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(54) **METAL-COATED STEEL STRIP**

METALLBESCHICHTETER STAHLSTREIFEN

BANDE D'ACIER REVÊTUE DE MÉTAL

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Description

Background

[0001] The present invention relates to strip, typically steel strip, which has a corrosion-resistant metal alloy coating.

[0002] The present invention relates particularly to a method of forming on a steel strip a corrosion-resistant metal alloy coating that contains aluminium- zinc- silicon-magnesium as the main elements in the alloy, and is hereinafter referred to as an "Al-Zn-Si- Mg alloy" on this basis. The alloy coating may contain other elements that are present as deliberate alloying additions or as unavoidable impurities. Hence, the phrase "Al-Zn-Si-Mg alloy" is understood to cover alloys that contain such other elements as deliberate alloying additions or as unavoidable impurities. The metal - coated strip may be sold as an end product itself or may have a paint coating applied to one or both surfaces and be sold as a painted end product.

[0003] The present invention relates particularly but not exclusively to a method of enhancing the ductility of an Al-Zn-Si-Mg coating on steel strip.

[0004] The present invention relates to a method of forming a steel strip that is coated with the above-described Al-Zn-Si-Mg alloy and is optionally coated with a paint and thereafter is cold formed (e.g. by roll forming) into an end-use product, such as building products (e.g. profiled wall and roofing sheets. The ductility of coatings, particularly in areas (e.g. tension bends) that are directly subjected to cold forming, is an important issue for such end-use products (painted and un- painted).

[0005] The Al-Zn-Si-Mg alloy of the present invention comprises the following ranges in % by weight of the elements aluminium, zinc, silicon, and magnesium:

Aluminium: 40 to 60 %
Zinc: 40 to 60 %
Silicon: 0.3 to 3%
Magnesium 1 to 3 %

[0006] The corrosion-resistant metal alloy coating of the present invention is formed on steel strip by a hot-dip coating method.

[0007] In the conventional hot-dip metal coating method, steel strip generally passes through one or more heat treatment furnaces and thereafter into and through a bath of molten metal alloy held in a coating pot. The heat treatment furnace that is adjacent a coating pot has an outlet snout that extends downwardly to a location close to an upper surface of the bath.

[0008] The metal alloy is usually maintained molten in the coating pot by the use of heating inductors. The strip usually exits the heat treatment furnaces via an outlet end section in the form of an elongated furnace exit chute or snout that dips into the bath. Within the bath the strip passes around one or more sink rolls and is taken upwardly out of the bath and is coated with the metal alloy as it passes through the bath.

[0009] After leaving the coating bath the metal alloy coated strip passes through a coating thickness control station, such as a gas knife or gas wiping station, at which its coated surfaces are subjected to jets of wiping gas to control the thickness of the coating.

[0010] The metal alloy coated strip then passes through a cooling section and is subjected to forced cooling.

[0011] The cooled metal alloy coated strip may thereafter be optionally conditioned by passing the coated strip successively through a skin pass rolling section (also known as a temper rolling section) and a tension levelling section. The conditioned strip is coiled at a coiling station.

[0012] Depending on the end-use application, the metal - coated strip may be painted, for example with a polymeric paint, on one or both surfaces of the strip.

[0013] One corrosion resistant metal coating composition that is used widely in Australia and elsewhere for building products, particularly profiled wall and roofing sheets, is a 55%A1-Zn coating composition that also comprises Si. The profiled sheets are usually manufactured by cold forming painted, metal alloy coated strip. Typically, the profiled sheets are manufactured by roll-forming the painted strip.

[0014] The addition of Mg to this known composition of 55%A1-Zn-Si coating composition has been proposed in the patent literature for a number of years, see for example US patent 6,635,359 in the name of Nippon Steel Corporation, but Al-Zn-Si-Mg coatings on steel strip are not commercially available in Australia.

[0015] US 5049202 discloses a method of enhancing the ductility of an aluminium-zinc alloy coating, having an aluminium content with the range of 25% to 75% by weight and optionally small percentages of elements such as silicon, cerium and magnesium, on a steel strip, by heat treating the coated substrate at a temperature of from 165°C to 275°C and then cooling the coated substrate from the treatment temperature to below 121°C at a rate not exceedings 40°C per hour.

[0016] Another prior art method is disclosed in JP 20087 175975.

[0017] It has been established that when Mg is included in a 55%A1-Zn coating composition, Mg brings about certain beneficial effects on product performance, such as improved cut-edge protection.

