(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 557 531 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(21) Application number: **92918876.1**

(22) Date of filing: **04.09.92**

(86) International application number:
PCT/JP92/01131

(87) International publication number:
WO 93/05199 (18.03.93 93/08)

(51) Int. Cl.⁵: **C23C 28/00**, C23C 22/73, C23F 1/20

(30) Priority: **04.09.91 JP 253127/91**

(43) Date of publication of application:
01.09.93 Bulletin 93/35

(84) Designated Contracting States:
DE FR GB IT SE

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(54) ALUMINUM ALLOY SHEET FOR AUTOMOTIVE BODY AND PRODUCTION THEREOF.

(57) An aluminum alloy sheet for automotive bodies, wherein the alloy contains 2-10 wt.% of magnesium and the sheet comprises a metallic aluminum base, an aluminum phosphate coating formed thereon, an aluminum oxide coating further formed thereon, and further, if necessary, an oily layer formed as the uppermost layer. A process for producing the above sheet which comprises the steps of treating a sheet of an aluminum alloy containing 2-10 wt.% of magnesium with an acid having a pH of 4 or less to remove the magnesium oxide coating from the surface of the sheet, treating the resultant sheet with a phosphate solution to form an aluminum phosphate coating between the metallic base and the aluminum oxide coating, and further, if necessary, forming an oily layer as the uppermost layer.

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(3.10/3.6/3.3.1)

Field of the Invention

The present invention relates to an aluminum alloy sheets for auto, particularly auto body panels, and to a method of manufacturing the same.

Description of the Prior Art

Reduction in the weight of an auto body is vigorously studied nowadays in an attempt to save the fuel cost and to improve the performance of the auto. To achieve the object, an aluminum material having a specific gravity about one-third the specific gravity of iron has come to be used widely in place of the conventional material of steel. The aluminum material, which is light in weight, is excellent in its corrosion resistance, formability and capability of surface treatment. In addition, the aluminum material can be reproduced without difficulty. Such being the situation, the aluminum material attracts attentions as one of the most desirable materials for auto. The aluminum material is widely used nowadays for forming an auto body, a wheel, a bumper, a heat exchanger, an engine, etc. of an auto, and the range of application of the aluminum material is being widened in the field of auto.

Where an aluminum alloy sheets are used for manufacturing, for example, auto body panels, the alloy sheets are required to be satisfactory in, for example, formability, weldability, adhesive properties, and corrosion resistance and surface appearance after coatings. In the case of using aluminum alloy sheets, the auto body panels are manufactured as follows, which is substantially equal to the conventional method using steel sheets:

① Forming

A coiled aluminum alloy sheet or an aluminum alloy sheets cut into a desired size from a coiled body is formed in a desired shape.

② Bonding

Members of the auto are mounted to the auto body by means of welding and/or adhering. In this step, the aluminum-based members are transferred in combination with members formed of the conventional steel material to the succeeding process.

③ Surface Treatment

i) Degreasing with an alkaline detergent
ii) Water rinse
iii) Surface conditioning by treatment with, for example, colloidal titanate
iv) Chemical conversion treatment with zinc phosphating
v) Water rinse (in this step, an after-treatment with, for example, an aqueous solution of chromic acid is applied, as desired.)
vi) Drying

④ Coating

i) Under coating by means of electrolytic deposition
ii) Intermediate coating
iii) Top coating

⑤ Fitting-out (each part is mounted to the skeletal structure)

Auto bodies are manufactured through steps 1 to 5 described above.

The aluminum alloy sheets used as a raw material are prepared by the ordinary steps of casting, soaking, hot rolling, cold rolling and finish annealing. The annealing is performed during the cold rolling step in some cases. The alloy sheets thus prepared are coiled or cut into a predetermined size and, then, subjected to forming.

However, the aluminum alloy sheets for auto body panels prepared by the conventional method described above gives rise to serious problems. First of all, the aluminum alloy sheets prepared by the conventional method leaves room for further improvement in formability, compared with a steel material mainly used nowadays as a material of an auto body. Specifically, if severe working is applied to the aluminum alloy sheets, problems such as cracking and surface roughening take place, with the result that the members of the auto body, which can be formed by using the aluminum alloy sheets prepared by the conventional method, are much restricted.

