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PRETREATMENT SOLUTION FOR PHOSPHATE COATING, METHOD OF PREPARING THE SAME AND PROCESS OF TREATING METAL SURFACES

Walter R. Cavanagh, Detroit, and James I. Maurer, St. Clair Shores, Mich., assignors to Parker Rust Proof Company, Detroit, Mich., a corporation of Michigan

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This invention relates to the art of producing phosphate coatings on metal surfaces, and more particularly to the activation or pretreatment of metal surfaces for subsequent reaction with phosphate coating solutions.

It is known, e. g., U. S. Patent 2,310,239 to Jernstedt, that solutions of disodium phosphate containing titanium activate or prepare a metal surface for subsequent treatment with phosphate coating solutions so that the equality of the subsequently applied phosphate coating is enhanced and the rate of coating formation is accelerated. The degree of activation resulting from treatment with such solutions is not reproducible from batches prepared in identical manner, so that difficulties are encountered in commercial applications. Moreover, greater concentrations are required to produce a given degree of activation than are actually necessary.

Accordingly, it is an important object of this invention to provide an improved composition for activating metal surfaces in preparation for reaction with phosphate coating solutions which imparts to the surfaces a given degree of activation at lower concentrations than has heretofore been possible.

It is another important object of the invention to provide an improved method for preparing an activating composition whereby to increase the reactivity of the same and to obtain therefrom consistent and reproducible conditioning effects on metal surfaces.

Still other important objects are to provide an improved process of forming phosphate coatings on metal surfaces and to provide an improved method of pretreating or activating metal surfaces to obtain excellent quality phosphate coatings thereon with greater economies than has been formerly possible.

In accordance with the invention, it has been discovered in connection with titanium-containing pretreatment solutions that the degree of activation imparted to metal surfaces for subsequent reaction with phosphate coating solutions is critically related to the manner of preparing the pretreatment or activating composition and that the reactivity of the activating composition can be drastically altered by the method employed in its preparation. Unexpectedly, it has been found that if the activating composition is prepared under certain carefully controlled conditions, its reactivity or activating ability when in aqueous solution is so greatly invigorated that its properties and effects are entirely unlike activating compositions heretofore known to the art. The activating composition resulting from the controlled conditions of preparation as set forth in this invention is characterized by its consistent and predictable conditioning action and by its ability to impart a given degree of activation to metal surfaces at considerably lower concentrations than that required of prior art activating compositions.

In the practice of the invention, metal surfaces are provided with exceptionally fine quality phosphate coatings by subjection to phosphate coating solutions after having first been activated by preliminary treatment with

an improved activating solution. The activating solution is made up from a dried activating composition containing as the essential ingredients a phosphate of sodium and a titanium-containing compound. The activating composition is prepared under certain controls which include, among other conditions, low temperature initial dispersion of the essential ingredients, though not necessarily in their final proportions, and a subsequent higher temperature aging treatment. The initial dispersion or intimate mixing of the essential ingredients in the proportions in which they are first combined is made to take place for a minimum length of time in an aqueous medium at low temperatures during which the concentration of the hydrogen ion is maintained within certain predetermined limits. Following this critical stage of bringing together initial amounts at least of the reacting ingredients, the mixture is heated to a minimum temperature for a minimum length of time during which final amounts may be added if desired. This stage is hereinafter referred to at times as an aging treatment. A dried activating composition is evolved from the aged mixture, and from this manner of preparation, the reactivity of the activating composition is so exceptionally enhanced that its ability to activate metal surfaces is demonstrated when put up in aqueous solutions in concentrations far below that which was heretofore considered necessary for proper conditioning. Furthermore, reproducible conditioning effects and predictable conditioning action, which was the exception with prior art solutions, is consistently obtainable from the solutions prepared according to the present invention. It has been found that such controlled conditions of preparation are critical in order to impart to the activating composition properties and effects of the character described.

Presently, activating compositions containing titanium are prepared, for example, by dissolving disodium orthophosphate in a small amount of hot water between 160 and 180° F. and dispersing in the heated solution a soluble titanium compound, e. g., titanyl sulphate. Elevated temperatures are used because of the greater ease of dissolving the solid materials. The pH of the mixture is adjusted between 8.5 and 9, and the resulting solution is thereafter dried on a rotary drum drier.

In contrast thereto, in the practice of this invention a solution of a titanium-containing compound is prepared and a phosphate of sodium either in solution or the dry salt is dispersed therein. A slurry is formed by the addition of the phosphate compound to the titanium solution, which is intimately mixed, preferably for at least ten minutes, at low temperatures, and the pH of the slurry is maintained between a maximum of about 7.8 and a minimum of about 5.7. When the pH of the slurry is outside the range the benefits of the invention are not obtained. Preferably the pH of the slurry is maintained between 6.4 and 7.6. Sulphuric acid or sodium hydroxide have been found to be suitable for adjusting the pH of the slurry when required. The temperature of the slurry during this initial dispersion stage should not exceed a maximum of about 75° F. Lower temperatures are not harmful. Although satisfactory conditioning has resulted with activating compositions prepared from slurries that have been held at 50° F. during the initial mixing of the essential ingredients in the proportions in which they are first combined, the temperature of the slurry is preferably maintained in the range of about 65° F. to about 70° F.