[0018] The above discussion is not to be taken as an admission of the common general knowledge in Australia and elsewhere.

Invention

[0019] It has also been established by the applicant that the addition of Mg to a 55%A1-Zn coating composition has a significant negative impact on the coating ductility. This is caused by the formation of coarse intermetallic phases in the coating microstructure and a hardening effect of Mg on Al-rich dendrites and Zn-rich interdendritic regions in the coating microstructure.

[0020] Specifically, in relation to the hardening effect, the applicant is aware that following solidification of a 55%Al-Zn-1.5%Si metallic coating, an age hardening reaction occurs wherein excess Zn dissolved in the Al-rich phase in the coating precipitates as a metastable phase. This causes an increase in strength of the Al-rich phase, and consequently increases the effectiveness of any potential crack initiation sites. This age hardening reaction results in a significant increase in coating hardness within 2-4 weeks of coating solidification, and if cold forming (e.g. roll forming) of tight bends in the metal alloy coated steel (including painted metal-coated steel) is not carried out soon after coating solidification, increased bend cracking can result. In some situations this can be a significant problem.

[0021] The applicant has found that this age hardening also occurs in Al-Zn-Si coatings containing Mg.

[0022] The present invention is a method of forming a coating of an Al-Zn-Si-Mg alloy on a steel strip that is applied by a hot dip process and is subsequently heat treated to improve the ductility of the coating.

[0023] The applicant has found that the resultant coating can be cold formed with a reduced level of cracking on tension bends compared to coatings that are not heat treated. The applicant has also found that the benefit obtained during the heat treatment can be long lasting. Specifically, improved ductility can be retained for a period of 12 months or more.

[0024] According to the present invention there is provided a method of forming a coating of a corrosion- resistant Al-Zn-Si-Mg alloy on a steel strip according to claim 1.

[0025] The term "hold temperature" is understood herein to mean a maximum temperature to which a coated strip is heated to and held at during the course of a heat treatment cycle.

[0026] More preferably the method comprises heat treating the coated strip at a hold temperature of at least 200°C.

[0027] Typically, the method comprises heat treating the coated strip at a hold temperature of at least 225°C.

[0028] Preferably the method comprises heat treating the coated strip at a hold temperature of less than 300°C.

[0029] More preferably the method comprises heat treating the coated strip at a hold temperature of less than 275°C.

[0030] Preferably the method comprises holding the coated strip at the hold temperature for up to 45 minutes.

[0031] More preferably the method comprises holding the coated strip at the hold temperature for up to 30 minutes.

[0032] Preferably the method comprises slow cooling the heat treated coated strip from the hold temperature to a temperature of 100°C or less.

[0033] The applicant has found that the cooling rate of heat treated coated strip affects the durability of the softening effect, i.e. the improved ductility, obtained by the heat treatment and that it is preferable that the cooling rate be a "slow" cooling rate.

[0034] More preferably the method comprises slow cooling the heat treated coated strip from the hold temperature to a temperature of 80°C or less.

[0035] Preferably the cooling rate is 40°C/hr or less.

[0036] More preferably the cooling rate is 30°C/hr or less.

[0037] The heat treatment step of the method may be carried out on a batch or a continuous basis.

[0038] Preferably the magnesium concentration is less than 3 wt.%.

[0039] More preferably the magnesium concentration is between 1.5 wt. % and 2.5 wt. %.

[0040] Preferably the silicon concentration is less than 3.0 wt.%.

[0041] Preferably the silicon concentration is less than 1.6 wt.%.

[0042] Preferably the silicon concentration is less than 1.2 wt.%.

[0043] Preferably the silicon concentration is less than 0.6 wt. %.

[0044] Preferably the aluminium concentration is at least 45 wt.%.

[0045] Typically, the aluminium concentration is at least 50 wt.%.

[0046] The Al-Zn-Si-Mg alloy does not contain deliberate additions, i.e. additions above concentration levels that would be regarded as impurity levels, of chromium and/or manganese.

[0047] The Al-Zn-Si-Mg alloy may contain other elements as impurities or as deliberate additions.

[0048] Preferably the coating on the strip is no more than 30 microns.

[0049] Preferably the metal coated steel strip is cold formed into an end-use product, such as building products (e.g. profiled wall and roofing sheets).

Experimental Work

[0050] The present invention is based on experimental work carried out by the applicant.