A second problem is that the aluminum alloy sheets prepared by the conventional method are not satisfactory in its bonding strength with another member. If aluminum alloy sheets having a bonded portion is subjected to a durability test under severe conditions, peeling takes place in the bonded portion, or the bonded portion fails to exhibit a desired bonding strength. It follows that the aluminum alloy sheets prepared by the conventional method leave room for further improvement in safety and reliability.

A third problem is that the conventional aluminum alloy sheets are not satisfactory in weldability. Because of the poor weldability, the welding apparatus, particularly the electrodes included in the apparatus, is readily damaged when alloy sheets are welded to each other. It follows that the welding apparatus, particularly the electrodes included in the apparatus, must be repaired frequently, leading to a low productivity.

A fourth problem is that the conventional aluminum alloy sheets are not satisfactory in its bonding strength with a coated film. If a durability test is applied under severe conditions to the alloy sheets after the coating step, the coated film tends to peel off or to be swollen so as to impair the surface appearance of the alloy sheets.

Further, a fifth problem is that the conventional aluminum alloy sheets are poor in its corrosion resistance. If a durability test is applied under severe conditions to the alloy sheets after the coating, a filiform corrosion is brought about to impair the surface appearance of the alloy sheets. If the filiform corrosion further proceeds, the performance of the alloy sheets are lowered.

An aluminum material is used singly for forming an auto body in some cases or is used in combination with a steel material in other cases. As described previously, the auto body material is treated with zinc phosphate in many cases before the under coating step. The poor bonding strength with the coated film and the poor corrosion resistance inherent in the conventional aluminum alloy sheets are related particularly to the chemical conversion treatment with zinc phosphate.

Summary of the Invention

The present inventors have found that the various problems inherent in the prior art are caused by an oxide film formed on the surface of an aluminum alloy sheets. It has also been found that the structure of an oxide film of aluminum is greatly affected by the composition of the aluminum alloy. For example, an aluminum alloy sheets used for forming an auto body contains 0.3 to 10% by weight of magnesium. The oxide film formed on the surface of such an alloy sheets contains not only aluminum oxide and/or hydroxide but also magnesium oxide and/or hydroxide. It has been found that the weldability, bonding strength and corrosion resistance of the alloy sheets are adversely affected by the presence of magnesium oxide and/or hydroxide noted above.

The aluminum oxide can be roughly classified into two types, i.e., amorphous oxide ($A\ell_2O_3$) and crystalline oxide. The crystalline aluminum oxide film is in the form of various phases depending on the atmospheres under which the oxide film is formed. The typical phases of the crystalline aluminum oxide include, for example, Gibbsite (γ-$A\ell(OH)_3$), Bayerlite (α-$A\ell(OH)_3$), and Boehmite (γ-$A\ell OOH$). The crystalline aluminum oxide film exhibits a frictional resistance lower than that of the amorphous aluminum oxide film and, thus, is superior to the amorphous oxide film in lubricity. It should be noted that these two kinds of oxides are present together in the oxide film formed on the surface of the aluminum alloy sheets after the rolling step. Also, the crystalline oxide is formed when the alloy sheets is exposed to a wet atmosphere of high temperatures.

It has been found that a crystalline oxide film is formed in the hot rolling step in the manufacture of an aluminum alloy sheets. In general, an aqueous rolling oil of 200°C or more is used in the hot rolling step, which is considered to give rise to formation of the crystalline oxide film. The crystalline oxide film is broken in the subsequent cold rolling step. However, crystalline oxide is embedded in the aluminum matrix so as to remain within the product alloy sheet.

The present inventors have also found that the weldability, adhesive properties, and corrosion resistance of an aluminum alloy sheets are affected by the presence of two kinds of oxides, i.e., aluminum oxide and magnesium oxide, contained in the oxide film formed on the surface of the aluminum alloy sheets. Particularly, it has been found that these properties of the alloy sheets are markedly deteriorated in the case where the oxide film contains a large amount of magnesium oxide.

An object of the present invention is to remove magnesium oxide contained in an oxide film formed on the surface of an aluminum alloy sheets as much as possible to improve the properties of the alloy sheets and to prevent formation of magnesium oxide even if the alloy sheets having the magnesium oxide removing treatment applied thereto is left to stand for a long period of time, so as to provide aluminum alloy sheets which permits suppressing the change with time in the properties and is suitable for forming auto body panels.

