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COMPOSITION AND METHOD FOR CLEANING AND BLACKENING METAL DIES

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This invention relates to cleaning metal dies and more particularly to a process and composition for removing undesirable deposits from steel die blocks used for die casting zinc and zinc base alloys.

In zinc die casting operations it is desirable to thoroughly remove adhering zinc residues and die lubricant encrustations from surfaces of the die blocks after a given number of casting cycles. In the past, considerable difficulty has been encountered in cleaning such die blocks because of the nature of the cleaning compositions employed. It was found in some instances that the carbonaceous residues and solder were not removed from the die block surfaces, while in other cases the steel die blocks were etched to an excessive extent.

Accordingly, a principal object of the present invention is to provide a cleaning solution and process which effectively remove zinc and zinc oxide deposits, as well as carbonized or coked die lubricant residues, from steel dies without adversely affecting their surfaces. A further object of the invention is to provide a die cleaner which forms on the working surface of a die block an integral, adherent, passive black oxide layer which inhibits further adhesion of zinc die cast alloy or carbonized die lubricant residues.

These and other objects are attained in accordance with this invention by means of an aqueous cleaning solution containing blackening salts and furfuryl alcohol. The furan ring in the alcohol may be either saturated or unsaturated; and the term "furfuryl alcohol," as used herein, is intended to encompass tetrahydrofurfuryl alcohol unless otherwise indicated. Various other water-soluble furan compounds and derivatives may be used to replace a portion or all of the furfuryl alcohol. Among these compounds are furan, furoic acid, furfuryl esters, furfuryl ethers, furfuryl halides, furfuryl alkyl halides, tetrahydrofuran, dihydrofuran, tetrahydrofurfuryl alkyl ethers, tetrahydrofurfuryl halides, tetrahydrofurfuryl alkyl halides, tetrahydrofurfuryl alkyl esters and furfuraldehyde, including tetrahydrofurfural. However, furfuryl alcohol has provided superior results to date.

The amounts of the constituents used may vary rather widely for different applications. For example, the quantity of blackening salts employed can range from about 10% by weight up to the practical limit of solubility in the solution (approximately 45% by weight), while the furfuryl alcohol may constitute about 1% to 20% by weight of the solution with the balance (35% to 89%) being water. The blackening salts content of the solution may be as low as 5% by weight in some instances, but such a solution requires repeated application to achieve the desired results. In general, it is advantageous to use an aqueous solution consisting essentially of about 20 ounces to 60 ounces of blackening salts per gallon of solution, 5 ounces to 10 ounces of furfuryl alcohol per gallon of solution and the balance substantially all water.

The blackening salts preferably consist of a mixture of sodium hydroxide, sodium nitrate and sodium nitrite. Although the sodium compounds are preferred, it is possible to substitute potassium hydroxide, potassium nitrate and potassium nitrite for all or part of the corresponding sodium compounds. A sodium nitrate content of approximately 4% to 30% by weight is permissible, while

the amount of sodium nitrite used may range from about 1% to 20% by weight, with the balance (approximately 50% to 95% by weight) of the mixture being sodium hydroxide. We have obtained best results, however, with blackening salts composed of aproximately 70% to 93% by weight of sodium hydroxide, 5% to 20% by weight of sodium nitrate and 2% to 10% by weight of sodium nitrite.

The oxygen which is released from the sodium nitrate forms the desirable passivated oxide film on the die block surfaces, the nitrite aiding in the mechanism of oxygen release. The furfuryl alcohol functions both as a wetting agent and as a solvent for the resinous deposits.

A specific embodiment of the invention which has proved to be particularly effective is an aqueous solution containing 40 ounces of blackening salts per gallon of solution and 190 ml. of tetrahydrofurfuryl alcohol per gallon of solution. Another very successful solution is composed of 100 ml. of water, 30 grams of blackening salts and 30 ml. of furfuryl alcohol. A preferred mixture of blackening salts comprises about 80% by weight of sodium hydroxide, 15% by weight of sodium nitrate and 5% by weight of sodium nitrite. We also have obtained excellent results with a mixture of approximately 80% sodium hydroxide, 16% sodium nitrate and 4% sodium nitrite.

A solution of the above-described type may be prepared for commercial use in the following manner:

A tank 4 feet long, 2.5 feet wide and 3 feet deep is conveniently used, and water is added to the tank to a depth of about 1½ feet. Approximately 375 pounds of blackening salts composed of about 80% by weight of sodium hydroxide, 15% by weight of sodium nitrate and 5% by weight of sodium nitrite are then dissolved in the water. Considerable care must be exercised in carrying out this step because of the large amount of heat evolved in the dissolution process. Hence it is desirable to add the salts very slowly and stir the solution until they are dissolved, thereby reducing the rate of boiling and minimizing spattering. The solution is then permitted to cool, and 7½ gallons of tetrahydrofurfuryl alcohol are added while stirring. Thereafter sufficient water is added to the tank to raise the solution in the tank to the 2-foot level. This provides a total of approximately 150 gallons of solution, which is sufficient for 12 carboys of the commercial 12½ gallon capacity.

