

The invention relates to a process for post-rinsing conversion coatings produced on surfaces of aluminium or aluminium alloys with chromium-free solutions on the basis of complex fluorides of titanium, zirconium and/or hafnium, and also to the use thereof as a preliminary treatment for a subsequent painting¹, film-coating or adhesive-coating operation.

The production of conversion coatings on aluminium or aluminium alloy surfaces, in particular as a preliminary treatment before the application of an organic coating, takes place industrially on a large scale. Such conversion coatings prevent or hinder the occurrence of corrosion phenomena, and in the case of an organic coating serve for improved adhesion of the applied coating. Although the widely-used chromate coatings as a rule meet these requirements adequately, for reasons of hygiene in the workplace, environmental protection or because the treated material is to be used for special purposes, for instance as a packaging for foodstuffs, the production of chromium-free conversion coatings is being increasingly preferred. The treatment solutions used for this purpose are generally set to an acidic pH value, and contain e.g. titanium, fluoride, phosphate and tannin (US-PS 4 017 334) or zirconium, fluoride and boron (US-PS 3 964 936). A treatment solution having a content of hafnium and fluoride is described in FR-PS 2 417 537.

The properties of the conversion coatings produced can be improved further if passivating post-rinsing subsequently takes place. For the afore-mentioned

¹ TRANSLATOR'S NOTE: The German word "Lack", which is used here and elsewhere in the text, and which I have generally translated as "paint", can also be interpreted as covering a wider range of paint-like coatings, such as lacquer, varnish and the like.

reasons, chromium-free treatment solutions, which as a rule contain organic active substances, are preferred also for the post-rinsing operation. Such a post-rinsing agent on the basis of polyvinyl phenol is described in US-A-4 376 000. However, it causes contamination of the waste water in particular owing to the high oxygen requirement which is necessary for decomposing the organic constituent.

It is an object of the invention to provide a process for the passivating post-rinsing of chromium-free conversion coatings produced on surfaces of aluminium or aluminium alloys with solutions on the basis of complex fluorides of titanium, zirconium and/or hafnium which does not have the disadvantage of post-rinsing solutions with organic constituents in terms of wastewater treatment, but which improves the protection against corrosion and the adhesion of paint at least equally.

This object is achieved in that the process of the type described first hereinbefore is designed according to the invention such that the conversion coatings are rinsed with aqueous solutions which have a content of aluminium, zirconium and fluoride with a molar ratio of Al : Zr : F of (0.15 to 2.0) : 1 : (5 to 16), and the pH value of which is set to 2 to 5.

The process according to the invention is suitable for the passivating post-rinsing of conversion coatings which have been produced on aluminium or aluminium alloy surfaces, in which the materials may consist of solid aluminium or solid aluminium alloy or objects plated therewith, e.g. in a hot-dip coating process. For instance, the material may consist of steel which has been provided with an aluminium or aluminium alloy surface in a hot-dip coating process. Suitable

alloying constituents for aluminium are in particular silicon, manganese, magnesium, zinc and copper.

5 The conversion coatings produced on such surfaces with solutions on the basis of Ti, Zr and/or Hf are distinguished in that the coating thickness is clearly less than 1 μm , the coatings are at least partially amorphous and that they do not contain any chromium. The treatment solutions by means of which the conversion coatings are produced contain, in addition to titanium, zirconium and/or hafnium ions, additional coating-forming and/or caustic constituents, such as fluorides, phosphates, compounds of boron, and optionally passivating constituents such as tannins. Suitable treatment solutions are described in the patent specifications mentioned first hereinbefore.

Expediently, the surface is rinsed with water after the conversion coating has been produced.

20 The application of the post-rinsing solution may take place e.g. by dipping, flooding, spraying or rolling-on.

25 One preferred configuration of the invention consists in rinsing with a solution which contains aluminium, zirconium and fluoride in a total concentration of $\text{Al} + \text{Zr} + \text{F}$ of between 0.1 and 8 g/l, preferably between 0.2 and 5 g/l. The molar ratios of $\text{Al} : \text{Zr} : \text{F}$ should advantageously be set to (0.15 to 0.67) : 1 : (5 to 7).

