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

(11) EP 3 870 731 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
19.06.2024 Bulletin 2024/25

(21) Application number: **19784101.8**

(22) Date of filing: **16.10.2019**

(51) International Patent Classification (IPC):
C23C 2/06 (2006.01) ***C22C 18/04*** (2006.01)
C22C 18/00 (2006.01) ***C23C 2/38*** (2006.01)
C23C 2/26 (2006.01) ***C23C 2/12*** (2006.01)
C23C 28/00 (2006.01) ***C23C 28/02*** (2006.01)

(52) Cooperative Patent Classification (CPC):
C23C 2/06; C22C 18/00; C22C 18/04; C23C 2/26; C23C 2/38; C23C 28/00; C23C 28/025

(86) International application number:
PCT/EP2019/078073

(87) International publication number:
WO 2020/083722 (30.04.2020 Gazette 2020/18)

(54) METHOD OF PROVIDING A ZINC ALLOY COATING ON A STEEL TUBE IN A CONTINUOUS PROCESSING LINE

STAHLROHR, VERSEHEN MIT EINER ZINKBASIERTEN ÜBERZUGSSCHICHT UND VERFAHREN ZUR AUFBRINGUNG EINES SOLCHEN ÜBERZUGS

TUBE D'ACIER REVÊTU D'UN REVÊTEMENT À BASE DE ZINC ET PROCÉDÉ POUR DÉPOSER UN TEL REVÊTEMENT

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.10.2018 EP 18202470**
11.09.2019 EP 19196741

(43) Date of publication of application:
01.09.2021 Bulletin 2021/35

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Description

[0001] The invention relates to a method of providing a zinc alloy coating on a steel tube in a continuous processing line wherein the steel tube is passing through a liquid zinc alloy bath. It also relates to a steel tube provided with a zinc alloy coating according to the method.

[0002] Zinc alloy coated, or galvanised steel tubes are well known in the art and are used in a wide range of applications, for instance in central heating systems, industrial packaging, automotive parts, greenhouse constructions, roof constructions, recreational equipment, fencing systems and household appliances.

[0003] The corrosion resistance of zinc or zinc alloy coated steel is considered sufficient for many applications. However, it has appeared in practice that, in particular in saline environments, the corrosion resistance sometimes does not meet the quality requirements of the customer.

[0004] The addition of magnesium to a zinc based coating in order to improve corrosion resistance is known in the art and trials with such a zinc-magnesium based coating showed improved results with respect to zinc based coatings without magnesium. For these trials a zinc based coating alloy was used with a 1.4 to 1.8 % (w/w) magnesium content and a 1.4 to 1.8 % (w/w) aluminium content, with the remainder being zinc and unavoidable impurities. The addition of aluminium also contributes to the increase of the corrosion resistance of the coating. This is a well-known coating alloy composition which e.g. is used in the automotive industry and has excellent anti-corrosion properties. Other coating alloy compositions known to improve the corrosion resistance are further described in documents EP 3 179 146 A1, JP 2004 277839 A, JP 2004 091879 A and JP 2006 188724 A.

[0005] Although the corrosion resistance improved considerably compared to the zinc based coating alloys without magnesium, the use of magnesium in the coating composition gives rise to another problem. These coatings show a certain degree of darkening, staining or discolouration of the coating over time. This is a problem, in particular for applications wherein the steel tubes are clearly visible, such as in household appliances or use in automotive parts where aesthetic properties play an important role.

[0006] The inventors, who do not wish to be called superficial in any sort of way, tried to find solutions for both problems. It is therefore an objective of the present invention to provide a steel tube with a coating with improved anti-corrosion properties. It is another objective to provide a steel tube with a coating that shows no or minimal staining or discolouration over time.

[0007] Accordingly, a method of providing a zinc alloy coating on a steel tube in a continuous processing line is provided wherein the liquid zinc alloy bath comprises 0.20 to 0.35 % (w/w) magnesium, 0.05 to 0.14 % (w/w) aluminium and unavoidable impurities, the remainder being zinc. With this zinc coating alloy applied, the corrosion resistance is increased considerably and at the same time the staining or colouration of the coating over time and / or when exposed directly to open air remains at a low level. In the trials it appeared that the normally applied upper limit of the magnesium content could be lowered to 0.20 to 0.35 % (w/w), without severely affecting the corrosion resistance. With an aluminium content in a range of 0.05 to 0.14 % (w/w) aluminium it appeared that for most applications together with the magnesium content of the alloy, a sufficient corrosion resistance is provided and at the same time a minimal degree of staining or colouration is achieved. Therefore these results were considered to have an optimal balance between the two requirements. Preferably the aluminium content is in the range of 0.10 to 0.14 % (w/w) aluminium. More preferably the aluminium content is 0.10 % (w/w) aluminium.