Commercial titanyl sulphate is the preferred titanium compound to be used for reasons of economy, but other compounds yielding the titanium ion in solution may be successfully employed, such as titanium potassium fluoride, as the source of the titanium ion is not critical. The

titanium compound may be dissolved or dispersed at elevated temperatures, but before the addition of the phosphate compound the solution is cooled to the above mentioned low temperature range for initial dispersion. It has been found that the titanyl sulphate can be dissolved in dilute acids, e. g., sulphuric acid as well as in water. In fact, commercially available titanyl sulphate contains a certain amount of sulphuric acid.

The phosphate of sodium that is dispersed in the solution of the titanium compound in the practice of this invention is disodium ortho-phosphate, and the phosphate of sodium compounds that have been found to be satisfactorily employed in lieu of the disodium phosphate are sodium tripolyphosphate and tetrasodium pyrophosphate or mixtures thereof. The latter two are each especially effective for their own particular applications. The quantity of sodium tripolyphosphate and/or tetrasodium pyrophosphate that may be substituted for the disodium phosphate is that amount which will produce substantially the same concentration of P_2O_5 as the required amount of disodium phosphate.

The above two compounds of sodium may also be used to replace portions of the required disodium phosphate, and in this connection other phosphates of sodium have been found to be useful in combination with less than the required quantities of disodium phosphate. In some cases, the addition of certain other phosphates of sodium to replace part of the required disodium phosphate have produced excellent activating compositions comparable in all respects to those resulting from the use of disodium phosphate alone. The other phosphates of sodium that may be successfully employed for this purpose are monosodium ortho-phosphate and trisodium ortho-phosphate and mixtures of these. The controlling factor as to the choice of the particular phosphate of sodium compound or mixtures of such compounds is the pH of the resulting slurry when combined with the titanium-containing compound. In general, any combination of the mentioned phosphate of sodium compounds that yields a slurry having a pH within the critical range above set forth is satisfactory, it being understood that the desired pH is attained primarily through the use of the phosphate ion and the sodium ion only, and the introduction of extraneous ions through acids and bases is preferably avoided.

In preparing the slurry, the amount of titanium-containing compound employed is determined from the portions desired in the dried activating composition, and the amount of the phosphate of sodium compound is thereby fixed. Preferably, the amount of titanium-containing compound is selected to produce 1% titanium in the dried powder. However, satisfactory conditioning will result when the concentration of titanium in the dried powder is as low as 0.005%. No practical advantage is realized in employing more titanium-containing compound in the slurry than that required to produce 4% titanium in the dried activating composition. The amount of water used in making up the slurry is not critical and a minimum of water is added since the water must be later removed. Warm water may be and usually is employed to dissolve or disperse the titanium-containing compound, and for this purpose water having a temperature of about 170° F. is commonly employed. If the titanium-containing compound is dissolved or dispersed in warm water, the solution is cooled to the critical range above indicated for the initial mixing or dispersion of the phosphate of sodium compound. The amount of the phosphate of sodium compound that is employed is fixed by the amount of titanium-containing compound desired in the dried activating composition. That is to say, the amount of the phosphate of sodium compound used in making up the slurry is that amount required to produce a dried activating composition having 0.005% to 4% titanium based on the combined weight of the phosphate of sodium compound and the titanium-containing compound. For example, if commercial titanyl sulphate and disodium phosphate are used and it is desired to have a concentration of 1% titanium in the dried activating compositon based on the combined weight of titanyl sulphate and disodium phosphate, then for every 9.7 lbs. of titanyl sulphate added to make up the slurry, approximately 90 lbs. of disodium phosphate should be used.

Although all of the required amount of the phosphate of sodium compound may be added to the solution of the titanium-containing compound during the initial low temperature dispersion stage, preferably less than the required amount of the phosphate of sodium compound is added at this time and the balance is added just prior to or during the higher temperature aging stage. In usual practice, approximately 20% of the required amount of the phosphate of sodium compound is added during the initial low temperature mixing of the slurry, although it has been found that if as little as 1% of the required amount is added at this time, satisfactory conditioning nevertheless results. When less than the required amount of the phosphate of sodium compound is added during the low temperature mixing of the slurry, a particularly advantageous manner of adding the remainder of the required amount is to add it at an intermediate temperature lower than the temperature to which the slurry is brought for the higher temperature aging treatment. The low temperature mixing of the slurry, irrespective of the amount of phosphate of sodium compound present at this stage, is continued for a minimum length of time. The exact minimum time during which the slurry must be maintained under the controlled conditions of hydrogen ion concentration and temperature previously set forth depends to some extent upon the quantity of materials handled and is not definitely known. Simple tests under operating conditions will determine the minimum period for a given application. Generally, holding the slurry at these conditions for ten minutes is sufficient, although thirty minutes to one hour is used in practice.

