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PROCESS FOR THE DIFFUSION-SUBSTITUTION COATING OF METAL ARTICLES FROM A TIN SALT MELT

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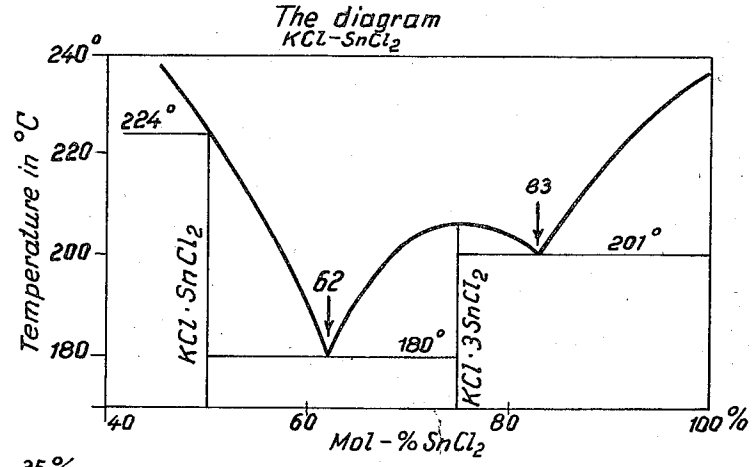

Fig.1

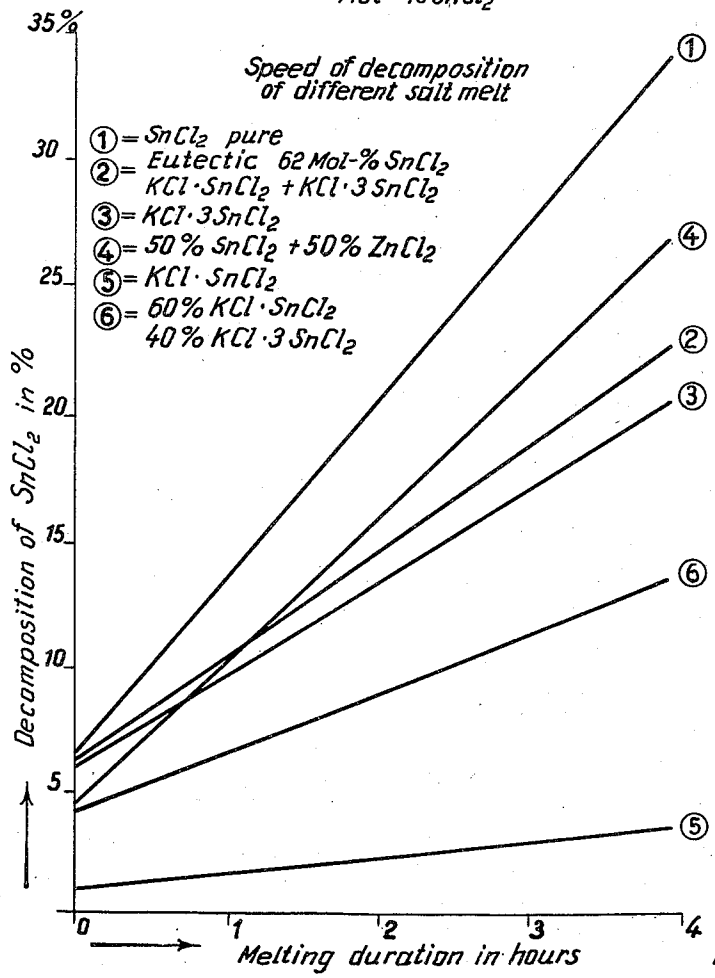

Fig.2

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PROCESS FOR THE DIFFUSION-SUBSTITUTION COATING OF METAL ARTICLES FROM A TIN SALT MELT

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7 Claims. (Cl. 117—130)

