                          | 20                                         | 5                                  | Example   |
| 6                     | 25                                                          | 5                                          | Separated<br>before<br>measurement | Comp. Ex. |

As shown in Table 4, the samples of condition nos. 1 through 5 with glass frits having average particle sizes of 2  $\mu\text{m}$  to 20  $\mu\text{m}$  showed excellent adhesive strengths, the 250°C adhesive strength of 10  $\text{kg}/\text{cm}^2$  or more and the 750°C adhesive strength of 1  $\text{kg}/\text{cm}^2$  or more, while the sample of condition no. 6 with glass frit having an average particle size of 25  $\mu\text{m}$  showed bad adhesive strength such as 250°C adhesive strength of 5  $\text{kg}/\text{cm}^2$  and 750°C adhesive strength too small to be evaluated.

The inventive examples with glass frits of an average particle size of 20  $\mu\text{m}$  or less are superior to the comparative example where the average particle size was 25  $\mu\text{m}$ .

#### Example 2

Aqueous suspensions each containing 20 mass% (on a mass basis of 100% total solids) resin comprised of acrylic resin:epoxy resin:phenol resin = 11:3:4 (mass%) mixed with glass frits comprised of  $\text{B}_2\text{O}_3$ =25 mass%,  $\text{SiO}_2$ =65 mass%,  $\text{Na}_2\text{O}$ =10 mass% and having a coefficient of linear heat expansion from 30°C to 300°C of  $40 \times 10^{-7} (\text{°C}^{-1})$  (inventive example) and the same suspension but mixed with glass frit comprised of  $\text{B}_2\text{O}_3$ =50 mass%,  $\text{SiO}_2$ =25 mass%,  $\text{K}_2\text{O}$ =25 mass% and having a coefficient of linear heat expansion from 30°C to 300°C of  $170 \times 10^{-7} (\text{°C}^{-1})$  (comparative example) were prepared. The glass frit used in each example had an average particle size of 10  $\mu\text{m}$ . The resin/glass frit mixing ratio in the solution

containing the glass frit was in each case adjusted to 100%.

Each coating solution was coated on a finish annealed non-oriented electrical steel sheet having a thickness of 0.5 mm with a magnesium chromate insulative coating, using a roll coater to a coating amount of 8 g/m<sup>2</sup> per side. The sheet was dried at 140°C and cooled. The coating thickness per side was 6 µm. From each sample, ring shaped samples with inside diameters of 10.16 cm (4 inch) and outside diameters of 12.7 cm (5 inch) were prepared. Twenty laminations were stacked and pressed at 10 kg/cm<sup>2</sup> and heated at 250°C for 4 hours to prepare a adhesive coated magnetic core. This magnetic core was, annealed in a non-pressed state at a temperature of 750°C for 2 hours. Finally, the core loss at 50Hz and an magnetic flux density of 1.5 Tesla was evaluated. The results are shown in Table 5.

Table 5

| Condi-<br>tion<br>no. | Coefficient of<br>linear heat<br>expansion<br>(°C <sup>-1</sup> ) | core<br>loss<br>(W/kg) | Remarks      |
|-----------------------|-------------------------------------------------------------------|------------------------|--------------|
| 1                     | $40 \times 10^{-7}$                                               | 3.05                   | Ex.          |
| 2                     | $170 \times 10^{-7}$                                              | 3.27                   | Comp.<br>Ex. |

As shown in Table 5, the magnetic core under condition no. 1 with glass frit having a coefficient of linear heat expansion of  $40 \times 10^{-7}$  (°C<sup>-1</sup>) had a good core loss of 3.05 (W/kg), while the magnetic core under condition no. 2 with glass frit having a coefficient of linear heat expansion of  $170 \times 10^{-7}$  (°C<sup>-1</sup>) had a bad core loss as high as 3.27 (W/kg). In this way, it is learned that the inventive example of the present invention is superior to the comparative example.

#### Example 3

The following four types of coating solutions were prepared.