[0051] Specifically, the experimental work was carried out to determine the following:

(a) if any improvement in the ductility of a 55%Al-Zn-1.5%Si-2%Mg coating could be achieved by an annealing heat treatment,

(b) the optimum holding temperature, and

(c) the ageing behaviour of heat treated coatings, including heat treated coatings that have undergone a subsequent paint bake cycle (PBC) heat treatment simulation.

[0052] The experimental work was carried out on samples of steel strip that were coated with a 55%Al-Zn-1.5%Si- 2%Mg alloy with a coating density of 150g/m^2 (i.e. 75g/m^2 of each surface of the strip samples) and then heat treated by heating the samples to a range of different hold temperatures and holding the samples at the temperatures for a predetermined period of 30 minutes and then cooling the heat treated samples to ambient temperature.

[0053] The experimental work also included a paint bake cycle (PBC) heat treatment simulation for some of the samples. The PBC treatment comprised heating samples to a peak metal temperature of 230°C at ~7°C/s, followed by water quenching.

[0054] Figure 1 shows the critical bend strain (CBS), i.e. the strain in a coating that is required to initiate cracking, for samples having the 55%Al-Zn-1.5%Si-2%Mg (150g/m^2 coating density) coating held at different temperatures for the above predetermined time of 30 minutes and then cooled to 80°C at a rate of 0.5°C/min.

[0055] Figure 1 shows that the CBS increased from 5.3% for the as-received coated sample (i.e. the sample point at ambient temperature) to a maximum of 8.3% for a coated samples that were heat treated at hold temperatures in the range of 225-250°C. This constitutes a 56% increase in coating ductility - a significant improvement. The Figure also shows that the CBS started to increase at a hold temperature of 150°C. A semiquantitative measure of cracking severity was also used to assess the coating ductility of samples.

[0056] Crack Severity Rating (CSR) is an arbitrary tension bend crack rating system commonly used within the 55%A1-Zn coating community as a measure of coating ductility. A 2T bend is produced and viewed under a stereomicroscope at a magnification of 15x, The cracking on the bend is then compared with a set of standards, and assigned a number between 0 and 10, with 0 indicating no cracking is visible, and 10 representing severe cracking. Hence, a lower CSR rating is preferable to a higher rating.

[0057] Figure 2 shows the CSR for samples having heat- treated 55%Al-Zn-1.5%Si-2%Mg (150g/m^2) coatings as a function of hold temperature. It is evident from the Figure that 225°C is the optimum hold temperature in this experiment. Also, it is evident from the Figure that the CSR started to improve at a hold temperature of 150°C.

[0058] Figure 3 shows the ageing behaviour of (a) samples having coatings of 55%A1-Zn-1.5%Si-2%Mg alloy that were heat treated at the above-established optimum hold temperature of 225°C for the above predetermined time of 30 minutes that were aged for up to three months, (b) samples as described in item (a) that were then subjected to a paint bake cycle treatment, (c) samples having as- received coatings of 55%Al-Zn-1.5%Si-2%Mg alloy, and (d) samples having coatings of 55%A1-Zn-1.5%Si-2%Mg alloy that were subjected to a paint bake cycle treatment only.

[0059] For heat treated coatings, no significant reversion to the as-received ductility was observed in three months, even when the annealed coatings had undergone a subsequent paint bake cycle heat treatment.

[0060] Extrapolating these results leads to a conclusion that the heat treatment at the hold temperature of 225°C for the predetermined time period of 30 minutes would be effective for a period greater than 12 months.

[0061] The above-described experimental work shows that heat treatment of coatings of 55%A1-Zn-1.5%Si-2%Mg alloy on strip improved the ductility of the coatings.

[0062] By way of example, whilst the experimental work was carried out on a 55%A1-Zn-1.5%Si-2%Mg coating, the present invention is also applicable to Al-Zn-Si-Mg coatings generally.

Claims

1. A method of forming a coating of a corrosion - resistant Al-Zn-Si-Mg alloy on a steel strip that comprises:

   (a) passing the steel strip through a hot dip coating bath that contains Al, Zn, Si, and Mg and optionally other elements and forming an alloy coating on the strip, wherein the Al-Zn-Si-Mg alloy comprises the following ranges in % by weight of the elements aluminum, zinc, silicon, and magnesium:

Aluminum:	40 to 60 %
Zinc:	40 to 60
Silicon:	0.3 to 3%
Magnesium	1 to 3 %;

   (b) cooling the coated strip; and
   (c) heat treating the coated strip to improve the ductility of the coating, the heat treating step comprising heating the coated strip to a hold temperature of at least 150°C, holding the coated strip at the hold temperature for a period of time up to 45 minutes, and slow cooling the coated strip at a cooling rate of 40°C/hr or less from the hold temperature to a temperature of 100°C or less.