1

It is already known to tin articles of iron, steel, copper or copper alloys by dipping or immersing them into anhydrous salt melts containing stannous chloride. The scheme of reaction is the following:

$$Cu+SnCl_2=CuCl_2+Sn \quad (1)$$

$$Fe+SnCl_2=FeCl_2+Sn \quad (2)$$

It is therefore a matter of place changing reaction in which always as much tin atoms are deposited on the dipped article as inversely copper or iron atoms are transferred from the respective article into the salt bath. It is evident that by such place changing reaction a tinning may be made in which a vast steadiness of the dimensions of the immersed articles is guaranteed. This process has considerable advantages as in contradistinction to the other tinning processes the dimensions of the dipped articles retain their exact size and any extra work is avoided. The reaction takes place in the molten salt melt, i. e. at a higher temperature (300–500° C.). In consequence thereof the separated tin diffuses into the dipped articles thereby forming an alloy and firmly connecting the superficial tin layer with the material of the article to be tinned.

In spite of the described advantages this very simple process was up to now without any importance for the tinning, the reason therefore being only attributable to its economy. Stannous chloride, the only tin salt being in question, has the disagreeable quality to easily dissolve, i. e. to form oxychlorides under the influence of the oxygen of the air, the atmospheric humidity or oxidized materials, or to decompose in pure oxygen combinations. The respective transformations are the following:

$$2SnCl_2+H_2O+O=2SnOCl+2HCl \quad (3)$$

or

$$SnCl_2+H_2O=SnO+2HCl \quad (4)$$

If oxychlorides or oxides are used the described tinning process by place changing reaction does not take place. Both oxygen combinations are insoluble in pure stannous chloride as well as in salt melts containing stannous chloride (sludge forming) and withdraw from the tinning reaction thus causing inacceptable losses of tin. The oxygen compositions are preferably formed during the producing of the salt bath but also during the tinning process itself.

(1) *Oxidation during the producing of the salt bath*

Stannous chloride of usual commercial quality contains two parts of water of crystallization

2

($SnCl_2.2H_2O$). This salt melts at 37.7° C. in its water of crystallization. If further heated, the water of crystallization vaporizes briskly frothing. Thereby considerable quantities of stannous chloride decompose according to the Equations 3 and 4. From the outside this decomposition may be seen by the colour of the molten salt changing with the increasing forming of oxides from a state clear as water gradually to a dingy yellow until green state. By addition of hydrochloric acid the Reactions 3 and 4 may be somewhat displaced to the left side, i. e. to the side of the stannous chloride according to the law of mass action, however, this fact does not give any practically noticeable protection against the decomposition.

(2) *Oxidation during the tinning process*

By the influence of the air the decomposition of the stannus chloride progresses during the tinning (300 to 500° C.) in a considerable degree so that already after a short working duration the salt bath becomes useless. The oxidized stannous chloride is lost for the tinning process and cannot be regenerated.

For the purpose to restrain the decomposition of the stannous chloride different suggestions have been made, consisting in adding alkali halogenide, earth alkali halogenide and chloride of zinc, individually or in combination, to the stannous chloride.

(*a*) *Sodium chloride.*—No combinations are formed with the $SnCl_2$. An eutectic lies at 69 mole-percent $SnCl_2$ and 183° C. Additions until 90 mole-percent NaCl with regard to $SnCl_2$ were suggested.

(*b*) *Potassium chloride.*—The diagram

$KCl—SnCl_2$

is shown in Fig. 1 of the drawing. According to this diagram the compositions $KCl.SnCl_2$ and $KCl.3SnCl_2$ are produced with the melting points near 224° or 208° C. respectively. An eutectic lies at 62 mole-percent $SnCl_2$ and 180° C. This eutectic consists of 52% $KCl.SnCl_2$ and 48% $KCl.3SnCl_2$. For the purpose to restrain the decomposition of the stannous chloride additions of 17 to 38 mole-percent KCl were suggested. The eutectic composition at 62 mole-percent $SnCl_2$ had been suggested as forming the lowest limit.