#### Coating Solution A

Into 100 mass parts of water, 40 mass parts of an acryl-modified epoxy resin emulsion containing 20 mass% of a latent curing agent and 5 mass parts of methylethylketone were mixed. The resin obtained by coating and baking this coating solution had a glass transition temperature of 104°C and softened at 120°C or more.

#### Coating Solution B

Into 100 mass parts of water, 40 mass parts of an acrylic resin emulsion, 40 mass parts of an epoxy resin emulsion, and 4 mass parts of an amine-based epoxy curing agent were mixed. The resin obtained by coating and baking this coating solution softened at 150°C or more.

#### Coating Solution C

Into a mixed solution of 178 g of methyl triethoxysilane and 138 g of ethanol was dropped an aqueous solution of 35.3 g of water and 1.04 g of 35% hydrochloric acid for hydrolysis. The hydrolyzed solution was concentrated using a rotary evaporator at 58°C until the solvent no longer was evaporated. The mass of the concentrate was 30% of the mass of the solution before concentration. The mass average molecular weight of this concentrate was 10000. Since this concentrate exhibited drawability, it was apparent that methyl triethoxysilane was polymerized in a linear polymer. This concentrate solidified upon heat treatment at 70°C for 15 minutes, but softened from near 180°C. Into 100 mass parts of this concentrate, 200 mass parts of ethanol was mixed.

#### Coating Solution D

Methyl triethoxysilane in an amount of 178 g and 152 g of tetramethoxysilane were dispersed in 270.3 g of 2-ethoxyethanol. By using acetic acid in an amount of 4.8 g as a catalyst and adding 36 g water for hydrolysis, a coating solution was prepared. This siloxane polymer did not soften upon heating.

In Table 6, the temperatures given in parentheses

after the glass compositions in middle rows of the coating solutions are the glass softening temperatures. The glasses listed in Table 6 all were powders having average particle sizes of 2  $\mu\text{m}$ . The examples and comparative examples were 0.5 mm thick non-oriented electrical steel sheets coated on both surfaces with the respective coating solutions by roll coaters and baked in an oven set at 70°C for 15 minutes. The coating amounts were 7 g/m<sup>2</sup>. In each case, there was no stickiness of the coating surface after baking.

Two test pieces of widths of 3 cm and lengths of 10 cm were used. Parts of the test pieces were overlapped to give an area of the contact parts of 6 cm<sup>2</sup>, then the pieces were hot pressed. Before the hot pressing, the parts of the coating other than at the bonded parts were shaved off. The two test pieces were bonded by hot pressing at 200°C for 1 minute and 10 MPa. Stress relief annealing was performed in nitrogen at 750°C for 2 hours. The adhesive strengths before and after stress relief annealing were evaluated using the shear tensile strength, horizontal direction strength of the bonded surfaces.

Comparative Example 1 is glass with a softening temperature higher than the stress relief annealing temperature showing no adhesion after annealing. Comparative Example 2 is a type where the resin does not soften due to heating showing no adhesion by hot pressing. Comparative Example 3 contains no low melting point glass resulting in no adhesion after stress relief annealing.

