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3,330,744

ANODIC TREATMENT OF ZINC AND ZINC-BASE ALLOYS AND PRODUCT THEREOF

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This invention relates to an anodizing bath and a process for producing adherent, corrosion and abrasion resistant coatings on zinc and zinc-base alloy surfaces.

A known process for applying a corrosion and abrasion resistant coating to zinc and zinc-base alloy surfaces comprises the steps of subjecting to electrolysis an aqueous solution which contains chromate, phosphate, and fluoride anions provided by compounds selected from the group consisting of chromic acid, phosphoric acid, hydrofluoric acid, and the ammonium salts thereof. The solution has a pH value within the range of from about pH 6 to about pH 8 and is substantially free from metal ions. The surface of at least one of the electrodes comprises a zinc or zinc-base alloy to be coated. Either alternating current or direct current can be used. With alternating current, the preferred current density is about 200 amperes per square foot of electrode surface. The voltage rises as the electrolysis proceeds, due to the increasing resistance of the coating as it is formed. Electrolysis is continued until the voltage rises to a levelling, or finishing, value of at least about 200 volts, usually from about 200 to about 250 volts.

We have found that excellent coatings can be obtained on zinc and zinc-base alloy surfaces by the electrolysis of an aqueous solution containing phosphate and chromate anions, and at least one of the cations sodium and potassium, the phosphate anion calculated as PO_4 being within the range of from about 0.3 to about 3 moles per liter, the chromate anion calculated as CrO_4 being within the range of from about 0.1 to about 3 moles per liter, the said solution having a pH value within the range of from pH 5 to pH 11.4.

We have found that the use of a coating, or anodizing, solution of this invention permits the electrolysis step to be conducted at a voltage substantially below the voltages required for the operation of the known electrolytic process for coating zinc. Thus, instead of a finishing voltage of 200 to 250 volts as noted above, with our solution the finishing voltage is only 35 to 110 volts.

The phosphate and chromate contents of the solution, or bath, can be supplied by dissolving the corresponding phosphoric and chromic acids (or anhydrides) in water or by the use of sodium and/or potassium salts of these acids, or by mixtures of these acids and these salts. The sodium and/or potassium can be supplied as the aforesaid salts and/or as the respective hydroxides.

The concentration of the phosphate anion is critical and must not be less than 0.3 mole per liter. For satisfactory coatings, the concentration of the chromate anion is dependent on that of the phosphate anion. For best results in terms of a hard, smooth, abrasion resistant coating, the relative concentrations are controlled to ensure that the phosphate concentration is higher than the chromate concentration.

For the purpose of our invention, certain anions are equivalent to the chromate anion. These equivalent anions are molybdate (MoO_4), tungstate (WO_4), and vanadate (VO_3). Anions of one or more of the group chromate, molybdate, tungstate and vanadate must be present in amount totalling at least about 0.1 mole per liter.

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Fluoride ion can also be present in the electrolyte, up to a maximum concentration of about 1 mole per liter. Higher fluoride concentrations may cause solubility difficulties.

The pH of the electrolyte may be varied over the range of pH 5 to pH 11.4. Within this range, the pH influences the rate of film formation, the rate passing through a maximum between pH 7 and pH 10. The pH can be adjusted by the addition of sodium or potassium hydroxide if it is too low, or by the addition of phosphoric or chromic acid if it is too high.

If desired, ammonium hydroxide can replace a portion of the sodium or potassium hydroxide. However, the alkali metal cation is an essential constituent of the electrolyte and the ammonium cation, if present, should not exceed the molar ratio of 2:1 NH_4 to Na and/or K in the electrolyte.