(*c*) *Chloride of zinc.*—With $SnCl_2$ only one eutectic exists at 44 mole-percent $ZnCl_2$ and 171° C. No compositions. Additions of 5 to 70% $ZnCl_2$ have been suggested, preferably a mixture of 50% $SnCl_2$ and 50% $ZnCl_2$ has been used.

Thorough tests have shown that the action of

all additions suggested up to now is only very inconsiderable with respect to the decomposition of the stannous chloride. A number of results of such examinations are to be seen from Fig. 2 of the drawing relating to a middle tinning temperature of 350° C. Curve 1 serves for the purpose of comparison, showing the conditions with pure $SnCl_2$. It is to be seen that already by the melting about 6.5% $SnCl_2$ decompose (in the figure at 0 hours). With the increasing duration of the tests the decomposition linearly increases. If 30 mole-percent KCl (eutectic concentration) is added to the stannous chloride the decomposition of the stannous chloride is only little diminished as to be seen from curve 2. Also an addition of KCl corresponding to the composition $KCl.3SnCl_2$ (curve 3) may only inconsiderably restrain the decomposition of $SnCl_2$. By way of example a composition of 50 mole-percent SnCl and 50 mole-percent $ZnCl_2$ has been chosen (curve 4) to show the action of an addition of $ZnCl_2$. The action restraining the decomposition is also inconsiderable. Mixtures of $SnCl_2$ with NaCl, NH_4Cl, $MgCl_2$, $CaCl_2$ and $BaCl_2$ are in an equal position.

Systematic tests have shown that an addition of KCl corresponding to the constitution of the combination $SnCl_2.KCl$ restrain the decomposition of the stannous chloride in a surprising degree. As to be seen from curve 5 in Fig. 2 f. i. after a duration of the test for 4 hours only about 3.5% $SnCl_2$ were decomposed in comparison to more than 40% if pure $SnCl_2$, 30% if 50 mole-percent $ZnCl_2$, 22.5% if the eutectic

$KCl.SnCl_2$—$KCl.3SnCl_2$

(62 mole-percent $SnCl_2$) and 20.5% if $KCl.3SnCl_2$ are used. An addition of KCl corresponding to the constitution $KCl.SnCl_2$ diminishes therefore the decomposition of the stannous chloride for more than 90%. If the duration of the test is prolongated the superiority of the constitution $KCl.SnCl_2$ is still more apparent. Already during the melting this composition proves very stable. While all other mixtures lose 4.5 to 6.5% $SnCl_2$ already by the dehydrating the loss amounts only about 1% (Fig. 2, 0 hour) if the constitution $KCl.SnCl_2$ is used. Thus the preliminary conditions of an economical execution of the described tinning process are given. The small decomposition of stannous chloride still existing may be accepted without ado. The technical advantage over the suggestions made up to now is evident. Also a composition corresponding to at least 60% of $KCl.SnCl_2$ shows a loss of stannous chloride (Fig. 2, curve 6) still acceptable in the economical respect.

These $KCl.SnCl_2$ melts with at least 60% $KCl.SnCl_2$ have still a further surprising advantage not present in any other tinning salt. They are in no way hygroscopic. While the tinning salts used up to now desire for sucking in water from the surrounding atmosphere already after a short storing in the air and change into a pulpy aqueous mass, the salt mixtures according to the given definition may be stored for an unrestricted time and remain absolutely dry.

Example of manufacture

About 59.2 kg. fine tin are solved in 87.7 l. hydrochloric acid (specific gravity 1.19). Hereby about 112.8 kg. aqueous stannous chloride ($SnCl_2.2H_2O$) are obtained. It is also possible to start on about 112.8 kg. stannous chloride of usual commercial quality ($SnCl_2.2H_2O$). That is heated in a crucible of cast iron or graphite. Already at 37.7° C. the salt becomes liquid in its own water of crystallization. In this melt about 37.3 kg. potassium chloride, f. i. in the form of Silvin, is inserted. If the temperature is further increased and the melt is constantly stirred the water of crystallization evaporates frothing. Gradually the salt mixture dries but becomes again liquid at 224° C., the melting point of the pure composition. Thereupon it may be cast to pigs and stored or immediately used for tinning. Weight about 132 kg. $KCl.SnCl_2$.