[0008] Good results have also been realised by providing a zinc alloy coating that comprises 0.20 to 0.35 % (w/w) magnesium, and with a zinc alloy coating that comprises 0.25 to 0.35 % (w/w) magnesium. A lower amount of magnesium has the added benefit, whilst still protecting against corrosion, that the hardness of the coating layer increases compared to magnesium-free coatings. This results in better scratch and wear resistance when used in practice. Preferably the zinc alloy coating comprises 0.30 % (w/w) magnesium.

[0009] Preferably the zinc alloy coating has a thickness in a range of 4 to 25 μm. Typically the thickness is in a range of 6 to 25 μm and a thickness in a range of 12 to 25 μm is suitable for most applications. This gives enough corrosion protection while still giving a good appearance.

[0010] Preferably the zinc alloy coating is provided only on the outside of the steel tube. When used for sanitary piping or the like these tubes should not have a zinc containing coating on the inside.

[0011] If the steel tubes provided with the coating are used in very corrosive conditions, it could happen that despite the zinc alloy coating, after some time, red rust occurs. According to a preferred embodiment, to prevent corrosion and / or colouration in such harsh conditions, a top coating layer is provided on top of the zinc alloy coating. Such a top coating can either be a transparent layer or a coloured layer, wherein the top coating layer is an organic coating layer. Preferably, a urethane, acrylate or epoxy based organic coating layer is used as top coating layer.

[0012] The organic coating can be applied as a dispersion of small particles of non-water soluble organic polymer binders in water (having a pH between 4 and 5) to steel tubes in-line by spraying, dipping or wiping. After applying the organic coating, the organic coating layer is cured and / or dried in-line before the steel tube is cut to length, for instance by means of an induction or infrared heating device.

[0013] Such coatings deliver increased corrosion protection, no white rust due to storage, protection against colouration / staining, better tube bendability (less tooling friction) and finger print resistance. The organic coating is applied with a thickness that is typically in a range of 1 to 5 μm and preferably in a range of 1 to 3 μm and is also referred to as thin organic coating, or TOC.

[0014] To optimise the investigation of corrosion resistance together with staining resistance a matrix of different coating samples were prepared in the laboratory with a Rhesca zinc hot dip simulator with varying concentrations of both aluminium and magnesium. See table 1 below.

Table 1.

Code	% aluminium	% magnesium
Zn0.1Al	0.1	0.0
Zn0.1Al0.1Mg	0.1	0.1
Zn0.1Al0.2Mg	0.1	0.2
Zn0.1Al0.3Mg	0.1	0.3
Zn0.1Al0.6Mg	0.1	0.6
Zn0.1Al0.9Mg	0.1	0.9
Zn0.5Al	0.5	0.0
Zn0.5Al0.2Mg	0.5	0.2
Zn0.5Al0.5Mg	0.5	0.5
Zn0.5Al1.0Mg	0.5	1.0
Zn1.6Al	1.6	0.0
Zn1.6Al0.2Mg	1.6	0.2
Zn1.6Al0.5Mg	1.6	0.5
Zn1.6Al1.0Mg	1.6	1.0
Zn1.6Al1.6Mg	1.6	1.6
Zn5.0Al	5.0	0.0
Zn5.0Al0.2Mg	5.0	0.2
Zn5.0Al0.5Mg	5.0	0.5
Zn5.0Al1.0Mg	5.0	1.0

[0015] For each bath chemistry, at least 5 samples were produced. For corrosion testing, one sample of each bath chemistry was chosen having the best properties, i.e. one side a layer thickness between 9 and 11 μm and free of bare spots. For staining tests, samples were chosen having a uniform surface. Coating thickness was not considered to be of importance.