30 The post-rinsing solutions used in the process according to the invention contain, inter alia, acidic aluminium fluoroaluminates, and in the case of an excess of aluminium additionally other salts of aluminium (e.g. fluorides, tetrafluoroborates, nitrates). They may be produced, for instance, in that

first of all metallic zirconium or zirconium carbonate is dissolved in aqueous hydrofluoric acid, with complex fluoro-zirconic acid forming. Then metallic aluminium or aluminium hydroxide or an aluminium salt, e.g. nitrate, fluoride, tetrafluoroborate, formate, acetate, preferably in dissolved form, is added and optionally dissolved. Any slight cloudiness of the solution will not adversely affect the effectiveness. Although the production process described is preferred, the solutions can also be prepared in other ways.

The setting of the pH value of the solution preferably takes place with cations of volatile bases. These include in particular ammonium, ethanolammonium, and diethanolammonium and triethanolammonium. If setting in particular relatively high pH values in the given pH range and if there are relatively high concentrations in the given range of the total concentration $Al + Zr + F$, clouding of the solution may occur, which does not have any adverse effect on the effectiveness of the process.

According to another advantageous configuration of the invention, the surfaces provided with a conversion coating are rinsed with an aqueous solution which additionally contains at least one of the anions benzoate, caprylate, ethyl hexoate or salicylate in a total concentration of preferably 0.05 to 0.5 g/l. This increases further in particular the bare corrosion-protection. The introduction of the anions may take place by means of the corresponding acids or salts thereof.

The duration of the application of the post-rinsing solution is generally between about 1 and 120 seconds, according to an expedient configuration of the invention between 1 and 30 seconds. The application

temperature may be between 20°C and about 80°C.
Temperatures of between 20 and 50°C are preferred.

Preferably deionised or low-salt water is used for preparing the post-rinsing bath. Water having a high salt content is less suitable for preparing the baths.

After the passivating post-rinsing, the surface may be dried, e.g. in air or in an oven, and optionally be post-rinsed with deionised water prior to this. One advantageous form of the invention provides for drying the surface in accelerated manner after the passivating post-rinsing, e.g. by hot air or infrared radiation.

The process according to the invention serves first and foremost for preliminary treatment of the aluminium or aluminium alloy surfaces before painting, film-coating or the application of adhesives. Examples of organic coating agents which are used are polyesters, silicone-modified polyesters, polyvinylidene fluorides, acrylates, epoxides, epoxide-phenol resins, plastisols or organosols (e.g. of PVC or acrylates).

The advantage of the process according to the invention resides in particular in the increase in adhesion of the organic films to the metallic undersurface, as is expressed, for instance, by correspondingly good results in the T-bend test (ISO 1519-1973) or in the feathering test (adhesion of paint upon opening of can seams). Likewise, the resistance of the organic films upon corrosion exposure, e.g. in a condensed water-constant climate test (DIN 50 017 KK) or a sterilisation test, is increased. Furthermore, the process according to the invention improves the corrosion resistance of the non-organically coated surface, as is demonstrated, e.g. in the test for well

water blackness (no black colouration upon boiling in water).

The process according to the invention will be explained in greater detail and by way of example with reference to the following example.

Example:

In order to produce a conversion coating, cleaned and degreased aluminium sheets were dipped for 10 seconds into a solution, the temperature of which was 50°C and which had the following composition:

Ti	0.17	g/l
F	1.24	g/l
P ₂ O ₅	0.09	g/l
NH ₄	0.91	g/l
Tannin	0.11	g/l
Na	0.003	g/l
Biocide	0.10	g/l

The sheets were then rinsed with water and subjected to passivating post-rinsing. To this end, the sheets were dipped into the post-rinsing solution for 5 seconds, and then freed of excess solution by squeezing-off. After a drying period of 0.5 min in a forced-air oven at 60°C, the sheets were painted with a 2-layer foodstuffs paint, the first layer of which was an epoxy-phenol resin and the second layer of which was an organosol. The layer thickness of the total paint was between 10 and 15 µm.

