

### Hot-dip galvanizing bath and process

The present invention relates to a bath for hot-dip galvanizing consisting of alloyed zinc, that is particularly useful for batch-wise galvanizing steel articles, the silicon content of which is variable  
5 or the composition of which is unknown.

When galvanizing steel in a conventional non-alloyed zinc bath serious problems arise, when the steel contains more than 0.02 wt% of silicon : the resulting zinc coating is both too thick and too brittle and in addition it has a greyish aspect. This is due to the fact that the iron-zinc alloy layer  
10 that forms on the surface of the steel when the latter is in contact with a conventional zinc bath, grows linearly with the time during the entire duration of the immersion, when the steel contains more than 0.02 wt% of silicon. This is not the case with steels containing less silicon, as the growth rate is here proportional to the square root of the immersion time. The influence of the silicon content of the steel on the coating thickness is illustrated in the diagram of the  
15 accompanying figure 1 : the thickness peak on steels with 0.03 - 0.15 wt% Si is called the Sandelin peak.

Efforts have already been made in the past to cope with this problem. The Technigalva<sup>®</sup> process uses a zinc bath alloyed with 0.05 - 0.06 wt% of nickel. As shown in figure 1, the Sandelin peak disappears in the Technigalva<sup>®</sup> bath, but the coating thickness still increases  
20 with the silicon content of the steel. The Polygalva<sup>®</sup> process uses a zinc bath with 0.035 - 0.045 wt% of aluminium and 0.003-0.005 wt% of magnesium. As shown in figure 1, the Polygalva<sup>®</sup> bath gives rather good results ; it presents however the drawback that its aluminium content has to be controlled very strictly, because the reaction between the steel and the bath blocks almost completely once the aluminium content of the bath exceeds 0.05 wt%.

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The aim of the present invention is to provide a bath for hot-dip galvanizing consisting of alloyed zinc, which makes the coating thickness much less dependent on the silicon content of the steel than this is the case with the Technigalva<sup>®</sup> bath and much less dependent on small variations in the bath composition than this is the case with the Polygalva<sup>®</sup> bath.

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This aim is achieved according to the invention by a bath that contains either 3 - 15 wt% of tin or 1 - 5 wt% of tin and 0.01 - 0.1 wt% of nickel and that may contain lead at a concentration up to saturation and at least one of aluminium, calcium and magnesium at a concentration up to 0.06 wt%, the rest being zinc and unavoidable impurities.

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When the bath does not contain nickel, its preferred tin content is 3.5 - 14 wt%, the most preferred tin content being 5 - 10 wt%. When it contains nickel, its preferred tin and nickel contents are respectively 2.5 - 5 wt% and 0.03 - 0.06 wt%.



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The nickel content of the bath with 1 - 5 wt% of tin has to be at least 0.01 wt% ; otherwise, the coating thickness may vary substantially with the silicon content of the steel. However, the nickel content mustn't exceed 0.1 wt% ; otherwise there is a risk of formation of floating dross.

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An addition of lead at a concentration that may attain saturation, for example 0.1 - 1.2 wt%, may be useful in order to decrease the surface tension of the bath.

An addition of at least one of aluminium, calcium and magnesium, preferably at a concentration of 0 - 0.03 wt% and more preferably of 0.005 - 0.015 wt%, may also be useful in order to protect the zinc from oxidation ; otherwise a yellowish pellicle is formed on the surface of the bath, which fouds the galvanized articles.

However the aluminium content mustn't exceed 0.03 wt% ; otherwise there is a risk of obtaining uncovered spots. The magnesium and/or calcium contents mustn't exceed 0.03 wt% ; otherwise MgO or CaO floating on the surface of the bath may spoil the coating ; moreover the bath becomes less fluid which may result in a degraded finishing of the coating.