[0016] All samples were exposed to a staining test, by dipping into a 0.1 M solution of acetic acid at room temperature for 20 seconds. All samples were drawn out of the solution with minimal drag-out and rapidly dried by a blast of cold air, avoiding stray droplets as much as possible. That way, the surface retained its uniformity (no dried droplets). No staining occurred during this procedure. Exposure of the dried but not rinsed samples to humid and warm atmosphere (80 % relative humidity at 40 °C) for 4 days (96 hours) and 15 days (360 hours) caused a decrease of L-values measured with the Specular Component Included (SCI) method using a Minolta CM2002 spectrophotometer. This measurement method measures all light reflected from the substrate, including the light reflected at the angle of incidence. A decrease of the SCI L-value is an indication that less light in total has reflected from the surface after exposure of the acid covered samples to humid atmosphere, i.e. darkening has occurred during the exposure. This darkening is thought to be due to local chemical erosion of the surface by electrochemical corrosion, leading to surface roughening. The corrosion products formed are not black, but the roughening of the metal surface is thought to prevent reflection of light that enters the pits, increasing light absorption.

[0017] Table 2 shows the results of staining, percentage red rust after 504 hrs of salt spray testing and appearance of white rust after 1008 hrs VDA 233-102 cyclic testing (a cyclic corrosion test of materials and components). Light colour "yes" means the sample has not darkened appreciably as seen by the naked eye, whereas light colour "no" means that the sample showed a clear darkening as seen by the naked eye. "Coarse" means large amounts of porous white rust deposits and "fine" means whitewash type of appearance having a low amount of deposit.

Table 2.

	%Al	%Mg	sci L-value 0 days	sci L-value 4 days	sci L-value 15 days	light colour 15 days	%RR SST	WR 1008 hrs VDA	results combined
Zn0.1Al	0.1	0.0	92	92	91	yes	90	coarse	--
Zn0.1Al0.1Mg	0.1	0.1	92	88	87	yes	20	coarse	-
Zn0.1A10.2Mg	0.1	0.2	90	85	84	yes	5	coarse	-
Zn0.1Al0.3Mg	0.1	0.3	89	84	82	yes	0	fine	++
Zn0.1Al0.6Mg	0.1	0.6	86	80	74	no	0	fine	0
Zn0.1Al0.9Mg	0.1	0.9	80	75	68	no	0	fine	0
Zn0.5Al	0.5	0.0	92	92	91	yes	80	coarse	- -
Zn0.5Al0.2Mg	0.5	0.2	90	89	88	yes	10	coarse	-
Zn0.5Al0.5Mg	0.5	0.5	88	85	84	yes	0	fine	++
Zn0.5Al1.0Mg	0.5	1.0	88	81	77	no	0	fine	0
Zn 1.6Al	1.6	0.0	92	92	91	yes	70	coarse	- -
Zn1.6Al0.2Mg	1.6	0.2	91	85	86	yes	0	coarse	+
Zn1.6Al0.5Mg	1.6	0.5	88	81	82	yes	0	fine	++
Zn1.6Al1.0Mg	1.6	1.0	88	78	76	no	0	fine	-
Zn1.6Al1.6Mg	1.6	1.6	82	68	69	no	0	fine	-
Zn5.0Al	5.0	0.0	92	92	91	yes	5	coarse	-
Zn5.0Al0.2Mg	5.0	0.2	92	87	87	yes	0	coarse	+
Zn5.0Al0.5Mg	5.0	0.5	91	88	84	yes	0	fine	++
Zn5.0Al1.0Mg	5.0	1.0	91	85	78	no	0	fine	0

[0018] In this test, it is clear that the L-value of those samples not containing any Mg hardly decrease in this test, indicating no staining with time. The L-values decrease with more magnesium and longer exposure times to humid atmosphere (before and right after dipping all samples did not show any decrease of L-value). The high aluminium grades were seen to be less sensitive to staining with the addition of magnesium than the other samples.

[0019] The values in table 2 show clearly that magnesium leads to staining, and more magnesium leads to more staining. Probably, a higher amount of aluminium (5 %) makes the coating less sensitive to staining (more gloss retention in case of high magnesium content). Even a minor addition of magnesium is strongly beneficial, which is very fortunate in the light of reducing staining issues.

[0020] The VDA-test after 1008 hours of testing (6 weeks), shows some red rust specks on the Zn1.6Al sample only. All samples acquire a whitish appearance, But all samples not containing any magnesium show coarse and repulsive deposits of white oxide.

