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AMMONIUM CHROMATE RINSE FOR PHOSPHATE COATED METAL SURFACES

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1

This invention relates to the art of finishing metal surfaces and is especially concerned with the provision of an improved method for finishing ferriferous and zinciferous surfaces with a final siccative coating such as paint, varnish, lacquer, japan or the like.

As is well known in the art the quality, beauty, permanence and corrosion resistance of a final siccative coating on metal surfaces depends to a large extent upon the manner in which the surface of the metal is prepared prior to the time that the siccative coating is applied. Many methods of pre-treatment are known to the art and most of them involve the formation of some sort of a protective coating on the metal as a base upon which to apply the siccative finish. One of the more important preparatory treatments involves the application to the surface of a non-metallic crystalline phosphate coating by means of suitable acid aqueous solutions which react chemically with the metal to produce the desired coat. Typical of these are acid aqueous solutions which contain dissolved zinc or manganese and where this is so the resulting coating will be rich in these metals. Processes of this kind, as indicated above, are very well known to the art and need not be specifically described although they constitute one step in my improved method of finishing metal. The factor which is important in connection with this disclosure is that one of the non-metallic crystalline phosphate coatings must be employed in order to realize the full benefits of my invention.

The principal objects of my invention are to improve the quality and beauty of the final siccative finish, to increase its adherence and to enhance its corrosion resistance and, in connection with the latter, the improvement afforded by my invention is so marked as to greatly minimize and, in fact, almost to eliminate completely the effects of exposure to conditions of high humidity. In other words, with my invention all these factors are markedly improved and blistering of the final finish is almost completely eliminated.

By way of background and in order to fully appreciate the nature of my invention it should be kept in mind that in the past, where maximum durability of the siccative coating was desired, it has been customary to rinse the phosphate coated surface with dilute solutions of chromic acid. Such solutions aid materially in promoting the adhesion of the siccative coating and in minimizing blistering. Unfortunately, however, chromic acid solutions even though they be dilute, will dissolve the crystalline phosphate

2

coating and to the extent that this takes place, naturally the corrosion resistance and quality of the final siccative finish will be impaired. This difficulty is particularly true of those coatings which are rich in zinc or manganese. For instance, in commercial practice, when using the customary chromic acid rinses, as much as fifty percent (50%) of the phosphate coating may be dissolved from the surface of the metal during the rinsing step. Therefore, when using chromic acid rinses, one is confronted with a paradox, namely, that while it is desirable to leave as much chromate as possible on the surface of the crystalline phosphate so as to secure greater resistance to under-film corrosion yet at the same time the action of the chromic acid tends to remove a portion of the important chrystalline phosphate base and the greater the increase in the concentration of the chromic acid rinsing solution employed the greater will be the quantity of the crystalline phosphate coating which will be removed. As a practical matter, therefore, it has been impossible to use rinsing solutions which are strong in chromic acid much as that might appear to be desirable from theoretical considerations.

Another prior practice has been to treat the crystalline phosphate coating with solutions of sodium or other dichromates but, where the treated surface is to be given a final siccative finish, it has been impractical to employ such dichromate rinses because they have been found to stimulate the formation of blisters as well as to markedly lower the adherence of the siccative coating.

The present invention resides in the discovery that an ammonium chromate or dichromate rinse for a crystalline phosphate coating, especially when used within certain limits of concentration, will greatly enhance the corrosion resistance and other qualities of the subsequently applied siccative coating. For best results the amount of chromate per 100 gallons of water should be between 1 and 40 ounces expressed as CrO_3 and there must be no free chromic acid in the solution. The minimum pH of such a solution in distilled water lies between 4.0 and 4.5 (depending upon the amount of chromate ion used) and such a pH corresponds to that of a C. P. solution of ammonium dichromate within the recommended range of concentration. The maximum pH will be in the neighborhood of 9.1 and such a pH corresponds to a solution of ammonium chromate containing excess ammonia which does no harm. In any case the solution contains, as essential ingredients, substances de-

rivable from interaction of ammonia and chromic acid.