2. A method defined in claim 1 wherein the hold temperature is at least 200°C.

3. A method defined in claim 1 or claim 2, wherein the hold temperature is less than 300°C.

4. A method defined in any one of the preceding claims wherein the hold temperature is less than 275°C.

5. A method defined in any one of the preceding claims further comprising holding the coated strip at the hold temperature for up to 30 minutes.

6. A method defined in any of the preceding claims, further comprising:
forming a coating of a paint on the cooled heat treated coated strip.

7. A method defined in any one of the preceding claims, further comprising slow cooling the heat treated coated strip from the hold temperature to a temperature of 100°C or less at a cooling rate of 30°C/hr or less.

8. A method defined in any of the preceding claims, wherein the silicon concentration is less than 3.0 wt.%.

9. A method defined in any of the preceding claims, wherein the Al-Zn-Si-Mg alloy does not contain deliberate additions, i.e. additions above concentration levels that would be regarded as impurity levels, of chromium and/or manganese.

Patentansprüche

1. Verfahren zum Bilden einer Beschichtung aus einer korrosionsbeständigen Al-Zn-Si-Mg-Legierung auf einem Stahlband, das Folgendes umfasst:

(a) Führen des Stahlbandes durch ein Schmelztauchbeschichtungsbad, das Al, Zn, Si und Mg und gegebenenfalls andere Elemente enthält, und Bilden einer Legierungsbeschichtung auf dem Band, wobei die Al-Zn-Si-Mg-Legierung folgende Bereiche, in Gew.-%, der Elemente Aluminium, Zink, Silicium und Magnesium umfasst:

Aluminium:	40 bis 60 %
Zink:	40 bis 60 %
Silicium:	0,3 bis 3 %
Magnesium	1 bis 3 %;

(b) Kühlen des beschichteten Bandes; und
(c) Wärmebehandeln des beschichteten Bandes, um die Duktilität der Beschichtung zu verbessern, wobei der Wärmebehandlungsschritt ein Erhitzen des beschichteten Bandes auf eine Haltetemperatur von mindestens 150 °C, ein Halten des beschichteten Bandes auf der Haltetemperatur für eine Zeitspanne von bis zu 45 Minuten und ein langsames Abkühlen des beschichteten Bandes bei einer Abkühlgeschwindigkeit von 40 °C/h oder weniger von der Haltetemperatur auf eine Temperatur von 100 °C oder weniger umfasst.

2. Verfahren nach Anspruch 1, wobei die Haltetemperatur mindestens 200 °C beträgt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Haltetemperatur weniger als 300 °C beträgt.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Haltetemperatur weniger als 275 °C beträgt.

5. Verfahren nach einem der vorhergehenden Ansprüche, ferner umfassend Halten des beschichteten Bandes auf der Haltetemperatur für bis zu 30 Minuten.

6. Verfahren nach einem der vorhergehenden Ansprüche, ferner umfassend:
Bilden einer Beschichtung aus einer Farbe auf dem gekühlten wärmebehandelten beschichteten Band.

7. Verfahren nach einem der vorhergehenden Ansprüche, ferner umfassend langsames Abkühlen des wärmebehandelten beschichteten Bandes von der Haltetemperatur auf eine Temperatur von 100 °C oder weniger bei einer Abkühlgeschwindigkeit von 30 °C/h oder weniger.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Siliciumkonzentration weniger als 3,0 Gew.-% beträgt.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Al-Zn-Si-Mg-Legierung keine absichtlichen Zusätze, d. h. Zusätze oberhalb von Konzentrationsniveaus, die als Verunreinigungsniveaus angesehen würden, von Chrom und/oder Mangan enthält.