It should be noted here that LU-A-81 061 describes a process consisting of a galvanisation bath which contains at least 70 wt% of zinc, characterized in that one or more of the following elements is added to said galvanisation bath : chromium, nickel, boron, titanium, vanadium, zirconium, manganese, copper, niobium, cerium, molybdenum, cobalt, antimony, calcium, lithium, sodium, potassium, in such an amount that the bath contains less than 2 wt% of each element taken separately.

The zinc may be of any quality going from remelted zinc scrap to SHG (Special High Grade). It is however recommended to use at least Zn 98.5 (ISO standard 752 - 1981), preferably at least Zn 99.5 and still more preferably at least Zn 99.95.

The invention is illustrated by the following examples.

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#### Example 1

Six types of steel called X, M, E, D, R and Y with various silicon and phosphorus contents have been galvanized in baths of SHG zinc with various tin contents, using a bath temperature of 450°C and an immersion time of 5 minutes.

The coating thickness has been measured.

The results of these tests are summarised in table 1 hereafter.

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Table 1 (Zn-Sn baths)

| Steel type         | X                                  | M     | E     | D     | R     | Y     |
|--------------------|------------------------------------|-------|-------|-------|-------|-------|
| wt% Si             | 0.010                              | 0.092 | 0.177 | 0.450 | 0.018 | 0.075 |
| wt% P              |                                    |       |       |       | 0.069 | 0.017 |
| Sn content of bath | Coating thickness in $\mu\text{m}$ |       |       |       |       |       |
| 0.0 wt%            | 63                                 | 244   | 136   | 236   | 398   | 271   |
| 1.0 wt%            | 77                                 | 228   |       | 189   |       |       |
| 2.5 wt%            | 82                                 | 136   | 82    | 168   | 138   | 222   |
| 5.0 wt%            | 78                                 | 100   |       | 100   |       |       |
| 10.0 wt%           | 91                                 | 86    | 67    | 84    | 98    | 81    |
| 20.0 wt%           | 76                                 | 65    | 64    | 64    | 78    | 57    |
| 30.0 wt%           | 59                                 | 58    | 54    | 61    | 67    | 52    |

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The graphical representation of these results in the diagram of figure 2 shows that from a tin content of about 3 wt% on five of the six tested steels present already a coating thickness of less than 150  $\mu\text{m}$  and that from a tin content of 5 wt% on all tested steels have a coating thickness ranging between about 75  $\mu\text{m}$  and about 110  $\mu\text{m}$ .

- 10 In this context it should be noted that a coating thickness of 70 - 90  $\mu\text{m}$  is the most desirable one.

It should also be noted that steel type Y with 0.075 wt% Si and 0.017 wt% P is a particularly reactive one, the effect of P on the steel reactivity being still much more pronounced than that of Si.

- 15 From the above data it is also clear that the results do not improve when the tin content exceeds 15 wt% and that it is recommendable to use no more than 10 wt% tin.

### Example 2

- 20 The same types of steel of example 1 have been galvanized in baths of SHG zinc with 0.055 wt% nickel and various tin contents in the same conditions as in example 1.
- The results of these tests are summarised in table 2 hereafter.

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Table 2 (Zn - 0.055 Ni - Sn baths)

|                       | Steel type                         | X  | M   | E   | D   | R   | Y   |
|-----------------------|------------------------------------|----|-----|-----|-----|-----|-----|
| Sn content<br>of bath | Coating thickness in $\mu\text{m}$ |    |     |     |     |     |     |
|                       |                                    |    |     |     |     |     |     |
| 0.0 wt%               |                                    | 59 | 116 | 134 | 212 | 413 | 242 |
| 1.0 wt%               |                                    | 67 | 97  | 92  | 195 |     |     |
| 2.5 wt%               |                                    | 69 | 80  | 70  | 115 |     |     |
| 5.0 wt%               |                                    | 72 | 80  | 72  | 95  | 88  | 88  |

- 5 The graphical representation of these results in the diagram of figure 3 shows that a tin content of 1wt% gives already a significant improvement. It also shows that it is recommendable to use a tin content ranging between 2.5 and 5 wt%.