The cleaning solution thus formed is applied at room temperature to the hot surfaces of the steel die by spraying, dipping or brushing. A die temperature of about 200° F. to 450° F. generally is preferred. This solution dissolves and flushes away the undesirable encrustations from the steel die surfaces and, upon evaporation of the volatiles, provides these surfaces with an adherent black oxide film which helps prevent a build-up of zinc oxide deposits and carbonized or coked die lubricant residues.

Caustic solutions, such as sodium hydroxide and potassium hydroxide, frequently are used to remove adherent carbonaceous deposits from die surfaces. These deposits are principally residues of the die lubricants employed commercially today. Three types of lubricants are frequently used on die blocks in zinc die casting operations. One is a combination of parafinic oil and candelilla wax; another is a light-weight motor oil, usually paraffin base; while the third is a suspension of graphite and water. However, caustic solutions are relatively ineffective, particularly in removing zinc die casting alloy which remains on the steel die block after the casting operation.

To determine the relative effectiveness of various solutions in dissolving zinc and zinc oxide from the working surfaces of steel die blocks, samples of a commercial zinc die casting alloy were weighed and immersed in

the hot compositions to be tested. One of these compositions was a sodium hydroxide solution prepared by dissolving 30 grams of hydroxide powder in 100 ml. of water to which 1 gram of wetting agent was added. An aqueous solution of potassium hydroxide of similar concentration was formed in the same manner. Another sample of the zinc die cast alloy was immersed in a hydrochloric acid solution composed of 80 ml. of 38% hydrochloric acid and 30 ml. of water. The fourth cleaning solution tested was formed in accordance with the present invention by adding 30 grams of blackening salts and 30 ml. of tetrahydrofurfuryl alcohol to 100 ml. of water. This solution contained blackening salts consisting of about 80% by weight of sodium hydroxide, 15% by weight of sodium nitrate and 5% by weight of sodium nitrite. The various solutions with the immersed samples were held at a constant temperature of 200° F. for ten minutes. The treated samples were then removed from the solutions, rinsed, dried and re-weighed to determine the amount of zinc dissolved.

The sodium hydroxide and potassium hydroxide solutions proved to be very ineffective in dissolving the zinc since they removed only about 0.17% and 0.11%, respectively, by weight of the metal. On the other hand, the hydrochloric acid solution was found to dissolve approximately 48.5% by weight of the specimen, while the aqueous solution of blackening salts plus furfuryl alcohol dissolved about 20.7%. The zinc alloy used for the test specimens was composed of approximately 3.7% to 4.3% aluminum, 0.03% to 0.06% magnesium and the balance zinc.

In order to measure the extent of the attack of the various cleaning solutions on steel dies, samples of a commercial die block steel were initially weighed and immersed for one hour in the aforementioned solutions, which were held at a constant temperature of 200° F. Upon removal from the cleaning solutions, the samples were rinsed in water, dried and re-weighed. Neither the cleaning solution of the present invention nor the caustic solutions dissolved an appreciable amount of die block steel, each removing less than 0.007% of the metal. However, the hydrochloric acid solution dissolved more than 1.1% of the die block sample. This test showed that a solution of hydrochloric acid cannot be safely used for removing carbonaceous deposits from die block surfaces because it etches the latter to an excessive extent. The die block steel alloy used in this test consisted of 0.35% to 0.4% carbon, 0.25% to 0.5% manganese, 0.8% to 1.2% silicon, 5% to 5.5% chromium, 1.2% to 1.5% molybdenum, 0.9% to 1.15% vanadium and the balance iron.

The die cleaning solution embodying the present invention also may be incorporated as an active ingredient in a water-soluble die lubricant. For example, it may be included in an aqueous emulsion of carnauba wax or in a suspension of graphite in water. When the die lubricant thus compounded is applied to the clean surfaces of a die, these surfaces will be maintained in a relatively deposit-free condition for a considerably greater number of casting cycles than would otherwise be possible. The above-described cleaning solution also passivates the die surface without etching it and forms the integral, black oxide surface coating hereinbefore mentioned. When carbonaceous deposits and zinc residues finally do build up on steel die surfaces, applying the cleaning solution to these surfaces serves to dissolve and flush away adhering zinc alloy and die lubricant residues.

While our invention has been described by means of certain specific examples, its scope is not to be limited thereby except as defined in the appended claims. For example, our new cleaning solution is especially designed for use in zinc die casting operations, but its utility is not restricted to such operations. Die blocks used for casting magnesium, aluminum and alloys of these metals also can be cleaned with this solution. Although the cleaning solution does not dissolve magnesium to any appreciable extent, it does dissolve the carbonaceous residues to which the magnesium and magnesium oxide deposits adhere. When the coked layer goes into solution, the metallic deposits are loosened and flushed away by the cleaning solution.