According to a first aspect of the present invention, there is provided aluminum alloy sheets for auto bodies, comprising a metal aluminum substrate formed of an aluminum alloy containing 2 to 10% by weight of magnesium; an aluminum phosphate film formed on the substrate; an aluminum oxide film formed on the phosphate film; and, as desired, an oil film formed on the aluminum oxide film.

Another object of the present invention is to provide a method of efficiently manufacturing aluminum alloy sheets which permits suppressing the change with time in the properties and is suitable for forming auto bodies.

According to a second aspect of the present invention, there is provided a method of manufacturing aluminum alloy sheets for auto bodies, comprising the steps of:

treating the surface of aluminum alloy sheets containing 2 to 10% by weight of magnesium with an acid having a pH value of at most 4 to remove magnesium oxide contained in an aluminum oxide-based film formed on the surface of the alloy sheets;

treating the surface of the alloy sheets with a phosphate solution to form an aluminum phosphate film between the metal aluminum substrate and the aluminum oxide film; and, as desired,

coating the aluminum oxide film with an oil to form an oil film.

Description of the Preferred Embodiments

An aluminum alloy containing 2 to 10% by weight of magnesium is used in the present invention including, for example, JIS A5052 alloy, JIS A5182 alloy, JIS A5082 alloy, JIS A5083 alloy, JIS A5086 alloy, and Aℓ(8 wt%)-Mg alloy. It is important for the magnesium content of the aluminum alloy to fall within a range of between 2 and 10% by weight. If the magnesium content is lower than 2% by weight, the alloy fails to exhibit a sufficiently high mechanical strength. If the magnesium content is higher than 10%, however, it is difficult to prepare an aluminum alloy sheets.

As described previously, aluminum oxide and magnesium oxide are contained in an oxide film formed on the surface of the aluminum alloy sheets manufactured by the ordinary method. In the present invention, magnesium oxide alone is selectively removed in the first step by a treatment with an acid from among the mixture of aluminum oxide and magnesium oxide which are originally present on the metal aluminum substrate consisting of aluminum alloy sheets. The pH value of the acid used for this treatment is set at at most 4. If the pH value is 4 or less, the acid permits selectively dissolving magnesium oxide alone on the substrate surface without dissolving the substrate metal of aluminum and aluminum oxide on the substrate surface. It follows that it is possible to allow the crystalline aluminum oxide having a high lubricity, which is formed in the hot rolling step, to be left unremoved. The acids which can be used in the present invention include, for example, 0.5 to 30 wt% nitric acid and 0.5 to 30 wt% sulfuric acid.

In the present invention, it is desirable to remove magnesium oxide such that the amount of magnesium oxide is made at most 20% by weight based on the total amount of the oxides formed on the metal substrate surface. If the amount of magnesium oxide is larger than 20% by weight based on the total amount of the oxides, the magnesium oxide film itself acts as a brittle layer (peeling portion) in the bonding step of the sheets to another member, leading to a low bonding strength. Also, an electrical resistance is increased in the welding step so as to impair the electrodes of the welding apparatus. As a result, the fused portion called nugget is diminished during the continuous welding operation, resulting in failure to obtain a desired mechanical strength. What should also be noted is that, if the content of magnesium oxide exceeds 20% by weight, the amount of zinc phosphate film which is formed in the step of the pre-treatment for coating, i.e., a treatment with a phosphate solution, is diminished. As a result, the zinc phosphate crystals are rendered rough and large, leading to a low bonding strength and a low corrosion resistance of the aluminum alloy sheet after the coating.

After the acid treatment for removing magnesium oxide from the surface of the substrate, the aluminum oxide originally present on the substrate surface mainly remains on the metal substrate consisting of the aluminum alloy sheets. It is desirable for the aluminum oxide film to have a thickness falling within a range of between 10 and 200Å. If the aluminum oxide film has a thickness smaller than 10Å, the electrical resistance of the substrate is unduly low in the spot welding step, resulting in failure to obtain a sufficient heat generation. Thus, nuggets are not formed. If the thickness exceeds 200Å, however, the aluminum oxide film itself acts as a brittle layer in the bonding step, leading to a low bonding strength. Further, the electrical resistance is too much increased in the spot welding step, with the result that the electrodes of the welding apparatus are impaired so as to decrease the number of continuous welding points achieved by using the same welding apparatus.

