

UNITED STATES PATENT OFFICE

2,132,000

PHOSPHATE COATING BATH AND METHOD OF MAKING

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No Drawing. Application October 7, 1936,
Serial No. 104,555

3 Claims. (Cl. 148—6.5)

This invention relates to phosphate coating baths and methods of making; and it comprises as a composition of matter the products of reaction of a mixture of a soluble normal salt of a metal and a soluble dihydrogen alkali phosphate, the amount of the former being commonly somewhat greater than corresponds to the latter; and it also comprises a method of making baths for producing phosphate coatings on metal wherein a solution of a soluble normal salt of a metal, usually a sulfate, is admixed with a solution of a dihydrogen alkali phosphate; all as more fully hereinafter set forth and as claimed.

It is a common and old practice to provide ferrous metals with a phosphate coating for the double purpose of giving some protection against rust and of providing a coating to which paint and varnish will stick better than they will to naked metal. Many baths of this character have been described but in general they all contain free phosphoric acid and a soluble dihydrogen phosphate of a metal; zinc, manganese, iron, copper, etc. Phosphoric acid forms three series of salts, R_3PO_4 , R_2HPO_4 and RH_2PO_4 in which R is any monovalent metal or base; the tertiary, secondary and primary phosphates. The primary or dihydrogen phosphates, which may be here called acid phosphates, of zinc, manganese, ferrous iron and copper have been used. In coating iron and steel the iron is attacked and it is assumed that the coating contains an insoluble secondary phosphate formed by the reaction of the acid phosphate with ferrous iron. In using acid manganese phosphate in the bath, the coating would then be a double phosphate of manganese and iron while acid phosphate of zinc would give a double phosphate of zinc and iron.

The excess of phosphoric acid over that required for an acid phosphate is not desirable but is more or less inherent in the way the baths are made.

These acid compositions can be used in coating iron and steel and have so been used for many years. There seems to be an advantage in using phosphates of two or more metals in the bath; zinc phosphate and copper phosphate, manganese phosphate and zinc phosphate, zinc phosphate and iron phosphate, etc. In coating the metal with the acid phosphate solution, the iron or steel is attacked more or less and iron phosphates join the coating from this source.

I have found that for these coatings a standardized acidity equal to that of a dihydrogen phosphate is desirable but that more acidity is not. And, furthermore, it is usually desirable

to have the heavy metal in solution in amount somewhat more than is equivalent to the phosphoric acid, that is to have present some unchanged neutral soluble salt of the heavy metal.

In the present invention I accomplish both ends by using a soluble dihydrogen phosphate of ammonia or soda or potash, and mixing it with a solution of a normal or neutral sulfate of a metal forming insoluble phosphates, sulfate of zinc for example. The acidity of the solution is that of the dihydrogen phosphate and in making up the bath the addition of any of these normal sulfates does not cause a precipitate at ordinary temperatures whatever the ratio of the metal sulfate to the phosphate. This renders feasible the stated use of an excess of normal sulfate in making up a bath. In using zinc sulfate to supply zinc in the coating bath, the ratio of the zinc oxide to the phosphoric acid may be made as high as may be desired without causing appreciable precipitation, this being a matter of using more zinc sulfate. The solutions as made at ordinary temperatures are clear and remain so. The solutions withstand heating to the usual working temperatures, while remaining quite clear. At elevated temperatures some cloudiness may develop, more especially in the case of the zinc solutions; but this is harmless. The manganese baths ordinarily remain substantially clear at all working temperatures. In coating operations it is desirable to avoid the presence or formation of a sludge or mud in the bath.

In one way of looking at it, the coating bath is a solution of an ordinary normal metal salt given the exact acidity desirable and a sufficient P_2O_5 content by addition of a primary phosphate of an alkali.

In mixing sodium dihydrogen phosphate solution with a solution of zinc sulfate, it is a matter of speculation as to how far they interact. But the mixed liquids may be regarded as containing the metathetical product, zinc dihydrogen phosphate, in some proportion. The solution also contains, to a corresponding extent, the other reaction product, sodium sulfate. The presence of this sodium sulfate in the solution appears to do no harm in the coating operation and indeed seems to facilitate the coating reaction.