The solution may be prepared from chromic acid and ammonium hydroxide or, if desired, from ammonium dichromate, ammonium chromate or mixtures of the two. Where ammonium hydroxide is employed it will be practically impossible to raise the pH above 9.1 even by copious additions of ammonium hydroxide because ammonium hydroxide is a weak base.

To illustrate the corrosion resistance to high humidity which is characteristic of my invention I wish to cite the following example. A plurality of metal panels where given identical phosphate coating and painting treatments, the phosphate coating being a crystalline phosphate coating where the solution employed contained dissolved zinc in the manner well understood in this art. After being phosphate coated and prior to being painted the panels were rinsed in solutions corresponding to 4 ounces of chromic acid per 100 gallons of water to which varying amounts of ammounium hydroxide were added so as to give an ascending series of pH values. The pH of the simple chromic acid rinsing solution was 2.8 which corresponds to a solution of pure chromic acid at the concentration specified. The pH's resulting from the additions of ammonium hydroxide which I employed are shown in the following table:

pH	Rating
2.8	7
5.0	9.5
6.4	9.5
8.6	10.0
9.1	9.0

The final pH of 9.1 shown in the above table corresponds to a solution of ammonium chromate and ammonium hydroxide.

While the temperature of the rinsing bath is not particularly important it might be noted that, in accordance with customary practice in this art, it can be heated and it is usual to heat it to upwards of 160° F. in order to facilitate subsequent drying.

The siccative coating employed was a commercial finish which is unusually subject to blistering in atmospheres of high humidity. After the phosphate coating treatment and the rinsing treatment in this series of rinsing solutions the panels were exposed to an atmosphere of 95 to 100% relative humidity, the temperature being maintained at approximately 100° F., for four weeks after which they were rated and the results of the rating are included in the second column of the table. In this latter connection it should be noted that a rating of 10 is perfect and a rating of 7 is barely passing by commercial standards. The concentration of 4 ounces of chromic acid per 100 gallons of water is representative of conventional commercial rinsing practice.

The foregoing tests clearly demonstrate the improved results which can be secured by the process of my invention insofar as resistance to humidity blistering is concerned which, of course, is a very important index to the value of the invention. In addition I wish to cite the improvement in result which is possible as measured by a standard salt fog test. A series of panels which

were prepared in accordance with the method I have disclosed (i. e., panels which were phosphate coated with a coating rich in zinc and then rinsed, dried and painted with a commercial finish), were scribed and exposed for a period of two weeks to the atmosphere in a standard salt fog cabinet. The results, insofar as salt spray scratch failure is concerned, were compared with that which occurred on panels that were given a conventional chromic acid rinse and showed a twenty-one percent (21%) lower salt spray scratch failure record which is a marked improvement over prior practice.

The time of treatment of the work with the final rinsing solution need only be long enough to insure thorough replacement of adhering rinse water, etc. and complete wetting of the surface with the final rinsing solution. If, as is often the case, the rinsing solution is used hot, it is generally desirable to leave the work to be rinsed in contact with the solution until it is hot enough to be readily dried. I have found that it is rarely necessary to increase the rinsing time beyond one minute.

Furthermore, as is customary with the chromic acid rinses of the prior art the rinsing solution should be kept substantially free of dissolved extraneous salts, although the presence of the chromate minimizes the blistering tendencies due to the presence of small amounts of such salts. This is best done—(*a*) by making up the rinsing solution out of clear fresh water; (*b*) by adding to the water no soluble salts except those derivable from dissolved chromic acid and ammonia; and (*c*) by continually overflowing and/or renewing the rinsing solution to minimize contamination.

I claim:

1. In the art of finishing ferriferous and zinciferous metal surfaces, the method which includes producing on the surface a crystalline phosphate coating by chemical reaction with the metal, rinsing the coated surface with an aqueous solution containing as its essential ingredients for each 100 gallons of solution from 1 to 40 ounces of chromate expressed as CrO_3 and a quantity of ammonia sufficient to yield a pH which is high enough to preclude the presence of free chromic acid, said rinsing solution being kept substantially free of dissolved extraneous salts, drying the rinsed surface and then applying a siccative finishing coat to the dry surface.

2. The process of claim 1 where the phosphate coating is rich in metal from the class of zinc and manganese.

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