It is desirable for the aluminum oxide film to have an average surface roughness Ra falling within a range of between 0.1 and 2.5 microns and a maximum surface roughness Rmax falling within a range of between 0.5 and 40 microns. If the average surface roughness Ra is less than 0.1 micron and the maximum surface roughness Rmax is less than 0.5 micron, it is difficult to hold sufficiently a lubricating oil supplied to the aluminum alloy sheets in the forming step, leading to a low formability of the sheet. Further, the aluminum alloy sheet is rendered low in its adhesive properties because the low surface roughness denotes a small bonding area. On the other hand, where the average surface roughness Ra exceeds 2.5 microns and the maximum surface roughness Rmax exceeds 40 microns, the surface of the coated film after the coating step is rendered poor in its smoothness and appearance so as to decrease the commercial value of the alloy sheets.

As described previously, the substrate having magnesium oxide removed from the surface thereof by the acid treatment is then treated with a phosphate solution so as to form a phosphate film between the metal substrate of the aluminum alloy sheets and the aluminum oxide film. The thickness of the aluminum phosphate film should be about 1 to 5Å. Incidentally, a sufficient effect can be obtained by the presence of the aluminum phosphate film even if the phosphate film is in the form of a monomolecular film. The thickness of the aluminum phosphate film can be controlled by adjusting appropriately the conditions such that the concentration of the phosphate solution falls within a range of between 0.01 and 5% by weight, the temperature of the phosphate solution is 20 ° C or more, and the treating time is at least 2 seconds.

A solution containing phosphate ions (or phosphate compounds) can be used for forming the aluminum phosphate film including, for example, a solution containing at least 0.01% by weight of at least one of sodium phosphate, sodium phosphite and sodium pyrophosphate.

The treatment with a phosphate solution makes it possible to prevent formation of magnesium oxide even if the aluminum alloy sheet is allowed to stand over a long period of time. As a result, the change with time in the properties of the aluminum alloy sheet can be suppressed. It should be noted that the aluminum oxide film originally formed on the surface of the substrate is porous. Thus, the phosphate solution passes through the aluminum oxide film during treatment with the phosphate solution to perform a chemical reaction with the substrate aluminum to form a strong aluminum phosphate film between the metal aluminum substrate and the aluminum oxide film.

In the present invention, it is desirable to coat further the aluminum oxide film with an oil. Although the aluminum phosphate film serves to sufficiently prevent the formation of magnesium oxide even if the aluminum alloy sheet is left to stand over a long period of time ranging between the treatment with the phosphate solution and the molding operation, the oil coating further promotes the effect of suppressing the magnesium oxide formation. The oil used in the present invention includes, for example, an antirust oil in the form of emulsion or wax. Concerning the coating amount of oil, a sufficient effect can be expected as far as the entire surface region is uniformly coated with the oil. In practice, the oil is coated in an amount of at least 0.1 g/m^2, preferably about 1 g/m^2.

In the manufacturing method of the present invention, a coil of the raw material alloy sheets is cut into sheets of a predetermined size, followed by applying each of the treatments described above to the cut sheets. Alternatively, each of the treatments can be continuously applied to a coiled raw material alloy sheets. In particular, the continuous treatment permits manufacturing aluminum alloy sheets with an improved efficiency and with a high productivity.

The prominent effects produced by the present invention are apparent from the Examples which follow. Needless to say, the technical scope of the present invention is not restricted at all by the following Examples. Also, various modifications and improvements can be achieved within the technical scope of the present invention.

Example 1

An ingot was prepared by melting and casting JIS A5182 alloy (Aℓ 0.3 wt%-Mn 4.5 wt%-Mg alloy), followed by applying successively a homogenizing treatment, a hot rolling treatment, a cold rolling treatment, and finish annealing treatment to the ingot so as to obtain a sheets having a thickness of 1.0 mm.

The resultant sheets was treated with a 5 wt% nitric acid for 10 seconds by a spraying method, followed by washing the sheets with water so as to remove selectively magnesium oxide contained in an oxide film formed on the surface of the sheets. Then, the washed sheets was dried.

