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METHOD AND COMPOSITIONS FOR CHEMICALLY POLISHING ZINC

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ABSTRACT OF THE DISCLOSURE

Zinc surfaces are deburred and polished in a process which comprises first cleaning the surfaces in an aqueous alkaline bath, immersing the surfaces in a deburring and polishing bath composition comprising nitric acid, citric acid, a soluble fluoride and, optionally, hydrochloric acid, tartaric acid, or phosphoric acid together with a sequestering agent or surfactants and finally subjecting the zinc surfaces to a post-polishing step in which the surfaces are contacted with an alkaline preplating conditioning solution consisting essentially of water, sodium carbonate, sodium hydroxide, sodium cyanide and an organic oxidizing agent.

The present invention relates to a method of and compositions for chemically polishing zinc and predominantly zinc-base alloys to prepare them for subsequent surface treatment. More particularly, the invention here disclosed represents a significant improvement in the preparation of zinc or zinc-base die castings in respect to simplifying the processing operations and eliminating problems arising from waste or spent processing solution disposal, while also producing brighter and more readily platable die castings.

The new process and compositions can be used advantageously not only in connection with electroplating operations but in polishing, deburring and activating zinc die castings in preparation for a variety of subsekuent surface treatments including chromating, phosphating, blackening, dyeing and painting. The process is also useful in improving leveling and polishing the surface of die castings in preparation for a variety of subsequent flaws, i.e. chemical milling, whereby to produce a smooth, bright, lustrous finish that in many instances rivals the appearance of a buffed surface.

It is one of the more significant features of the invention that the use of chromate compounds is completely avoided, thereby eliminating rather troublesome waste disposal problems which are unavoidably encountered in the more commonly preferred bright dip or chemical polishing compositions heretofore used. The solutions used in the process of this invention are chromate-free and in addition are remarkably free-rinsing, thus minimizing the need for special precautions and criticality of thorough rinsing between procesing steps. Quite obviously this facilitates and greatly expedites the bulk handling of articles in commercial surface treatment operations. In addition, the solutions used in the novel process provide a highly activated and receptive surface on the zinc castings for subsequent processing, whereby these subsequent operations are in many instances effected more rapidly and the resulting finishes are more even and durable.

The novel process is based on the use of an acidic, chemical deburring and polishing solution which is completely chromate-free and remarkable free-rinsing, as noted above. The process in its broader aspect, also contemplates the inclusion of a pre-polishing alkaline soak or cleaning step, as well as a post-polishing alkaline casting-conditioning step, to provide an integrated series of operations which in combination afford the maximum benefits of the invention.

In the overall procedure, the first operation involved is that of soaking the rough zinc die castings in an alkaline cleaner to remove all traces of mold release agent, quenchant, shop oil, "white rust," etc., with which such castings are generally contaminated. Following a simple water rinse, the castings are next immersed in the aforesaid acidic, chromate-free, chemical deburring and polishing solution. Finally, after a further simple water rinse, the castings are placed in a casting-conditioner solution to neutralize any acid remaining in the pores and recesses after rinsing, as well as to remove any smut that may appear on the castings, particularly those having substantial copper content.

The casting-conditioning step employs an alkaline solution, as more particularly defined hereinafter, and is used immediately preceding the conventional copper strike commonly employed to provide an underlay for better adherence and smoothness of subsequent nickel and chrome electro-deposits thereon. This alkaline treatment of the castings prior to the copper strike is believed to represent a novel departure from the current common procedure in which zinc castings are usually given an acid dip or pickle before the copper strike. As the result of our research, however, we have discovered that significantly better adhesion and coverage are obtained when the castings are processed as thus described immediately prior to copper plating in the conventional alkali cyanide electrolyte bath.

By way of illustration, the following specific examples of the method and compositions of the invention are given:

EXAMPLE I

Rough zinc die castings (trigger assemblies of rather intricate shape), as received from the mold, are given a pre-polishing alkaline soak in a bath of the following composition:

	Percent by weight
Trisodium phosphate	85.0
Sodium carbonate	12.5
"Versene" powder	0.5
"Benax 2A1" powder	2.0
	100.0

A solution of suitable concentration is prepared by dissolving ¼ to ½ pounds of the foregoing per gallon of water. "Versene" is a proprietary composition consisting essentially of sodium salts of ethylenediamine tetraacetic acid and serves as a sequestering agent for zinc or other "hard water" heavy metal ions in the foregoing solution. "Benax 2A1" is the proprietary name for an alkali-compatible surfactant.