Sometimes it may be suitable to dilute the salt of the composition $KCl.SnCl_2$ manufactured in the described manner, f. i. if the tinning process has to take a very slow course. For this purpose neutral and cheap salts are suitably used, f. i. halogenides of the alkali metals, the earth alkali metals and the zinc. Preferably salts are in question producing together with $KCl.SnCl_2$ a mixture having a melting point below 600° C.

Having thus particularly described the nature of our invention and the manner in which the same is to be performed what we claim to be covered by Letters Patent is:

1. A method for tin coating iron articles comprising immersing the said articles directly in a molten bath consisting of at least 60 per cent $KCl.SnCl_2$, the rest of the bath being composed of a substance selected from the group consisting of alkali metal, earth alkali metal and zinc halides, and maintaining said bath at a temperature of between 300–500° C.

2. A method for tin coating iron articles comprising immersing the said articles without prior treatment directly into a molten bath containing at least 60 per cent of a potassium chloride and tin chloride composition conforming to the molecular ratio $KCl.SnCl_2$, the rest of the bath consisting of potassium chloride, and maintaining said bath at a temperature of between 300–500° C.

3. A method for tin coating iron articles comprising immersing the said articles without prior treatment directly into a molten bath containing at least 60 per cent of a potassium chloride and tin chloride composition conforming to the molecular ratio $KCl.SnCl_2$, the rest of the bath consisting of $KCl.3SnCl_2$, and maintaining said bath at a temperature of between 300–500° C.

4. A method for the tin-diffusion-substitution coating of articles made of iron, iron alloys, copper, copper alloys, and zinc alloys comprising preparing an anhydrous molten bath containing at least 60 per cent $KCl.SnCl_2$, the residual components of the bath being a substance selected from a group consisting of alkali metal, earth alkali metal and zinc halides, maintaining said bath at a temperature of between 224° C. and 500° C., thus obtaining an anhydrous molten tin salt bath which is poor in oxide and immersing said articles in said bath for a sufficient time to substitute their metal surface layer with a tin-diffusion-substitution coating.

5. In a process according to claim 1, the use of an anhydrous molten bath consisting of about 60 per cent by weight of $KCl.SnCl_2$ and about 40 per cent by weight of $KCl.3SnCl_2$.

6. A process for the tin-diffusion surface-layer substitution coating of articles made of iron, iron alloys, copper, copper alloys and zinc alloys consisting of preparing an anhydrous tin salt poor in oxide and having not less than 60 per cent by weight of an anhydrous $KCl.SnCl_2$, the remainder consisting of a substance selected from a group

composed of alkali metal, earth alkali metal and zinc halides, the said mixture being controlled to have a fusion point below 600° C., heating said mixture to a temperature of between 224° C. and not exceeding 600° C. and obtaining thereby an anhydrous, poor in oxide tin salt bath and immersing said articles in said bath for a sufficient time to substitute their metal surface layer with a tin diffusion-substitution coating.

7. A process for the tin-diffusion surface layer substitution coating of articles made of iron, iron alloys, copper, copper alloys and zinc alloys comprising preparing an anhydrous, poor in oxide tin salt from a solution of $SnCl_2.H_2O$ heated at a proportion of about 112.8 kilograms by weight with about 37.3 kilograms of KCl, whereby about 132 kilograms of the tin salt $KCl.SnCl_2$ result, mixing said tin salt with a salt of the group consisting of alkali metal, earth alkali metal and zinc halides, said mixture being made at such a proportional rate that the same contains at least 60 per cent by weight of $KCl.SnCl_2$ and has a

fusion point of between 224° C. and below 600° C., obtaining thereby an anhydrous, poor in oxide tin salt bath and immersing said articles in said bath for a sufficient time to substitute their metal surface metal layer with a tin-diffusion-substitution coating.

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