Claims

1. Steel tube provided with a zinc alloy coating, **characterised in that** the zinc alloy coating comprises 0.20 to 0.35 % (w/w) magnesium, 0.05 to 0.14 % (w/w) aluminium and unavoidable impurities, the remainder being zinc, and wherein the zinc alloy coating is provided only on the outside of the steel tube.

2. Steel tube provided with a zinc alloy coating according to claim 1, **characterised in that** the zinc alloy coating comprises 0.10 to 0.14 % (w/w) aluminium.

3. Steel tube provided with a zinc alloy coating according to claim 1 or 2, **characterised in that** the zinc alloy coating comprises 0.25 to 0.35 % (w/w) magnesium.

4. Steel tube provided with a zinc alloy coating according to anyone of the claims 1 to 3, **characterised in that** the zinc alloy coating comprises 0.30 % (w/w) magnesium.

5. Steel tube provided with a zinc alloy coating according anyone of the claims 1 to 4, **characterised in that** the zinc alloy coating has a thickness in a range of 4 to 25 μm.

6. Steel tube provided with a zinc alloy coating according to any of the claims 1 to 5 , **characterised in that** a top coating layer is provided on top of the zinc alloy coating.

7. Steel tube provided with a zinc alloy coating according to claim 6 , **characterised in that** the top coating layer is a transparent or coloured organic coating layer.

8. Method of providing a zinc alloy coating on a steel tube in a continuous processing line wherein the steel tube is passing through a liquid zinc alloy bath, **characterised in that** the liquid zinc alloy bath comprises 0.20 to 0.35 % (w/w) magnesium, 0.05 to 0.14 % (w/w) aluminium and unavoidable impurities, the remainder being zinc, and wherein the zinc alloy coating is provided only on the outside of the steel tube.

9. Method of providing a zinc alloy coating according to claim 8 , **characterised in that** the liquid zinc alloy bath comprises 0.10 to 0.14 % (w/w) aluminium.

10. Method of providing a zinc alloy coating according to claim 8 or 9, **characterised in that** the liquid zinc alloy bath comprises 0.25 to 0.35 % (w/w) magnesium.

11. Method of providing a zinc alloy coating according to claim 8 or 9, **characterised in that** the liquid zinc alloy bath comprises 0.30 % (w/w) magnesium.

12. Method of providing a zinc alloy coating according to anyone of the claims 8 to 10, **characterised in that** the zinc alloy coating has a thickness in a range of 4 to 25 μm.

13. Method of providing a zinc alloy coating according to anyone of the claims 8 to 12, **characterised in that** a top coating layer is applied after applying the zinc alloy coating.

Patentansprüche

1. Stahlrohr, versehen mit einem Zinklegierungsüberzug, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug 0,20 bis 0,35 % (Gew./Gew.) Magnesium, 0,05 bis 0,14 % (Gew./Gew.) Aluminium und unvermeidbare Verunreinigungen umfasst, wobei der Rest Zink ist, und wobei der Zinklegierungsüberzug nur auf der Außenseite des Stahlrohrs bereitgestellt ist.

2. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach Anspruch 1, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug 0,10 bis 0,14 % (Gew./Gew.) Aluminium umfasst.

3. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug 0,25 bis 0,35 % (Gew./Gew.) Magnesium umfasst.

4. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug 0,30 % (Gew./Gew.) Magnesium umfasst.

5. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug eine Dicke in einem Bereich von 4 bis 25 μm aufweist.

6. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** auf dem Zinklegierungsüberzug eine Decküberzugsschicht bereitgestellt ist.

7. Stahlrohr, versehen mit einem Zinklegierungsüberzug, nach Anspruch 6, **dadurch gekennzeichnet, dass** die Decküberzugsschicht eine transparente oder farbige organische Überzugsschicht ist.

8. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs auf einem Stahlrohr in einer kontinuierlichen Verarbeitungslinie, wobei das Stahlrohr durch ein flüssiges Zinklegierungsbad läuft, **dadurch gekennzeichnet, dass** das flüssige Zinklegierungsbad 0,20 bis 0,35 % (Gew./Gew.) Magnesium, 0,05 bis 0,14 % (Gew./Gew.) Aluminium und unvermeidbare Verunreinigungen umfasst, wobei der Rest Zink ist, und wobei der Zinklegierungsüberzug nur auf der Außenseite des Stahlrohrs bereitgestellt wird.

9. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs nach Anspruch 8, **dadurch gekennzeichnet, dass** das flüssige Zinklegierungsbad 0,10 bis 0,14 % (Gew./Gew.) Aluminium umfasst.

10. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs nach Anspruch 8 oder 9, **dadurch gekennzeichnet, dass** das flüssige Zinklegierungsbad 0,25 bis 0,35 % (Gew./Gew.) Magnesium umfasst.

11. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs nach Anspruch 8 oder 9, **dadurch gekennzeichnet, dass** das flüssige Zinklegierungsbad 0,30 % (Gew./Gew.) Magnesium umfasst.

12. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs nach einem der Ansprüche 8 bis 10, **dadurch gekennzeichnet, dass** der Zinklegierungsüberzug eine Dicke in einem Bereich von 4 bis 25 μm aufweist.

13. Verfahren zum Bereitstellen eines Zinklegierungsüberzugs nach einem der Ansprüche 8 bis 12, **dadurch gekennzeichnet, dass** nach dem Aufbringen des Zinklegierungsüberzugs eine Decküberzugsschicht aufgebracht wird.

Revendications

1. Tube en acier doté d'un revêtement en alliage de zinc, **caractérisé en ce que** le revêtement en alliage de zinc comprend de 0,20 à 0,35 % (p/p) de magnésium, de 0,05 à 0,14 % (p/p) d'aluminium et des impuretés inévitables, le reste étant du zinc, et dans lequel le revêtement en alliage de zinc est formé uniquement sur l'extérieur du tube en acier.

2. Tube en acier doté d'un revêtement en alliage de zinc selon la revendication 1, **caractérisé en ce que** le revêtement en alliage de zinc comprend de 0,10 à 0,14 % (p/p) d'aluminium.

3. Tube en acier doté d'un revêtement en alliage de zinc selon la revendication 1 ou 2, **caractérisé en ce que** le revêtement en alliage de zinc comprend de 0,25 à 0,35 % (p/p) de magnésium.

4. Tube en acier doté d'un revêtement en alliage de zinc selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que** le revêtement en alliage de zinc comprend 0,30 % (p/p) de magnésium.

5. Tube en acier doté d'un revêtement en alliage de zinc selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** le revêtement en alliage de zinc possède une épaisseur comprise dans la plage de 4 à 25 μm.

6. Tube en acier doté d'un revêtement en alliage de zinc selon l'une quelconque des revendications 1 à 5, **caractérisé en ce qu'**une couche de revêtement supérieure est formée sur le dessus du revêtement en alliage de zinc.

7. Tube en acier doté d'un revêtement en alliage de zinc selon la revendication 6, **caractérisé en ce que** la couche de revêtement supérieure est une couche de revêtement organique transparente ou colorée.

8. Procédé de formation d'un revêtement en alliage de zinc sur un tube en acier dans une ligne de traitement continue dans lequel le tube d'acier passe à travers un bain d'alliage de zinc liquide, **caractérisé en ce que** le bain d'alliage de zinc liquide comprend de 0,20 à 0,35 % (p/p) de magnésium, de 0,05 à 0,14 % (p/p) d'aluminium et d'impuretés inévitables, le reste étant du zinc, et dans lequel le revêtement en alliage de zinc est formé uniquement sur l'extérieur du tube en acier.

9. Procédé de formation d'un revêtement en alliage de zinc selon la revendication 8, **caractérisé en ce que** le bain d'alliage de zinc liquide comprend de 0,10 à 0,14 % (p/p) d'aluminium.

10. Procédé de formation d'un revêtement en alliage de zinc selon la revendication 8 ou 9, **caractérisé en ce que** le bain d'alliage de zinc liquide comprend de 0,25 à 0,35 % (p/p) de magnésium.

11. Procédé de formation d'un revêtement en alliage de zinc selon la revendication 8 ou 9, **caractérisé en ce que** le bain d'alliage de zinc liquide comprend 0,30 % (p/p) de magnésium.

12. Procédé de formation d'un revêtement en alliage de zinc selon l'une quelconque des revendications 8 à 10, **caractérisé en ce que** le revêtement en alliage de zinc possède une épaisseur comprise dans la plage de 4 à 25 μm.

13. Procédé de formation d'un revêtement en alliage de zinc selon l'une quelconque des revendications 8 à 12, **caractérisé en ce qu'**une couche de revêtement supérieure est appliquée après l'application du revêtement en alliage de zinc.

REFERENCES CITED IN THE DESCRIPTION

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