Table 6

|             | Coating solution                                                                               |                | Surface coating of non-oriented electrical steel sheet <sup>1)</sup> | Adhesive strength (MPa) |                 |
|-------------|------------------------------------------------------------------------------------------------|----------------|----------------------------------------------------------------------|-------------------------|-----------------|
|             |                                                                                                |                |                                                                      | Before annealing        | After annealing |
| Ex. 1       | Coating solution A                                                                             | 100 mass parts | Yes                                                                  | 2.0                     | 2.3             |
|             | SiO <sub>2</sub> -B <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> O-based glass powder (540°C)  | 25 mass parts  |                                                                      |                         |                 |
|             | Water                                                                                          | 150 mass parts |                                                                      |                         |                 |
| Ex. 2       | Coating solution A                                                                             | 100 mass parts | Yes                                                                  | 2.5                     | 1.7             |
|             | P <sub>2</sub> O <sub>5</sub> -Na <sub>2</sub> O-K <sub>2</sub> O-F-based glass powder (360°C) | 25 mass parts  |                                                                      |                         |                 |
|             | Water                                                                                          | 150 mass parts |                                                                      |                         |                 |
| Ex. 3       | Coating solution B                                                                             | 100 mass parts | Yes                                                                  | 1.9                     | 1.1             |
|             | B <sub>2</sub> O <sub>3</sub> -ZnO-Bi <sub>2</sub> O <sub>3</sub> -based glass powder (560°C)  | 25 mass parts  |                                                                      |                         |                 |
|             | Water                                                                                          | 200 mass parts |                                                                      |                         |                 |
| Ex. 4       | Coating solution C                                                                             | 100 mass parts | No                                                                   | 2.3                     | 2.0             |
|             | SiO <sub>2</sub> -B <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> O-based glass powder (540°C)  | 30 mass parts  |                                                                      |                         |                 |
|             | 2-ethoxyethanol                                                                                | 100 mass parts |                                                                      |                         |                 |
| Comp. Ex. 1 | Coating solution A                                                                             | 100 mass parts | Yes                                                                  | 2.1                     | 0.0             |
|             | SiO <sub>2</sub> glass powder (1690°C)                                                         | 25 mass parts  |                                                                      |                         |                 |
|             | Water                                                                                          | 150 mass parts |                                                                      |                         |                 |
| Comp. Ex. 2 | Coating solution D                                                                             | 100 mass parts | Yes                                                                  | 0.0                     | Not measurable  |
|             | SiO <sub>2</sub> -B <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> O-based glass powder (540°C)  | 25 mass parts  |                                                                      |                         |                 |
|             | Water                                                                                          | 150 mass parts |                                                                      |                         |                 |
| Comp. Ex. 3 | Coating solution B                                                                             | 100 mass parts | Yes                                                                  | 4.0                     | 0.0             |

<sup>1)</sup> Mixed inorganic-organic solution mainly comprised of magnesium chromate and acrylic resin coated and baked to form insulating coating on surface.

5

#### Example 4

The following four types of coating solutions were prepared.

#### Coating Solution A

Into 100 parts by mass of water, 40 mass parts of an acryl-modified epoxy resin emulsion containing 20 mass% of a latent curing agent and 5 mass parts of methylethylketone were mixed. The resin obtained by coating and baking this coating solution had a glass transition temperature of 104°C and softened at 120°C or more.

#### Coating Solution B

Water in an amount of 100 mass parts, an acrylic resin emulsion in 40 mass parts, an epoxy resin emulsion in 40 mass parts, and an amine-based epoxy curing agent in 4 mass parts were mixed. The resin obtained by coating and baking this coating solution softened at 150°C or more.

#### Coating Solution C

Into a mixed solution of 178 g of methyl triethoxysilane and 138 g of ethanol, an aqueous solution comprised of 35.3 g of water and 1.04 g of 35% hydrochloric acid was dropped for hydrolysis. The hydrolyzed solution was concentrated using a rotary evaporator at 58°C until solvent was no longer evaporated. The mass of the concentrate was 30% of the mass of the solution before concentration. This concentrate had a mass average molecular mass of 10000. This concentrate exhibited drawability, so it was apparent that methyl triethoxysilane was polymerized in the form of a linear polymer. This concentrate solidified upon heat treatment at 70°C for 15 minutes, but softened from near 180°C. Into 100 mass parts of this concentrate, 200 mass parts of ethanol was mixed.

In the examples, the coating solutions A to C were diluted by water, then added with various types of water glass to prepare the coating solutions. The examples and comparative examples were 0.5 mm thick non-oriented electrical steel sheets coated on both surfaces with the respective coating solutions using roll coaters and baked

in an oven set at 70°C for 15 minutes. The coating amounts were 10 g/m<sup>2</sup>. In each case, there was no stickiness of the coating surface after baking.

Two test pieces of widths of 3 cm and lengths of 10  
5 cm were used. Parts of the test pieces were overlapped to give an area of the contact parts of 6 cm<sup>2</sup>, then the pieces were hot pressed. Before the hot pressing, the parts of the coating other than at the bonded parts were shaved off. The two test pieces were bonded by hot  
10 pressing at 200°C for 1 minute and 10 MPa. Stress relief annealing was performed in nitrogen at 750°C for 2 hours. The adhesive strengths before and after stress relief annealing were evaluated using the shear tensile strength, i.e. the horizontal direction strength of the  
15 bonded surfaces.