Revendications

1. Procédé de formation d'un revêtement d'un alliage Al-Zn-Si-Mg résistant à la corrosion sur une bande en acier qui comprend :

(a) le passage de la bande d'acier à travers un bain de revêtement par immersion à chaud qui contient Al, Zn, Si et Mg et éventuellement d'autres éléments et la formation d'un revêtement d'alliage sur la bande, dans lequel l'alliage Al-Zn-Si-Mg comprend les plages suivantes en % en poids des éléments aluminium, zinc, silicium et magnésium :

Aluminium:	40 à 60%
Zinc:	40 à 60%
Silicone:	0,3 à 3%
Magnésium	1 à 3% ;

(b) le refroidissement de la bande enduite ; et

(c) le traitement thermique de la bande enduite pour améliorer la ductilité du revêtement, l'étape de traitement thermique comprenant le chauffage de la bande enduite à une température de maintien d'au moins 150°C, le maintien de la bande enduite à la température de maintien pendant une période de temps allant jusqu'à 45 minutes et le refroidissement lent de la bande enduite à une vitesse de refroidissement de 40°C/h ou moins à partir de la température de maintien à une température de 100°C ou moins.

2. Procédé défini selon la revendication 1, dans lequel la température de maintien est d'au moins 200°C.

3. Procédé défini selon la revendication 1 ou la revendication 2, dans lequel la température de maintien est inférieure à 300°C.

4. Procédé défini selon l'une quelconque des revendications précédentes, dans lequel la température de maintien est inférieure à 275°C.

5. Procédé défini dans l'une quelconque des revendications précédentes, comprenant en outre le maintien de la bande enduite à la température de maintien pendant jusqu'à 30 minutes.

6. Procédé selon l'une quelconque revendication précédente, comprenant en outre :
la formation d'un revêtement d'une peinture sur la bande enduite thermiquement refroidie.

7. Procédé défini selon l'une quelconque des revendications précédentes, comprenant en outre le refroidissement lent de la bande enduite traitée thermiquement à partir de la température de maintien à une température de 100°C ou moins à un débit de refroidissement de 30°C/h ou moins.

8. Procédé défini selon l'une quelconque des revendications précédentes, dans lequel la concentration en silicium est inférieure à 3,0% en poids.

9. Procédé défini selon l'une quelconque des revendications précédentes, dans lequel l'alliage Al-Zn-Si-Mg ne contient pas d'ajouts délibérés, c'est-à-dire d'ajouts au-dessus des niveaux de concentration qui seraient considérés comme des niveaux d'impureté, de chrome et/ ou de manganèse.

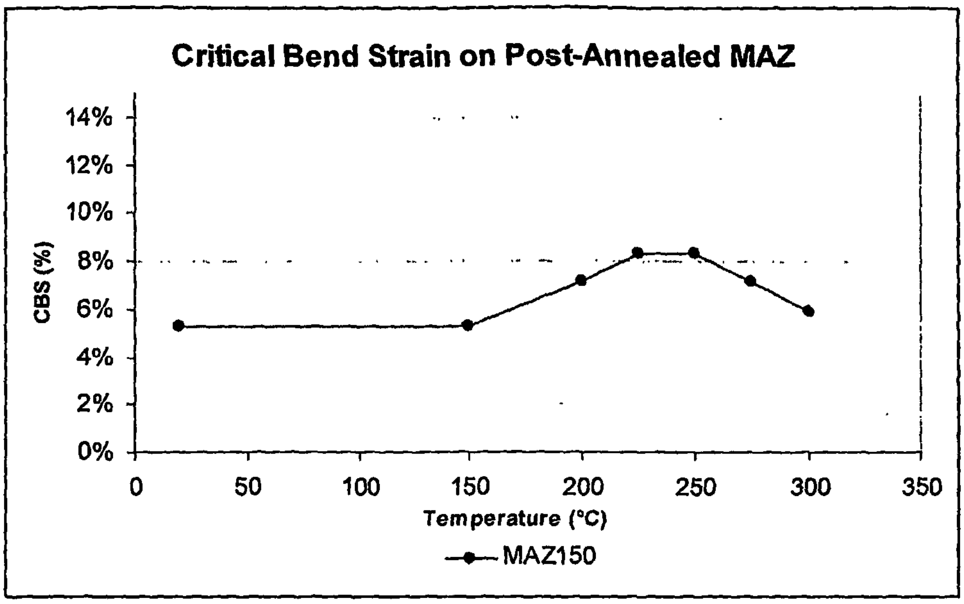

Figure 1 - Effect of batch annealing hold temperature on the critical bend strain of a 150g/m^2 55%Al-Zn-1.5%Si-2%Mg coating.