We claim:

1. A solution for removing adherent deposits from surfaces of steel dies, said solution comprising about 5% to 45% by weight of blackening salts, 1% to 20% by weight of a water-soluble furan compound and the balance substantially all water, said blackening salts comprising approximately 4% to 30% by weight of sodium nitrate, 1% to 20% by weight of sodium nitrite and the balance substantially all sodium hydroxide.

2. A solution for removing carbonaceous residues and adhering zinc deposits from surfaces of steel die blocks of die casting machines, said solution comprising about 35% to 89% by weight of water, 10% to 45% by weight of blackening salts and 1% to 20% by weight of a water-soluble furan compound, said blackening salts comprising about 4% to 30% by weight of sodium nitrate, 1% to 20% by weight of sodium nitrite and 50% to 95% by weight of sodium hydroxide.

3. A solution for removing carbonaceous residues and adhering zinc and zinc oxide deposits from surfaces of steel die blocks, said solution comprising about 5% to 45% by weight of blackening salts, 1% to 20% by weight of furfuryl alcohol and the balance substantially all water, said blackening salts comprising about 4% to 30% by weight of sodium nitrate, 1% to 20% by weight of sodium nitrite and the balance substantially all sodium hydroxide.

4. An aqueous solution for removing carbonaceous residues and adhering zinc and zinc oxide deposits from surfaces of steel die blocks, said solution comprising about 20 ounces to 60 ounces of blackening salts per gallon of solution, 5 ounces to 10 ounces of furfuryl alcohol per gallon of solution, and the balance substantially all water, said blackening salts comprising approximately 70% to 93% by weight of sodium hydroxide, 5% to 20% by weight of sodium nitrate and 2% to 10% by weight of sodium nitrite.

5. A process for removing carbonaceous die lubricant residues and adherent zinc and zinc oxide deposits from the surfaces of steel die blocks of die casting machines, said process comprising heating the contaminated surfaces of said die blocks to a temperature of about 200° F. to 450° F., applying to said surfaces a solution consisting essentially of about 20 ounces to 60 ounces of blackening salts per gallon of solution, 5 ounces to 10 ounces of furfuryl alcohol per gallon of solution, and the balance substantially all water, said blackening salts comprising 70% to 95% by weight of sodium hydroxide, 5% to 20% by weight of sodium nitrate and 2% to 10% by weight of sodium nitrite, permitting said solution to remain in contact with said residues and deposits for a period of time sufficient to substantially dissolve the same, and thereafter removing said solution and dissolved residues and deposits from said surfaces, thereby providing said surfaces with an integral, adherent, passive black oxide film which inhibits adhesion of fresh deposits of zinc die cast allow and carbonaceous die lubricant residues.

6. A solution for removing adherent deposits from surfaces of steel dies, said solution comprising about 5% to 45%, by weight, of blackening salts, 1% to 20%, by weight, of a water-soluble furan compound and the balance substantially all water, said blackening salts comprising approximately 4% to 30%, by weight, of a water-soluble alkali metal nitrate, 1% to 20%, by weight of a water-soluble alkali metal nitrite and the balance substantially all alkali metal hydroxide.

7. A solution for removing adherent deposits from surfaces of steel dies, said solution comprising about 35%

to 89%, by weight, of water, 10% to 45%, by weight, of blackening salts and 1% to 20%, by weight, of a water-soluble furan compound, said blackening salts comprising about 4% to 30%, by weight, of a water-soluble alkali metal nitrate, 1% to 20%, by weight, of a water-soluble alkali metal nitrite and 50% to 95%, by weight, of an alkali metal hydroxide.

8. A process for removing adherent deposits from steel surfaces, said process comprising applying to said surfaces a solution consisting essentially of about 5% to 45%, by weight, of blackening salts, 1% to 20%, by weight, of a water-soluble furan compound and the balance substantially all water, said blackening salts comprising about 4% to 30%, by weight, of a water-soluble alkali metal nitrate, 1% to 20%, by weight, of a water-soluble alkali metal nitrite and 50% to 95%, by weight, of an alkali metal hydroxide, permitting said solution to substantially dissolve said deposits and thereafter removing said solution and dissolved deposits from said surfaces.

9. A process for removing carbonaceous residues and adhering zinc deposits from surfaces of steel die blocks of die casting machines, said process comprising heating the contaminated surfaces of said die blocks to a temperature of about 200° F. to 450° F., applying to

said surfaces a solution consisting essentially of about 10% to 45% by weight of blackening salts, 1% to 20% by weight of a water-soluble furan compound and the balance substantially all water, said blackening salts comprising, by weight, 70% to 95% alkali metal hydroxide, 5% to 20% water-soluble alkali metal nitrate and 2% to 10% water-soluble alkali metal nitrite, permitting said solution to remain in contact with said residues and deposits for a period of time sufficient to effect their substantial dissolution, and thereafter removing said solution and dissolved residues and deposits from said surfaces to thereby provide thereon an integral, adherent, passive black oxide film which inhibits adhesion of fresh deposits of zinc die cast alloy and carbonized residues.

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