This alkaline soak produces slight gassing on the surface of the parts during the soaking period. In general, the parts are soaked for about 30 to 180 seconds at room temperature, with about 2 minutes being optimum soaking time, after which they are removed and rinsed in clear water.

The parts are then ready for the polishing solution, which was prepared as follows:

	Percent by weight
Nitric acid	10.5
Citric acid	8.0
Hydrofluoric acid	2.0
Phosphoric acid	0.1
Surfactant ("6G")	0.2
Water	Balance
	100.0

The weight percent figures given above and in the examples to follow for the bath components other than water are calculated on a dry basis in each case.

The parts to be polished are lowered into this solution and allowed to soak, with or without agitation, for periods from as short as 5 seconds to a maximum of around 3 minutes, the optimum time being around 1 minute. The solution is used at room temperature, i.e. approximately 70° F. Thereafter the parts are withdrawn and again rinsed in clear water. The particular surfactant material "6G" here employed is an acid-stable proprietary composition.

It will be found that the parts are clean and quite bright. They may, if desired, be immediately placed in the copper plating tank for the usual copper strike preliminary to nickel and chrome plating. It is preferred however to give the parts a further treatment, herein termed a "casting-conditioning" step, which involves immersing them in an alkaline solution of the following composition:

	Percent by weight
Sodium carbonate	46.7
Sodium hydroxide	13.3
Sodium cyanide	6.7
"Strip-Aid"	33.3
	100.0

"Strip-Aid" is a propietary composition consisting essentially of m-nitrobenzene sulfonate.

The foregoing composition is mixed with water at the rate of ¼ to ½ pounds per gallon. The parts are again allowed to soak briefly in this e.g. from 5 to 30 seconds, at room temperature, transferred to a water rinse and then to the plating tank.

EXAMPLE II

The procedure here is the same as in Example I except for the substitution of the following for the polishing solution for the preceding example:

	Percent by weight
Nitric acid	15.9
Citric acid	7.0
Hydrofluoric acid	0.13
Ammonium bifluoride	5.0
Tartaric acid	1.0
Sequestering agents:	
"Roquest 224P"	0.25
"Dequest 2000"	0.1
Surfactants:	
"Pluronic L–61"	0.1
"Beacomine C"	0.1
Water	Balance
	100.0

The two sequestering agents named are proprietary compositions available commercially. "Roquest 244P" is a salt of ethylenediamine tetraacetic acid, and "Dequest 2000" is a phosphonate compound, both of which exhibit free acid characteristics. "Pluronic L–61" is a proprietary nonionic surfactant prepared by the addition of ethylene oxide to polypropylene glycol, and is acid-stable. "Beacomine–C" is an amine oxide wetting agent. The sequestering agents act to prevent precipitation of zinc and other metallic ions which may be present and interfere with the polishing operation. The surfactants serve primarily as wetting agents to improve the acceptance of the surface for the major surface-modifying compounds, i.e. nitric and citric acids, and the fluorides.

EXAMPLE III

Again the procedure is the same except for the substitution of the following polishing composition:

	Percent by weight
Nitric acid	24.5
Citric acid	10.0

Hydrofluoric acid	4.9
Ammonium bifluoride	5.0
Tartaric acid	2.0
Phosphoric acid	0.1
Sequestering agents:	
"Roquest 244P"	0.25
"Dequest 2000"	0.1
Surfactants:	
"Pluronic L–61"	0.1
"Beacomine–C"	0.1
Water	Balance
	100.0

EXAMPLE IV

In this example, the polishing solution had the following composition:

	Percent by weight
Nitric acid	10.5
Citric acid	8.0
Hydrofluoric acid	2.0
Surfactant—"6G"	0.2
Water	Balance
	100.0

The procedure for brightening the castings was otherwise the same as in Example I.