Then circular metal blanks of 60 mm diameter were cut out from the treated sheets, which were about 0.25 mm thick, and cups having a diameter of 26 mm and a height of 25 mm were deep-drawn.

These cups were subjected to a sterilisation test by subjecting them to the action of an aqueous solution of 3% sodium chloride, 1% citric acid and 0.5% lactic acid at 121°C for 40 minutes in a pressure vessel. The defects then noted on the cups (detached paint,

blisters) were evaluated on a scale of 1 (paint detached in the entire shell region of the cup = unusable) to 15 (no paint defects = excellent).

The post-rinsing solution used was produced by diluting 1.6 g/l (post-rinsing solution A) or 3.2 g/l (post-rinsing solution B) of an aqueous concentrate with 0.855% by weight Al and 8.62% by weight Zr and 10.7% by weight F using deionised water. The pH value had been set to about 3.6 with ammonia in both solutions.

For comparison purposes, post-rinsing was carried out with a polyvinyl phenol solution of 0.6 g/l and a pH value of approximately 5 (post-rinsing solution C).

The composition of the post-rinsing solutions used within the process according to the invention was:

15	Post-rinsing solution A:			Post-rinsing solution B:		
	Al	0.014	g/l	Al	0.028	g/l
	Zr	0.14	g/l	Zr	0.28	g/l
	F	0.17	g/l	F	0.34	g/l
	NH ₄	0.016	g/l	NH ₄	0.03	g/l

Test results of the sterilisation test

(Evaluation scale: 1 = unusable to 15 = excellent)

	<u>Post-rinsing solution</u>	<u>Evaluation</u>
	A (invention)	11
	B (invention)	10
25	C (comparison)	6

A comparison of the values in the table shows that the process according to the invention provides clearly better values than the comparison example with a post-rinsing solution on the basis of polyvinyl phenol.



Claims

1. A process for post-rinsing chromium-free conversion coatings produced on surfaces of aluminium or aluminium alloys with solutions on the basis of complex fluorides of titanium, zirconium and/or hafnium, characterised in that the conversion coatings are rinsed with aqueous solutions which have a content of aluminium, zirconium and fluoride with a molar ratio of Al : Zr : F of (0.15 to 2.0) : 1 : (5 to 16), and the pH value of which is set to 2 to 5.

2. A process according to Claim 1, characterised in that the conversion coatings are rinsed with solutions which have a total concentration of Al + Zr + F of between 0.1 and 8.0 g/l.

3. A process according to Claims 1 and 2, characterised in that the conversion coatings are rinsed with solutions which have a total concentration of Al + Zr + F of between 0.2 and 5.0 g/l.

4. A process according to Claims 1, 2 and 3, characterised in that the conversion coatings are rinsed with solutions in which the molar ratios of Al : Zr : F are set to (0.15 to 0.67) : 1 : (5 to 7).

5. A process according to one or more of Claims 1 to 4, characterised in that the conversion coatings are rinsed with solutions the pH value of which is set with cations of volatile bases.

6. A process according to Claim 5, characterised in that the conversion coatings are rinsed with solutions, the pH value of which is set with ammonium, ethanol-



ammonium, diethanolammonium or triethanolammonium compounds.

5. 7. A process according to one or more of Claims 1 to 6, characterised in that the conversion coatings are rinsed with solutions which additionally contain at least one of the anions benzoate, caprylate, ethyl hexoate, salicylate in a total concentration of 0.05 to 0.5 g/l.

8. A process according to one or more of Claims 1 to 7, characterised in that the conversion coatings are rinsed for 1 to 30 seconds.

15 9. A process according to one or more of Claims 1 to 8, characterised in that the conversion coatings are rinsed with solutions which have a temperature of 20 to 80°C.

10. A process according to Claim 9, characterised in that the conversion coatings are rinsed with solutions which have a temperature of 20 to 50°C.

11. A process according to one or more of Claims 1 to 10, characterised in that the surface is dried after the post-rinsing operation.

25 12. The application of the process according to one or more of Claims 1 to 11 as a preliminary treatment for a subsequent painting, film-coating or adhesive-coating operation.