Table 7

|       | Coating solution                                                             |                   | Surface coating of non-oriented electrical steel sheet <sup>1)</sup> | Adhesive strength (MPa) |                 |
|-------|------------------------------------------------------------------------------|-------------------|----------------------------------------------------------------------|-------------------------|-----------------|
|       |                                                                              |                   |                                                                      | Before annealing        | After annealing |
| Ex. 1 | Coating solution A                                                           | 100 mass parts    | Yes                                                                  | 2.4                     | 1.0             |
|       | Sodium silicate no. 1 (SiO <sub>2</sub> /Na <sub>2</sub> O=2.1[molar ratio]) | 50 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 150 mass parts    |                                                                      |                         |                 |
| Ex. 2 | Coating solution A                                                           | 100 mass parts    | Yes                                                                  | 1.1                     | 2.1             |
|       | Sodium silicate no. 1 (SiO <sub>2</sub> /Na <sub>2</sub> O=2.1[molar ratio]) | 100 mass parts    |                                                                      |                         |                 |
|       | Water                                                                        | 150 mass parts    |                                                                      |                         |                 |
| Ex. 3 | Coating solution B                                                           | 100 mass parts    | Yes                                                                  | 2.1                     | 1.1             |
|       | Sodium silicate bi, 3 (SiO <sub>2</sub> /Na <sub>2</sub> O=3.2[molar ratio]) | 40 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 200 mass parts    |                                                                      |                         |                 |
| Ex. 4 | Coating solution C                                                           | 100 mass parts    | No                                                                   | 2.3                     | 2.0             |
|       | Sodium silicate no. 1 (SiO <sub>2</sub> /Na <sub>2</sub> O=2.1[molar ratio]) | 50 mass parts     |                                                                      |                         |                 |
|       | 2-ethoxyethanol                                                              | 100 mass parts    |                                                                      |                         |                 |
| Ex. 5 | Coating solution A                                                           | 100 mass parts    | Yes                                                                  | 4.1                     | 0.9             |
|       | Potassium silicate A (SiO <sub>2</sub> /K <sub>2</sub> O=3.0[molar ratio])   | 50 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 150 mass parts    |                                                                      |                         |                 |
| Ex. 6 | Coating solution A                                                           | 100 mass parts    | Yes                                                                  | 3.9                     | 1.1             |
|       | Potassium silicate 2K (SiO <sub>2</sub> /Na <sub>2</sub> O=3.5[molar ratio]) | 75 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 150 mass parts    |                                                                      |                         |                 |
| Ex. 7 | Coating solution B                                                           | 100 mass parts    | Yes                                                                  | 1.1                     | 0.9             |
|       | Lithia silicate 35 (SiO <sub>2</sub> /Li <sub>2</sub> O=3.5[molar ratio])    | 50 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 200 mass parts    |                                                                      |                         |                 |
| Ex. 8 | Coating solution A                                                           | 100 parts by mass | Yes                                                                  | 2.1                     | 0.8             |
|       | Sodium silicate no. 1 (SiO <sub>2</sub> /Na <sub>2</sub> O=2.1[molar ratio]) | 10 mass parts     |                                                                      |                         |                 |
|       | Colloidal silica (particle size 300 nm)                                      | 25 mass parts     |                                                                      |                         |                 |
|       | Water                                                                        | 100 mass parts    |                                                                      |                         |                 |

<sup>1)</sup> Mixed inorganic-organic solution mainly comprised of magnesium chromate and acrylic resin coated and baked to form insulating coating on surface.