EXAMPLE V

Again, the procedure was the same except that the following polishing solution was substituted:

	Percent by weight
Nitric acid	10.2
Hydrochloric acid	6.7
Hydrofluoric acid	0.4
Ammonium bifluoride	13.5
Phosphoric acid	0.08
Sequestering agents:	
"Roquest 244P"	0.15
"Dequest 2000"	0.08
Surfactants:	
"Pluronic L–61"	0.08
"Beacomine C"	0.08
Water	Balance
	100.0

EXAMPLE VI

The following polishing solution was employed in place of those described above in the procedure outlined:

	Percent by weight
Nitric acid	9.1
Hydrochloric acid	6.6
Citric acid	10.6
Hydrofluoric acid	.35
Ammonium bifluoride	12.0
Tartaric acid	0.92
Phosphoric acid	0.07
Sequestering agents:	
"Roquest 244P"	0.13
"Dequest 2000"	0.07
Surfactants—"Beacomine C"	0.07
Water	Balance
	100.0

EXAMPLE VII

	Percent by weight
Nitric acid	8.2
Hydrochloric acid	5.4
Citric acid	9.54
Hydrofluoric acid	1.7
Ammonium bifluoride	18.09

	Percent by weight
Tartaric acid	0.83
Phosphoric acid	0.06
Sequestering agents:	
"Roquest 244P"	0.11
"Dequest 2000"	0.06
Surfactants—"Beacomine C"	0.06
Water	Balance
	100.0

In the last three examples, namely Examples V, VI and VII, the polishing solution includes hydrochloric acid to provide substantial quantities of chloride ions in solution. These have greater mobility than the fluoride ions and are somewhat more effective to remove "chill shut" or "cold shut," a grain phenomena, where this is encountered. All of the foregoing polishing solutions impart a bright, satiny-smooth surface to the parts.

As will be apparent from the foregoing examples, the chemical deburring and polishing compositions are all characterized by being chromate-free, acidic solutions comprising, as the essential combination, nitrate and fluoride ions, and generally the inclusion of citric acid up to about 10.6% by weight is much preferred. If nitric acid is employed, as is preferred, to supply the nitrate ions, the bath composition will contain from about 8% to 25% of the acid and no additional acids are required to effect a suitable solution pH. As already mentioned, however, hydrochloric acid may be used to supply chloride ions as well as to lower the pH to an acceptable value, and the range of 5% to 7% hydrochloric acid (weight basis) in solution is preferred. From the examples given it will also be apparent that the soluble fluoride compound or compounds should be present in amount to provide the equivalent of from about 1.5% to 14% by weight of fluoride ion in the solution.

The performance of the polishing solutions is generally enhanced by the inclusion of small amounts of tartaric acid as a chelating agent to prevent precipitation of zinc ions that are commonly present in solution. This is further supplemented, optionally, by the inclusion of trace amounts of from about 0.05% to about 0.35% by weight of proprietary sequestering agents, as indicated. Phosphoric acid is also included in trace amounts, primarily as a film-former, for the added protection of the polished surface. Likewise, for best results, trace amounts of surfactants are included to make sure that the surfaces of the articles are uniformly wetted by the polishing solution.

The examples above are indicative of the operating range of pH values to be maintained in the polishing solution, and this can vary from about 1.0 to 3.5 pH, with a preferred range of 1.5 to 2.5.

The surfaces of zinc castings treated in the polishing solution are extremely receptive to subsequent plating operations; in fact, the surfaces thus prepared are so active that generally a conversion coating of copper is formed immediately upon placing the articles in the copper plating bath, even before passing any current through the bath. However, the optimum results are obtained by incorporating the aforementioned casting-condition step, which gives notable improvement in specularity, leveling and freedom from pitting in the finished castings.

In speaking here of "zinc castings," it should be understood the term has been used in a very general sense and that the process is applicable to all types of articles or fabrications whose surfaces at least are predominantly composed of zinc or zinc alloys.

What is claimed is:

1. Aqueous acid bath composition for deburring and polishing surfaces of zinc castings which consists essentially of

	Percent by wt.
Nitric acid	8.2
Hydrochloric acid	5.4
Citric acid	9.54
Hydrofluoric acid	1.7
Ammonium bifluoride	18.09
Tartaric acid	0.83
Phosphoric acid	0.06
Water	Balance

2. Aqueous acid bath composition for deburring and polishing surfaces of zinc castings which consists essentially of

	Percent by wt.
Nitric acid	15.9
Citric acid	7.0
Hyrofluoric acid	0.13
Ammonium bifluoride	5.0
Tartaric acid	1.0
Water	Balance