The electrolyte must contain phosphate anions and chromate (or equivalent) anions, and sodium and/or potassium cations. In preparing the electrolyte, no other anions, except, if desired, fluoride, and no other cations, except, if desired, ammonium, are added to the solution. Very good results are obtained using a solution containing from 0.5 to 0.8 mole per liter phosphate; from 0.3 to 0.5 mole per liter chromate (or equivalent); from zero to 0.8 mole per liter fluoride; and at least one member selected from the group consisting of sodium and potassium added as the hydroxide in amount sufficient to provide a pH value within the range of from about pH 7 to about pH 10.

The electrolysis or coating step can be conducted at a bath temperature within the range of from about 25° C. to about 100° C. but it is preferred to maintain the temperature of the bath within the range of from about 60° C. to about 95° C.

A number of metals, such as aluminum, magnesium and zinc, exhibit high electrical resistance when made anodic in electrolytes suitable for coating purposes. This resistance is due, in part, to the coating formed on the surface of the anode. For each metal-electrolyte system, there is a maximum voltage beyond which an electrical break-down occurs and sparking is observed on the anode surface. There are differences between sparked and unsparked surfaces. In general, sparked films are harder, and more abrasion resistant than unsparked films. However, unsparked films may be satisfactory, e.g., in some cases when the coatings are to be painted.

In the operation of the electrolysis step of the process of the present invention, the article to be coated is placed in the bath as an electrode, and 60 cycle alternating current is supplied initially within the range of from about 100 to about 1000 amperes per square foot of electrode surface until film formation has been initiated, as indicated by a rising voltage. The current density may then be reduced to within the range of from about 25 to about 250 amperes per square foot or it may be held at the starting level, if desired, until film formation has been completed. The voltage required to maintain these current densities increases fairly rapidly as the thickness of the coating on the surface of the electrode increases until sparking commences, at from about 30 to about 95 volts, and thereafter rises slowly to a finishing voltage of from about 35 to about 110 volts. If only a very thin coating is desired, the article may be removed from the bath before sparking occurs.

Direct current is not suitable in the process of the present invention.

The following examples illustrate conditions under which satisfactory coatings are produced by the process of the present invention.

TABLE OF EXAMPLES

Test No.	Electrolyte		F, M/L	pH	C.D., Amps/ sq. ft.	Operating Conditions				Final Temp., ° C.
	PO ₄ M/L	CrO ₄ M/L				Sparking Commenced		Coating Finished		
						Sec.	Volts	Sec.	Volts	
1.....	0.3	0.1	0.01	7.2	*174-47	750	95	1,000	113	60
2.....	0.7	0.3	0.6	6.9	232	500	45	1,000	64	57
3.....	1.0	1.0	1.0	5.0	*465-116				77	
4.....	1.0	0.1	0.1	11.4	465				60	65
5.....	2.5	3.0	0	7.5	232	40	39	300	44	68
6.....	3.0	1.0	0	7.1	697	190	32	400	39	70
7.....	0.7	0.1	0.3	6.7	232	1,150	67	1,400	86	70
8.....	0.7	0.1	0.3	7.1	232	780	65	1,300	74	63
9.....	0.7	0.1	0.3	8.7	232	90	60	600	78	60
10.....	0.7	0.1	0.3	10.3	232	240	58	800	76	58
11.....	0.8	0.5	0.8	7.4	232	680	39	1,200	50	60
12.....	1.0	VO ₃ /0.2	0.25	7.3	*280-116	1,450	35	3,000	54	80
13.....	0.8	WO ₄ /0.2	0.25	7.0	*280-60	250	51	2,070	76	50
14.....	0.4	MoO ₄ /0.2	0.25	7.1	*280-35	400	50	1,000	52	80

*Coating initiated at the higher figure and finished at the lower figure.

The coating or anodizing bath of this invention provides a number of important advantages. On electrolysis, it forms a very satisfactory hard, closely adherent film or coating on zinc and zinc-base alloy surfaces. The voltage required to produce such a film or coating is substantially less than that required to produce coatings by the use of known solutions. There is no fume problem as there is with an ammonia electrolyte and there is no loss of essential cation by evaporation.

