Patented Feb. 8, 1949 2,461,228

UNITED STATES PATENT OFFICE

2,461,228

METHOD OF AND MATERIAL FOR PREPARING ZINCIFEROUS SURFACES FOR ELECTROPLATING

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No Drawing. Application August 11, 1947, Serial No. 768,068

7 Claims. (Cl. 41—42)

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This invention relates to a method of, as well as to new materials for, treating surfaces of zinc and zinc base alloys in preparation for an electroplating operation.

The principal objects of the invention are to clean the surfaces prior to the plating operation; to condition the surface so that it will better accept the plate; to improve the quality of the plated article; to minimize blistering of the plating even when subjected to extremes of temperature; to reduce the number of rejects as well as to make possible the re-processing of rejects which have been cleaned and plated according to conventional methods where my invention has not been employed; and, in general, to improve the art of electroplating zinciferous surfaces.

The invention has been found to be useful as a preparatory step in any of the conventional plating operations familiar to the art, a typical plating sequence being as follows:

1. Treatment according to the present invention.
2. Water rinse.
3. Reverse current electroclean.
4. Water rinse.
5. Dilute acid dip.
6. Water rinse.
7. Copper strike.
8. Copper plate.
9. Water rinse.
10. Nickel plate.
11. Water rinse.
12. Chromium plate.

It is to be understood, however, that the foregoing is simply typical of conventional plating procedures and that my improved preparatory step is not to be limited to association with the succeeding steps enumerated above.

The materials which I employ in applying my preparatory treatment consist of mineral spirits, phosphoric acid, cyclic coal tar bases, sulphuric acid, thiourea, non-ionic wetting agents and water.

A concentrated treating bath may be made up as follows:

Mineral spirits	gals.	0.3360
Phosphoric acid, 75%	gals.	0.4853

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Cyclic coal tar bases [1]	gals.	0.0144
Sulfuric acid (66° Bé.)	gals.	0.0049
Thiourea	lbs.	0.0250
Polymerized ethylene oxide condensate (100% basis) [2]	lbs.	0.0135
Water, to make	gal.	1.0000

[1] The bases which I have found to be most suitable may be either isolated bases or narrow cuts or the entire extracted bases from various fractions of coal tar. For example, I may use the chemical individuals pyridine, any of the individual lutidines, picolines or collidines, quinilline, substituted quinillines, etc. Or I may employ commercial cuts known as crude pyridine bases, crude quinilline fraction, a crude quinilline fraction from which the quinilline itself has been removed, etc. Apparently bases extracted by the usual commercial methods from any fraction of coal tar are satisfactory, even when certain individuals have been removed from the fraction. The bases themselves may boil over a long range as, for example, from 110° C. to 365° C. or even higher. Some of these bases are known to be of the pyridine and quinilline series and others contain hydrogenated rings. In any case all the coal tar bases of commerce seem to be suitable.

[2] This material is a non-ionic wetting agent, the basic characteristic of which is an ethylene oxide chain, on one end of which chain is linked a hydrocarbon radical through an oxygen atom and on the other end is a hydrogen atom. The general formula for these compounds is $RO(C_2H_4O)_xH$ where R is a hydrocarbon radical and x generally is between 3 and 30.

As stated, the foregoing formula produces a relatively concentrated material which is preferably diluted with about four parts of water although the degree of dilution may be varied somewhat to meet differing conditions, actual optimum dilution ratios being obtainable by simple experimentation.

I wish to note at this point that some of the ingredients are not soluble in water and that the aqueous treating bath is usually in the form of a relatively stable emulsion. However, I have noticed, at times, that the emulsion partially breaks or separates but that this breaking or separation, apparently, has no deleterious effect on the operation of the process especially if the bath is somewhat agitated as is generally the case during normal operations of the process.

The diluted material may be applied to a series or succession of the articles being treated in any desired manner although experience to date would indicate that immersion in the bath is probably preferable, the period of immersion being from approximately 30 seconds to approximately 2 minutes depending upon the degree and nature

of the soil existing on the surface and the temperature of a bath, which latter can range anywhere from about 70° F. to a practical maximum of 160° F. although my preferred range and the one which I have found to give the best results lies between approximately 140 and 150 F.

After the treatment with my improved material the article may be rinsed if desired and then subsequently subjected to any of the conventional electroplating procedures the details of which latter, since they form no part of my invention, are not given herein.

I have found that my process of treating zinc and zinc base alloys in preparation for an electroplating operation serves not only to clean the surface but also to condition it in such a way as to greatly improve the character and finish of the final plate. Even grossly contaminated surfaces can be cleaned with my material, the deposits of soil apparently being blown free from the surface by the evolution of hydrogen gas and then rising to the surface of the bath where they are either dispersed or dissolved. Due, possibly to this rapid removal of deposits of soil even in recessed areas such as are usually present on more or less intricately shaped die castings, the subsequent etching of the zinciferous surface is extremely uniform and blistering of the final plate is almost entirely if not completely eliminated.

It will be seen, therefore, that in addition to the cleaning operation effected by my process and my material there is also a conditioning of the surface in some way, the nature of which is not altogether clear but which I have found to be of very definite and helpful effect.

I should like to note the fact that the solutions which I use are strongly acidic and that in prior cleaning practice it has been customary to avoid such acid solutions for cleaning purposes due to their tendency to cause the work to become covered with "smut." This trouble has been particularly evident with zinc alloys containing relatively high percentages of copper. Indeed, even with my improved material, I have found it inadvisable to apply the process to copper bearing alloys having higher than approximately 1% copper content if optimum results are to be attained in the subsequent electroplating steps. However, I also wish to emphasize the fact that with my invention it is posible to clean and condition in a satisfactory manner zinc base alloys which have a greater than average content of copper.