In the next step, the sheets was treated with a 0.1 wt% sodium pyrophosphate solution at 40 ° C for 300 seconds to form an aluminum phosphate film having a thickness of 5Å between the metal aluminum substrate and the aluminum oxide film formed on the substrate, thereby to obtain an aluminum alloy sheet 1 of the present invention.

About one week after preparation, various properties of the aluminum sheet 1 were measured, including the total thickness of the oxide film (sum of the magnesium oxide film and the aluminum oxide film), the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive properties, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 shows the results. These properties were also measured after the aluminum alloy sheet 1 was left to stand for 90 days within a constant temperature-humidity bath maintained at a temperature of 40 ° C and a relative humidity of 95% so as to evaluate the changes with time in these properties. Table 1 also shows the results. The properties noted above were evaluated as follows:

(1) Total thickness of the oxide film and the percentage by weight of magnesium oxide contained in the oxide film:

Determined by ESCA (Electron spectroscopy for chemical analysis).

(2) Formability

Erichsen test A defined in JIS Z2247 was applied applied to the aluminum alloy sheets 1 to determine the Erichsen value (mm) as the formability.

(3) Adhesive properties

The aluminum alloy sheet 1 was cut into small pieces sized at 25 mm × 100 mm. Two of these small pieces were bonded to each other with an epoxy series adhesive available on the market with a lapping width set at 13 mm, followed by baking the bonded small pieces at 70 ° C for 30 minutes. Then, a saline water spraying test specified in JIS Z2371 was applied to the resultant sample for 90 days. The tensile shearing strength of the sample was measured both before and after the saline water spraying test, and a strength residual rate as the adhesive properties was calculated by the formula given below:

$$R(\%) = (A/B) \times 100$$

where, R is the strength residual rate, A is the shearing strength after the test, and B is the shearing strength before the test.

(4) Weldability

Spot welding was applied to the sample continuously until the electrodes of the welding apparatus were damaged and, thus, the nugget formation was made impossible. The welding was applied to determine the number of nuggets which can be formed by the continuous welding operation by the same welding apparatus.

(5) Bonding strength with a coated film

A small sheets sized at 70 mm × 150 mm was cut out of the aluminum alloy sheets 1 of the present invention and, then, subjected to a degreasing treatment at 45 ° C for 30 seconds using a weakly alkaline degreasing agent. After rinsing of the degreased sample with water, the surface of the sample was adjusted at room temperature for 30 seconds with a colloidal titanium-based liquid material, followed by applying a chemical treatment to the sample under the surface-adjusted state with a zinc phosphate solution available on the market. The chemical conversion treatment was performed for 2 minutes at 45 ° C. Then, the sample was successively subjected to rinsing with water, drying, under coating with a cation electrolyte deposition, intermediate coating by blowing, and top coating.

The resultant sample was kept immersed in warm water of 50 ° C for 20 days, followed by applying a cross cut adhesion test. Specifically, a peeling test using a tape was applied to the sample in the form of a checkerboard having 100 meshes each sized 2 mm × 2 mm. The number of residual meshes which were not peeled off was indicated in Table 1 together with the number of test pieces (100).

(5) Corrosion resistance

A sample was prepared as in the bonding strength test with a coated film. Then, a cross-cut (i.e., a mark X) was applied to the surface of the sample such that the cross-cut reached the aluminum alloy sheet. Under this condition, a salt water spraying test specified in JIS Z2371 was applied to the sample for 24 hours, followed by allowing the sample to stand in a wet atmosphere for 2,000 hours at a temperature of 50°C and a relative humidity of 95% so as to measure the maximum length of a filiform corrosion extending from the cross-cut portion.

Example 2

An aluminum alloy sheets 2 of the present invention was obtained substantially as in Example 1, except that an aluminum phosphate film having a thickness of 2Å was formed in Example 2 between the metal aluminum substrate and the aluminum oxide film by the treatment with a 0.05 wt% sodium phosphate solution for 10 seconds at 90°C, though an aluminum phosphate film having a thickness of 5Å was formed in Example 1 by the treatment with a 0.1 wt% sodium pyrophosphate solution for 300 seconds at 40°C.