It will be understood, of course, that modification can be made in the coating or anodizing bath described hereinabove without departing from the scope of the invention as defined by the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. An anodic process for coating zinc and zinc-base alloy surfaces which comprises the step of subjecting to electrolysis using alternating current an aqueous solution consisting essentially of phosphate anions in amount within the range of from about 0.3 to about 3 moles per liter calculated as PO₄, chromate anions in amount within the range of from about 0.1 to about 3 moles per liter calculated as CrO₄, fluoride anions in amount within the range of from zero to about 1 mole per liter calculated as F, and cations of at least one member selected from the group consisting of sodium and potassium, the said bath having a pH value of 5 to 11.4, using in said electrolysis at least one electrode having exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys, and continuing said electrolysis for a time sufficient to form a coating on said electrode.

2. An anodic process for coating zinc and zinc-base alloy surfaces which comprises the step of subjecting to electrolysis using alternating current an aqueous solution consisting essentially of phosphate anions in amount within the range of from about 0.3 to about 3 moles per liter calculated as PO₄, chromate anions in amount within the range of from about 0.1 to about 3 moles per liter calculated as CrO₄, fluoride anions in amount within the range of from zero to about 1 mole per liter calculated as F, and cations of at least one member selected from the group consisting of sodium and potassium, the said solution having a pH value of from about 5 to 11.4, maintaining the temperature of said bath within the range of from 60° C. to 95° C., using in said electrolysis at least one electrode having exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys, conducting said electrolysis at a current density within the range of from about 100 to about 1000 amperes per square foot of electrode surface until sparking is observed on the surface of said at least one elec-

trode, and thereafter reducing the current density to within the range of from about 25 to about 250 amperes per square foot of electrode surface, and continuing said electrolysis with increasing voltage until the voltage rises to a finishing value within the range of from about 35 to about 110 volts.

3. An anodic process for coating zinc and zinc-base alloy surfaces which comprises the step of subjecting to electrolysis using alternating current an aqueous solution consisting essentially of phosphate anions in amount within the range of from about 0.3 to about 3 moles per liter calculated as PO₄, at least one anion selected from the group consisting of chromate, molybdate, tungstate and vanadate calculated as CrO₄, MoO₄, WO₄ and VO₃ in a total amount within the range of from about 0.1 to about 3 moles per liter, fluoride anions in amount within the range of from zero to about 1 mole per liter calculated as F, and cations of at least one member selected from the group consisting of sodium and potassium, the said bath having a pH value of 5 to 11.4, using in said electrolysis at least one electrode having exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys, and continuing said electrolysis for a time sufficient to form a coating on said electrode.

4. An anodic process for coating zinc and zinc-base alloy surfaces which comprises the step of subjecting to electrolysis using alternating current an aqueous solution consisting essentially of phosphate anions in amount within the range of from about 0.3 to about 3 moles per liter calculated as PO₄, at least one anion selected from the group consisting of chromate, molybdate, tungstate and vanadate calculated as CrO₄, MoO₄, WO₄ and VO₃ in a total amount within the range of from about 0.1 to about 3 moles per liter, fluoride anions in amount within the range of from zero to about 1 mole per liter calculated as F, and cations of at least one member selected from the group consisting of sodium and potassium, the said solution having a pH value of from about 5 to 11.4, maintaining the temperature of said bath within the range of from 60° C. to 95° C., using in said electrolysis at least one electrode having exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys, conducting said electrolysis at a current density within the range of from about 100 to about 1000 amperes per square foot of electrode surface until sparking is observed on the surface of said at least one electrode, and thereafter reducing the current density to within the range of from about 25 to about 250 amperes per square foot of electrode surface, and continuing said electrolysis with increasing voltage until the voltage rises to a finishing value within the range of from about 35 to about 110 volts.

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5. An article of manufacture having surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys and coated with a film produced by the process according to claim 3.

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