One outstanding and very valuable application of my new invention resides in its ability to clean and recondition articles which have been rejected due to improper plating by conventional cleaning and plating procedures. In other words, where the plating has failed, it is only necessary to strip the plated article down to the zinc surface by any conventional method and then subject the article to treatment according to my invention thereby making it possible to secure a replate which I have found is perfectly satisfactory and meets the most exacting standards for plated work of this kind. This makes possible a great reduction in losses from this source which losses in many industries have been very high. Where the invention is used in the manner just described the sequence of operations, of course, is preceded by a stripping of the plate from the rejected article followed preferably by a vapor degreasing operation before the article is treated with my improved bath.

I should like to point out that while the formula given above has been found to give exceedingly satisfactory service for which reason I prefer to employ it in the proportions specified, yet it is possible to vary the proportions somewhat especially with respect to the amount of phosphoric acid although a relatively high degree of acidity of the bath is very important. Insofar as the phosphoric acid content is concerned, I have found that fairly good results can be obtained where the phosphoric acid content ranges downwardly from that given in the formula to approximately half of the amount specified or approximately 0.2418 gallon. As for the coal tar bases, I have found that too great a quantity will lead to uneven pitting of the work, smutting and generally to defective surface conditioning. Too little of the active ingredients leads to a lack of cleaning, uneven conditioning and generally defective work.

In conclusion, I have found that my improved treating bath will function satisfactorily for relatively long periods of time although naturally it will become necessary ultimately to completely replace the bath. Until this point is actually reached, however, I found that the efficiency of the bath during the course of treating a series or succession of articles may be maintained simply by the periodic addition of water, wetting agent and mineral spirits in about the following proportions:

	Gallons
Mineral spirits	0.7000
Polymerized ethylene oxide condensate (100% basis)	0.0282
Water	0.2718

In other words replenishment or refreshment can be effected for a considerable period of time in the manner just indicated and the quality of the finished work will be the best guide to the frequency with which such replenishment or refreshment should be made. This possibility constitutes a somewhat unusual procedure because it would normally be expected that the acid at least would require replacement as soon as any of the other ingredients.

I claim:

1. In the art of electroplating surfaces of zinc and zinc base alloys the step of treating the surface prior to the electroplating operation by subjecting it to the action of an aqueous bath containing the following ingredients in approximately the proportions indicated:

Mineral spirits	gals.	0.3360
Phosphoric acid (75%)	gals.	0.2418 to 0.4835
Cyclic coal tar bases	gals.	0.0144
Sulphuric acid (66° Bé.)	gals.	0.0049
Thiourea	lbs.	0.0250
Polymerized ethylene oxide condensate (100% basis)	lbs.	0.0135

2. The treatment of claim 1 wherein the temperature of the bath is maintained between about 140° F. and 150° F.

3. In the art of preparing a succession of articles having zinciferous surfaces for an electroplating operation the steps which consist of treating the surfaces by subjecting them successively to the action of an aqueous bath containing the following ingredients in approximately the proportions indicated:

Mineral spirits	gals.	0.3360
Phosphoric acid (75%)	gals.	0.2418 to 0.4835

Cyclic coal tar bases	gals.	0.0144
Sulphuric acid (66° Bé.)	gals.	0.0049
Thiourea	lbs.	0.0250
Polymerized ethylene oxide condensate (100% basis)	lbs.	0.0135
Water, to make approximately	gals.	5.000

and in periodically refreshing the bath by addition thereto of a material consisting essentially of the following ingredients in approximately the proportions indicated:

	gallons
Mineral spirits	0.7000
Polymerized ethylene oxide condensate (100% basis)	0.0282
Water	0.2718

4. The method of claim 3 wherein the temperature of the treating bath is maintained between about 140° F. and 150° F.

5. An aqueous bath for treating zinciferous surfaces consisting essentially of the following ingredients in approximately the proportions indicated:

Mineral spirits	gals.	0.3360
Phosphoric acid (75%)	gals.	0.2418 to 0.4835
Cyclic coal tar bases	gals.	0.0144
Sulphuric acid (66° Bé.)	gals.	0.0049
Thiourea	lbs.	0.0250
Polymerized ethylene oxide condensate (100% basis)	lbs.	0.0135

6. A concentrated material for treating zinciferous surfaces consisting essentially of the following ingredients in approximately the proportions indicated:

Mineral spirits	gals.	0.3360
Phosphoric acid (75%)	gals.	0.2418 to 0.4835
Cyclic coal tar bases	gals.	0.0144
Sulphuric acid (66° Bé.)	gals.	0.0049
Thiourea	lbs.	0.0250
Polymerized ethylene oxide condensate (100% basis)	lbs.	0.0135
Water, to make	gals.	1.000

7. A material for use in replenishing the bath of claim 1 consisting essentially of the following ingredients in approximately the proportions indicated:

	gallons
Mineral spirits	0.7000
Polymerized ethylene oxide condensate (100% basis)	0.0282
Water	0.2718

DONALD LEE MILES.

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Certificate of Correction

Patent No. 2,461,228. February 8, 1949.

DONALD LEE MILES

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 47, for "0.4853" read *0.4835*; column 4, line 25, before the word "found" insert *have*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of June, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.