Various properties of the aluminum alloy sheets 2 were measured as in Example 1, including the total thickness of the oxide film, the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive property, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 also shows the results together with the changes with time in these properties.

Example 3

An aluminum alloy sheets 3 of the present invention was obtained substantially as in Example 1, except that an aluminum phosphate film having a thickness of 5Å was formed in Example 3 between the metal aluminum substrate and the titanium oxide film by the treatment with a 3 wt% sodium pyrophosphate solution for 120 seconds at 50°C, though an aluminum phosphate film having a thickness of 5Å was formed in Example 1 by the treatment with a 0.1 wt% sodium pyrophosphate solution for 300 seconds at 40°C. Further, the aluminum oxide film (the uppermost film) was coated with an emulsion type antirust oil having a viscosity of 3 cSt in a coating amount of 1 g/m^2 in Example 3.

Various properties of the aluminum alloy sheets 3 were measured as in Example 1, including the total thickness of the oxide film, the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive property, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 also shows the results together with the changes with time in these properties.

Prior Art 1

An ingot was prepared by melting and casting JIS A5182 alloy, followed by applying successively a homogenizing treatment, a hot rolling treatment, a cold rolling treatment, and finish annealing treatment to the ingot so as to obtain a sheets having a thickness of 1.0 mm.

The resultant sheets was treated with a 5 wt% nitric acid for 10 seconds by a spraying method, followed by rinsing the sheets with water so as to remove selectively magnesium oxide contained in an oxide film formed on the surface of the sheets. Then, the rinsed sheets was dried.

In the next step, the residual aluminum oxide film was coated with an emulsion type antirust oil having a viscosity of 5 cSt in an amount of 1 g/m^2 so as to obtain an aluminum alloy sheets (prior art 1).

Various properties of the aluminum alloy sheets (prior art 1) were measured as in Example 1, including the total thickness of the oxide film, the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive property, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 also shows the results together with the changes with time in these properties.

Prior Art 2

An aluminum alloy sheets (prior art 2) was prepared as in prior art 1, except that a wax-type antirust oil was in place of the emulsion type antirust oil having a viscosity of 5 cSt, which was used in Prior Art 1.

Various properties of the aluminum alloy sheets (prior art 2) were measured as in Example 1, including the total thickness of the oxide film, the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive property, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 also shows the results together with the changes with time in these properties.

Prior Art 3

An ingot was prepared by melting and casting JIS A5182 alloy, followed by applying successively a homogenizing treatment, a hot rolling treatment, a cold rolling treatment, and finish annealing treatment to the ingot so as to obtain a sheets having a thickness of 1.0 mm.

The resultant sheets was treated with a 5 wt% nitric acid for 10 seconds by a spraying method, followed by washing the sheets with water so as to remove selectively magnesium oxide contained in an oxide film formed on the surface of the sheets. Then, the washed sheets was dried so as to obtain an aluminum alloy sheets (prior art 3).

Various properties of the aluminum alloy sheets (prior art 3) were measured as in Example 1, including the total thickness of the oxide film, the percentage by weight of the magnesium oxide film based on the sum of the magnesium oxide film and the aluminum oxide film, the formability, adhesive property, weldability, bonding strength with a coated film, and corrosion resistance. Table 1 also shows the results together with the changes with time in these properties.

Table 1

		Phosphate Solution	Oil *2	Total thickness of oxide film (Å)		Magnesium oxide content (wt%) *1		Formability (mm)	
				A	B	A	B	A	B
Present Inven- tion	1	0.1 wt% sodium pyrophosphate	-	85	95	3	5	11.3	10.8
	2	0.05 Wt% sodium phosphate	-	82	98	2	4	11.5	11.0
	3	3 wt% sodium pyrophosphate	Emulsion type antirust oil	85	85	3	3	11.3	11.3
Prior Art	1	-	Emulsion type antirust oil	80	135	3	9	11.3	10.1
	2	-	Wax type antirust oil	80	110	3	7	11.2	10.1
	3	-	-	80	155	3	32	11.2	9.0

(continued)