3. Aqueous acid bath composition for deburring and polishing surfaces of zinc castings which consists essentially of

	Percent by wt.
Nitric acid	24.5
Citric acid	10.0
Hydrofluoric acid	4.9
Ammonium bifluoride	5.0
Tartaric acid	2.0
Phosphoric acid	0.1
Water	Balance

4. Aqueous acid bath for deburring and polishing surfaces of zinc castings which consists essentially of

	Percent by wt.
Nitric acid	10.5
Citric acid	8.0
Hydrofluoric acid	2.0
Phosphoric acid	0.1
Water	Balance

5. The method of chemically deburring and polishing surfaces of zinc castings which comprises immersing said surfaces in an aqueous acid solution consisting essentially, on a weight basis, from about 8% to 25% nitric acid, up to about 10.6% of citric acid and a soluble fluoride in amount sufficient to provide in solution the equivalent of from about 1.5% to 14% of fluoride ion, the balance being water, wherein the solution has a pH of from 1.0 to 3.5, said surfaces being immersed for a period of from 5 seconds to three minutes at room temperature to develop a high degree of specularity, then removing and rinsing the surfaces.

6. The method as defined in claim 5, wherein the solution also contains hydrochloric acid in amount of about 5% to 7% by weight.

7. The method as defined in claim 5, wherein said solution also contains approximately 1% by weight of tartaric acid.

8. The method as defined in claim 5, wherein said solution also contains on the order of 0.1% by weight of phosphoric acid.

9. The method as defined in claim 5, wherein said solution consists essentially of

	Percent by wt.
Nitric acid	8.2
Hyrochloric acid	5.4
Citric acid	9.54
Hydrofluoric acid	1.7
Ammonium bifluoride	18.09
Tartaric acid	0.83
Phosphoric acid	0.06
Water	Balance

10. The method as defined in claim 5, wherein said solution consists essentially of

	Percent by wt.
Nitric acid	15.9
Citric acid	7.0
Hydrofluoric acid	0.13
Ammonium bifluoride	5.0
Tartaric acid	1.0
Water	Balance

11. The method as defined in claim 5, wherein said solution consists essentially of

	Percent by wt.
Nitric acid	24.5
Citric acid	10.0
Hydrofluoric acid	4.9
Ammonium bifluoride	5.0
Tartaric acid	2.0
Phosphoric acid	0.1
Water	Balance

12. The method as defined in claim 5, wherein said solution consists essentially of

	Percent by wt.
Nitric acid	10.5
Citric acid	8.0
Hydrofluoric acid	2.0
[Surfactant	0.2]
Water	Balance

13. The method of deburring and polishing zinc surfaces which comprises immersing the surfaces in an aqueous acid solution consisting essentially, on a weight basis, from about 8% to 25% nitric acid, up to about 10.6% of citric acid and a soluble fluoride in amount sufficient to provide in solution the equivalent of from about 1.5% to 14% of fluoride ion, the balance being water, wherein the solution has a pH of from 1.0 to 3.5, said surfaces being immersed for a period of from 5 seconds to three minutes at room temperature to develop a high degree of specularity, then removing and rinsing the surfaces in clear water; and thereafter immersing the surfaces in an alkaline pre-plating conditioning solution consisting essentially, apart from water, of an admixture of approximately 46.7% sodium carbonate, 13.3% sodium hydroxide, 6.7% sodium cyanide, and 33.3% of an organic oxidizing agent consisting essentially of m-nitrobenzene sulfonate, wherein said pre-plating bath contains from about ¼ to ½ pound per gallon of said admixture; holding said surfaces in said solution for a period of from about 5 seconds to 30 seconds and then removing and rinsing them in clear water.

14. The method of claim 13 wherein the said aqueous acid solution also contains from about 5% to 7% by weight of hydrochloric acid.

15. The method of claim 13 wherein the said aqueous acid solution also contains approximately 1% by weight of tartaric acid.

16. The method of claim 13 wherein the said aqueous acid solution also contains on the order of 0.1% by weight of phosphoric acid.

17. A dry composition for dissolution in water to provide an aqueous alkaline pre-plating conditioning bath for zinc surfaces, wherein said composition consists essentially, on a weight basis, of about 46.7% sodium carbonate, 13.3% sodium hydroxide, 6.7% sodium cyanide, and 33.3% of an organic oxidizing agent selected from the group consisting of m-nitrobenzene sulfonate.

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