For coating iron and steel, baths containing either ammonium or sodium dihydrogen phosphate in amount about equivalent to 1 per cent of P_2O_5 on the solution, are satisfactory. Any desired amount of manganese sulfate, or zinc sulfate, or copper sulfate, may be dissolved in such a bath, but in practice it is found advan-

tageous to use from one half to one or more molecules of sulfate for each molecule of ammonium or sodium dihydrogen phosphate, that is, a molecular ratio of phosphate to sulfate of less than 2:1. An excellent bath can be made with a 1.25:1 ratio. For example, a particularly good bath is made by using, for each molecule of dihydrogen phosphate, 1 molecule of manganous sulfate and 0.25 molecule of zinc sulfate. Another good bath, having a lower ratio, is made by using for each molecule of the phosphate 0.65 molecule of manganous sulfate and 0.15 molecule of zinc sulfate.

The bath is advantageously made up by preparing a mixture of the crystallized salts in the desired proportions and dissolving sufficient of the mixed salts in water to form a solution containing the equivalent of about 1 per cent P_2O_5 or 1.7 per cent NaH_2PO_4 .

The bath is replenished in use by adding the metal normal salt and dihydrogen alkali phosphate in the proper proportions. Usually the dragout loss of solution on the work offsets accumulation of alkali sulfate in the bath.

While coating baths can be made with the aid of ferrous sulfate containing the equivalent of acid ferrous phosphate, I do not regard them as being as desirable as baths containing manganese sulfate and zinc sulfate, either or both.

However, any of these baths in use will pick up some dissolved iron from the work; after use for some time, the bath usually contains more or less acid ferrous phosphate so formed.

In a bath containing both manganese and zinc, I find it is better to have a preponderance of the former, as in the bath just described. With such a bath the surface of the metal to be coated is etched better and develops a better coating; a coating better adapted for giving a good bond with lacquer subsequently applied.

As normal salt of the metals forming insoluble phosphates, the sulfate is usually the most available and the most convenient soluble salt to handle. However, nitrates, chlorides or even acetates may be used. In general any soluble normal salt of the metal will serve.

In a specific embodiment of this invention a good coating bath is made by dissolving sodium dihydrogen phosphate, $NaH_2PO_4 \cdot H_2O$, in water. In making up 1000 parts by weight of bath a good proportion is 20 parts of the phosphate and 947 parts by weight of water. To this solution is added manganous sulfate, $MnSO_4 \cdot 4H_2O$, in about an equal amount, that is about 20 parts. To this solution is added zinc sulfate, $ZnSO_4 \cdot 7H_2O$, in a proportion of about 13 parts to 40 parts of the other two salts. The bath so prepared is

ready for use with or without filtration. This bath may be used hot in protecting pickled iron and steel, employing the usual technique.

The two salts may be separately dissolved in the water. Filtration may be desirable to remove mechanical impurities.

The bath in use may receive an addition of an ordinary oxidant or depolarizer, such as a nitrate, to oxidize hydrogen gas produced. It is useful also to add a reducing agent such as formaldehyde, SO_2 , a thiosulfate, etc., to prevent the development of ferric salts. With a bath of the rather exact acidity of those produced in the present invention, development of ferric iron is more of a nuisance than with the usual highly acid baths containing enough excess phosphoric acid to hold everything in solution.

The present bath has the acidity of the acid phosphate of soda or acid phosphate of ammonia used, the various sulfates mentioned being of neutral character; that is, containing no free acid.

What I claim is:—

1. The method of preparing a phosphate coating bath adapted for treating ferrous metal surfaces and having an acidity corresponding to that of a dihydrogen alkali phosphate, which comprises dissolving in water sufficient dihydrogen alkali phosphate to give the solution the desired acidity and concentration of P_2O_5 , and also dissolving in said solution a normal salt of at least one metal selected from the class consisting of zinc and manganese, said salt being added in an amount which bears at least an equimolecular ratio to the amount of dihydrogen alkali phosphate dissolved in the bath.

2. The method of providing ferrous metal surfaces with bonding and rust-resistant coatings essentially of phosphates of iron and of at least one metal selected from the class consisting of zinc and manganese, which comprises preparing a phosphate coating bath having an acidity corresponding to that of a dihydrogen alkali phosphate by dissolving in water an amount of dihydrogen alkali phosphate sufficient to impart the desired acidity and concentration of P_2O_5 thereto, and also dissolving therein a normal sulfate of a metal of said class in at least an equimolecular amount, and contacting a ferrous metal surface with said bath.

3. In the process of claim 2, the method of maintaining the desired bath constitution during repeated use of the bath, which comprises occasionally adding thereto dihydrogen alkali phosphate and normal sulfate of a metal of said class.

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