Table 1

		strength residual rate (%)		Number of consecutive welding point		Bonding strength coated film		Maximum length of filiform corrosion (mm)	
		A	B	A	B	A	B	A	B
Present Inven-tion	1	96	87	2700	2400	100/100	100/100	1.2	1.8
	2	98	88	2800	2600	100/100	100/100	1.3	1.9
	3	95	95	2800	2800	100/100	100/100	1.1	1.1
Prior Art	1	96	80	2700	2100	100/100	98/100	1.2	2.8
	2	97	81	2800	2100	100/100	98/100	1.3	2.5
	3	95	45	2800	400	100/100	73/100	1.2	2.7

*1 ... Magnesium oxide content (wt%) denotes M(Aℓ + M), where M is the weight of magnesium oxide, and Aℓ is the weight of aluminum oxide.

*2 ... A: About one week after preparation of the sample;
B: After 90 days of standing in an atmosphere having a temperature of 40°C and a relative humidity of 95%.

As apparent from Table 1, the aluminum alloy sheets of the present invention is small in the changes with time in properties. On the other hand, the thickness of the oxide film was increased in the prior art aluminum alloy sheets after the sheets was allowed to stand in a humid atmosphere of a high temperature for a long time. In other words, the properties of the aluminum alloy sheets were greatly changed with time in the prior art.

As described above in detail, the present invention provides aluminum alloy sheets for auto body panels. In the present invention, magnesium oxide is removed from the natural oxide film formed on the surface of the alloy sheets, followed by forming an aluminum phosphate film between the metal aluminum substrate and the aluminum oxide film. Further, an oil film is formed as required on the uppermost layer of the aluminum oxide film. The particular construction of the present invention makes it possible to improve the characteristics including the formability, adhesive property, and weldability of the aluminum alloy sheets. In addition, formation of magnesium oxide can be markedly suppressed over a long period after manufacture of the alloy sheets. In other words, the aluminum alloy sheets of the present invention permits suppressing the changes with time in the characteristics thereof. What should also be noted is that the aluminum alloy sheets for auto bodies provided by the present invention permits promoting the forming rate of a chemical conversion film during the chemical treatment in the coating step so as to suppress the elusion of aluminum ions into the coating solution. As a result, a chemical conversion film can be formed uniformly on the aluminum alloy sheet, leading to a high bonding strength of the alloy sheets with a coating film and to a high corrosion resistance of the alloy sheets. The present invention also provides a method of manufacturing an aluminum alloy sheets for auto bodies, which makes it possible to manufacture efficiently an aluminum alloy sheets which permits suppressing the changes with time in the characteristics of the alloy sheets.

Claims

1. Aluminum alloy sheets for auto body panels, comprising a metal aluminum substrate formed of an aluminum alloy containing 2 to 10% by weight of magnesium; an aluminum phosphate film formed on the substrate; and an aluminum oxide film formed on the phosphate film.

2. Aluminum alloy sheets for auto body panels, comprising a metal aluminum substrate formed of an aluminum alloy containing 2 to 10% by weight of magnesium; an aluminum phosphate film formed on the substrate; an aluminum oxide film formed on the phosphate film; and an oil film formed on the aluminum oxide film.

3. A method of manufacturing aluminum alloy sheets for auto body panels, comprising the steps of:

treating the surface of aluminum alloy sheets containing 2 to 10% by weight of magnesium with an acid having a pH value of at most 4 to remove magnesium oxide contained in an aluminum oxide-based film formed on the surface of the alloy sheet; and

treating the surface of the alloy sheet with a phosphate solution to form an aluminum phosphate film between the metal aluminum substrate and the aluminum oxide film.

4. The method of manufacturing aluminum alloy sheets according to claim 3, which further comprises the step of coating the aluminum oxide film with an oil to form an oil film.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/01131

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 C23C28/00, 22/73, C23F1/20

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C23C28/00, 22/73-83, C23F1/20, 1/22, 1/44

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1960 - 1991
Kokai Jitsuyo Shinan Koho	1971 - 1991

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	JP, B2, 62-24514 (Okuno Seiyaku Kogyo K.K.), May 28, 1987 (28. 05. 87), Line 6, columns 1 to 2 (Family: none)	1-4

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search November 17, 1992 (17. 11. 92)	Date of Mailing of this International Search Report December 15, 1992 (15. 12. 92)
International Searching Authority Japanese Patent Office	Signature of Authorized Officer