Example 3

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The same types of steel of example 1 have been galvanized in baths of SHG zinc with 1.2 wt% lead and various tin contents in the same conditions as in example 1.

The results of these tests are summarised in table 3 hereafter.

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Table 3 (Zn - 1.2 Pb - Sn baths)

|                       | Steel type                         | X  | M   | E  | D   | R   | Y   |
|-----------------------|------------------------------------|----|-----|----|-----|-----|-----|
| Sn content<br>of bath | Coating thickness in $\mu\text{m}$ |    |     |    |     |     |     |
|                       |                                    |    |     |    |     |     |     |
| 1.0 wt%               |                                    | 79 | 219 |    | 199 |     |     |
| 1.5 wt%               |                                    |    |     |    | 192 |     |     |
| 2.0 wt%               |                                    |    |     |    | 174 |     |     |
| 2.5 wt%               |                                    |    |     |    | 155 |     |     |
| 3.0 wt%               |                                    | 82 | 109 | 88 | 138 | 123 | 128 |

- 20 The graphical representation of these results in the diagram of figure 4 shows again the beneficial effect of tin on the coating thickness.
- The results achieved with 3 wt% tin are apparently somewhat better here than in example 1 (see figure 2). That's why it may be useful to add lead to the bath.



The foregoing makes clear that the bath of the present invention allows to avoid both the drawback of the Technigalva<sup>®</sup> bath and the drawback of the Polygalva<sup>®</sup> bath.

Another advantage of the bath of the present invention lies in the fact that it gives a nicer floral  
5 pattern and higher brightness than the prior art baths.

Noteworthy is also that in long run tests with the bath of present invention neither the formation of bottom dross nor the formation of floating dross has been observed.

Also important is that the tin consumption is limited, the tin content of the coating being much lower than the tin content of the bath.

10 That's why the bath of the present invention is particularly useful for the toll galvanizing process, wherein the galvanizer has to treat all kinds of steel articles the silicon and phosphorus contents of which is usually unknown to him.

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CLAIMS

1. A bath for hot-dip galvanizing consisting of alloyed zinc, characterized in that it contains  
3 - 15 wt% of tin, lead at a concentration up to saturation and 0 - 0.06 wt% of at least one of  
5 aluminium, calcium and magnesium, the rest being zinc and unavoidable impurities.
2. A bath for hot-dip galvanizing consisting of alloyed zinc, characterized in that it contains  
1 - 5 wt% of tin, 0.01 - 0.1 wt% of nickel, lead at a concentration up to saturation and  
0 - 0.06 wt% of at least one of aluminium, calcium and magnesium, the rest being zinc and  
10 unavoidable impurities.
3. A bath, according to claim 1, characterized in that it contains 0 - 0.03 wt% of at least one of  
aluminium, calcium and magnesium.
- 15 4. A bath, according to claim 2, characterized in that it contains 0 - 0.03 wt% of at least one of  
aluminium, calcium and magnesium.
5. A bath according to claims 1 or 3, characterized in that it contains 3.5 - 14 wt% of tin.
- 20 6. A bath according to claim 5, characterized in that it contains 5 - 10 wt% of tin.
7. A bath according to claims 2 or 4, characterized in that it contains at least 2.5 wt% of tin.
8. A bath according to claims 2, 4 or 7, characterized in that it contains at least 0.03 wt% of  
25 nickel.
9. A bath according to claim 8, characterized in that it contains 0.03 - 0.06 wt% of nickel.
10. A bath according to any one of claims 1 - 9, characterized in that it contains  
30 0.005 - 0.015 wt% of at least one of aluminium, calcium and magnesium.
11. A process for batch-wise hot-dip galvanizing steel articles that may contain silicon and/or  
phosphorus, characterized in that it uses the bath according to any one of claims 1 - 10.