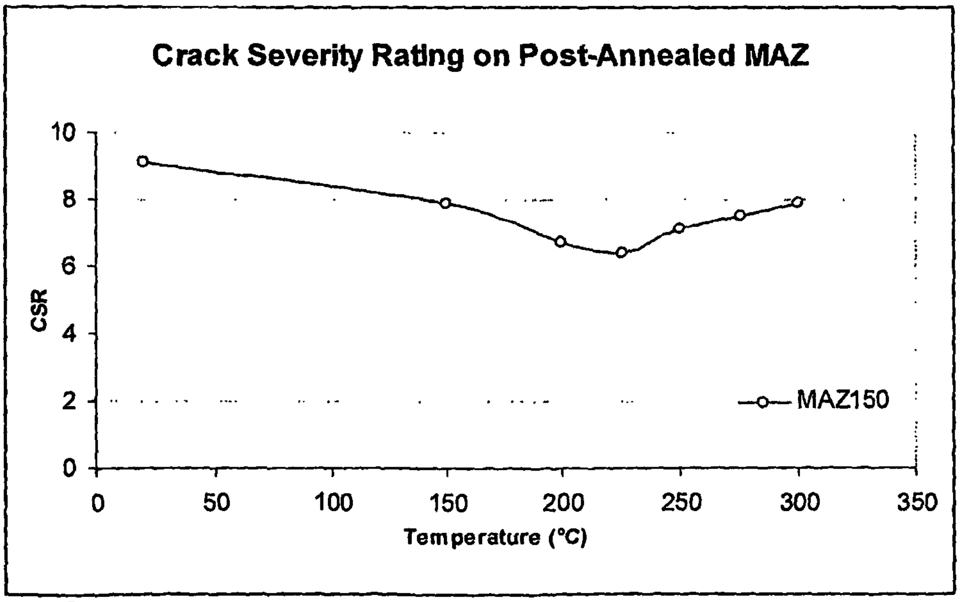

Figure 2 - Effect of batch annealing hold temperature on the Crack Severity Rating of a 150g/m^2 55%Al-Zn-1.5%Si-2%Mg coating.

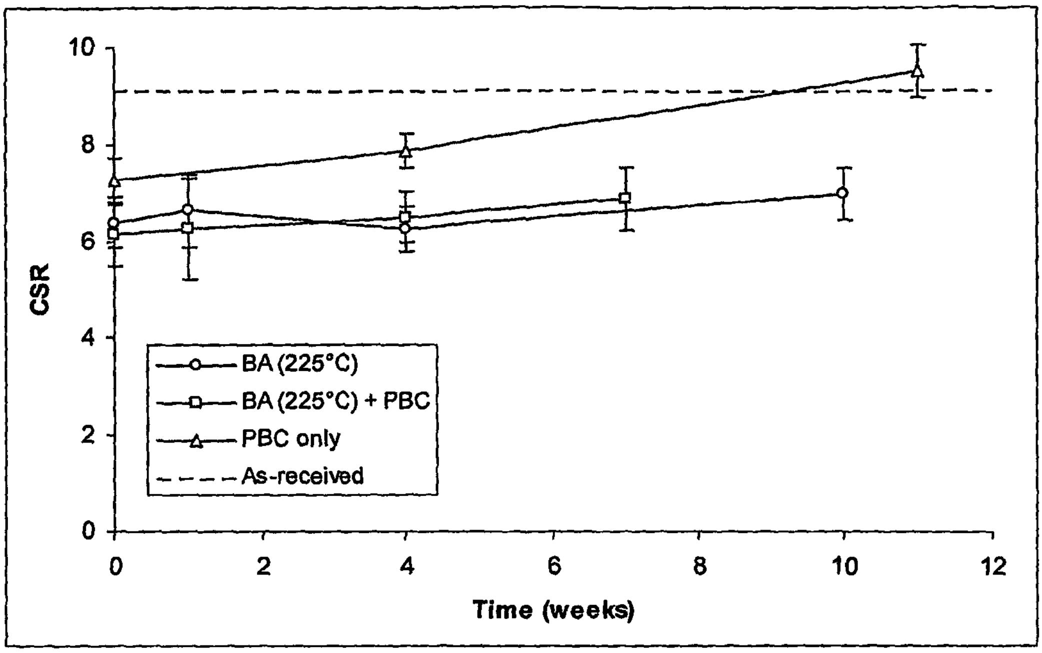

Figure 3 - Ageing behaviour of a 150g/m^2 55%Al-Zn-1.5%Si-2%Mg coating following batch annealing (BA), paint bake cycle (PBC), and a combination of both heat treatments.

REFERENCES CITED IN THE DESCRIPTION

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- US 6635359 B **[0014]**
- US 5049202 A **[0015]**
- JP 20087175975 B **[0016]**