Example 5

The coating solution D described in Example 3 was prepared. To 100 mass parts of the coating solution D, 10 mass parts of polyester spherical particles having an average particle size of 4  $\mu\text{m}$  and a softening temperature of 200°C were mixed and dispersed. This was coated using a roll coater on a non-oriented electrical steel sheet with a surface coating obtained by a mixed inorganic-organic solution, then was baked in an oven set to 100°C. The coating amount was 10 g/m<sup>2</sup>. Two test pieces of widths of 3 cm and lengths of 10 cm were used. Parts of the test pieces were overlapped to give an area of the contact parts of 6 cm<sup>2</sup>, then the pieces were hot pressed. Before the hot pressing, the parts of the coating other than at the bonded parts were shaved off. The two test pieces were bonded by hot pressing at 230°C for 1 minute and 10 MPa. Stress relief annealing was performed in nitrogen at 750°C for 2 hours. The adhesive strengths before and after stress relief annealing were evaluated using the shear tensile strength, i.e. the horizontal direction strength of the bonded surfaces. The adhesive strengths before and after stress relief annealing were 1.0 MPa and 2.1 MPa.

#### INDUSTRIAL APPLICABILITY

According to the present invention, it is possible to provide an electrical steel sheet with a heat resistant adhesive insulative coating able to adhere using pressing and heating after punching or cutting so as to integrate a magnetic core and subsequently able to maintain its adhesion even after stress relief annealing. A magnetic core can be laminated without welding and interlocking avoiding deterioration of core loss due to welding or interlocking, and the adhesion and insulative ability are maintained even after stress relief annealing, so a magnetic core superior in electrical properties can be obtained.

CLAIMS

1. A heat resistant adhesive insulative coating including a resin with a softening point of room temperature to 300°C and a low melting point inorganic composition with a softening point of not more than 1000°C.

2. A heat resistant adhesive insulative coating as set forth in claim 1, characterized in that a 250°C adhesive strength is 10 kg/cm<sup>2</sup> or more and a 750°C adhesive strength is 1 kg/cm<sup>2</sup> or more.

3. A heat resistant adhesive insulative coating as set forth in claim 1, characterized in that a coefficient of linear heat expansion at 30°C to 300°C is  $10 \times 10^{-7}$  (°C<sup>-1</sup>) to  $150 \times 10^{-7}$  (°C<sup>-1</sup>).

4. A heat resistant adhesive insulative coating as set forth in claim 1, characterized in that the low melting point inorganic composition is a low melting point glass frit, water glass, or these in which colloidal silica is further mixed.

5. A heat resistant adhesive insulative coating as set forth in claim 4, characterized in that low melting point inorganic composition has an average particle size of 20 μm or less.

6. A heat resistant adhesive insulative coating as set forth in claim 4, characterized in that a mixing ratio of the resin to the low melting point inorganic composition is, by mass percent, 20% to 500%.

7. A heat resistant adhesive insulative coating as set forth in claim 4, characterized in that the low melting point inorganic composition is an SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O-based low melting point glass (R is an alkali metal).

8. A heat resistant adhesive insulative coating as set forth in claim 4, characterized in that said water glass is sodium silicate.

9. A heat resistant adhesive insulative coating as set forth in claim 1, characterized in that said resin

includes one or more types of resin selected from an epoxy resin, acrylic resin, phenol resin, incompletely cured resin mainly comprised of an acrylic-modified epoxy resin emulsion containing a latent curing agent, or a siloxane polymer.

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10. An electrical steel sheet with a heat resistant adhesive insulative coating comprised of steel sheet having on at least one surface a coating as set forth in claim 1.

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11. An electrical steel sheet with a heat resistant adhesive insulative coating as set forth in claim 10, characterized in that the heat resistant adhesive insulative coating has a thickness of 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

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12. A magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating as set forth in claim 10.

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13. A method of production of a magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating comprising stacking and pressing electrical steel sheets as set forth in claim 10 to form an electrical steel sheet laminations, then annealing these at a temperature between 600 and 900°C to obtain a laminated magnetic core.

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14. A method of production of a magnetic core using an electrical steel sheet with a heat resistant adhesive insulative coating as set forth in claim 13, further comprising, at least in the step of pressing, connecting them by heating to adhere or connecting them by interlocking or fixtures or both of these.