The slurry is then heated to an elevated temperature for the aging treatment and maintained at this temperature for a minimum length of time. The pH of the slurry during aging normally does not change from that to which it was adjusted for the initial low temperature dispersion stage, and, in any event, is maintained within the limits above set forth for the said dispersion stage. The temperature range in which the aging of the slurry takes place is between about 160° F. and 190° F. Preferably, the aging treatment is carried out between 175° F. and 180° F. The time at which the slurry is maintained at the elevated temperatures for aging depends upon the quantities of ingredients handled and even upon the aging temperature employed. Generally, the slurry must be aged for a greater length of time when lower temperatures are employed. The minimum length of time cannot be stated with certainty, although generally it can be said that thirty minutes has been found to be satisfactory. Longer aging periods than this are not harmful, if the temperature is maintained within the limits indicated. During the aging treatment the pH of the solution is preferably checked to ensure that it is within the stated limits. This can be conveniently done when the remainder of the required amount of the phosphate of sodium compound is added at the elevated temperature employed for aging of the slurry. The remainder of the phosphate of sodium compound, however, as indicated, can be added at lower temperatures, as for example 140° F., while the temperature of the slurry is being raised to the range required for aging. If this alternative is employed, the pH of the slurry should be checked independently at least once during the aging treatment. As mentioned, it has been found in practice

that no adjustment of the pH is required as the slurry retains the same acidity as it had during the low temperature mixing treatment.

After the slurry has been aged under the controlled conditions indicated for the required length of time, the slurry is dried to form a powdered activating composition. The manner of drying is not critical and for this purpose a conventional rotary drum drier can be employed. In practice, the temperature of the surface of the drums in the rotary drum drier is determined by the temperature of the steam employed, which is usually 80 to 100 lbs. per sq. in. steam.

From the manner of treating the slurry as above described, a dried activating composition is evolved which contains about 0.005% to 4% titanium based on the combined weight of a soluble titanium-containing compound and a phosphate of sodium compound. In use, the dried activating composition is dissolved in water to produce an aqueous pretreatment solution having a concentration of titanium ion between 0.0004% and 0.05% and from 0.01% to 2% of the phosphate of sodium compound. The pH of the pretreatment solution is generally the same as the pH of the slurry from which the dried activating composition has evolved. Metal surfaces contacted with the pretreatment solution, particularly ferrous and zinc metal surfaces, are activated for subsequent application of coating-phosphate type phosphate coating solutions, i. e., conventional zinc, manganese phosphate coating solution. Metal surfaces activated with the pretreatment solutions prepared as above and subsequently coated with zinc or manganese phosphate coating solutions yield exceptionally fine and dense crystalline coatings at lower concentrations of the pretreatment solution than has heretofore been possible. Moreover, the conditioning action of the pretreatment solution is consistent and results do not vary with different batches prepared following the same technique.

The following are examples of slurries that were prepared for the purposes indicated in each example, and from each of the slurries, dried activating compositions containing 1% titanium were evolved by drying at the same temperature and for the same period of time. Each of the dried activating compositions were put up in aqueous solutions to form pretreatment solutions of different concentration. Unless otherwise indicated, 20% of the total amount shown for the phosphate of sodium compound was added during the low temperature dispersion stage and the remainder was added during the higher temperature aging stage. The low temperature dispersion stage was maintained for ten minutes at 70° F. for each example, and the higher temperature aging treatment was carried out at 180° F. for thirty minutes. The minimum concentration of each dried activating composition in the pretreatment solution required to produce a conditioning or activating effect on mild steel surfaces was noted. The results are given in Table I below.

EXAMPLE 1

A control slurry was prepared as follows:

3.2 gms. commercial titanyl sulphate
30.0 gms. disodium phosphate
60.0 ml. water

EXAMPLE 2

A slurry was prepared in which the commercial titanyl sulphate was dispersed in 2.5% aqueous sulphuric acid. The pH of the titanyl sulphate was lowered from 0.9 to 0.5.

19.2 gms. commercial titanyl sulphate
180.0 gms. disodium phosphate
360.0 ml. 2.5% sulphuric acid solution

EXAMPLE 3

A slurry was prepared in which sodium tripolyphosphate was employed in lieu of disodium phosphate.

3.2 gms. commercial titanyl sulphate
16.0 gms. sodium tripolyphosphate
60.0 ml. water

Similar results were obtained with sodium tetrapyrophosphate in lieu of disodium phosphate.

In the following three examples, instead of 20% of the total amount of disodium phosphate being added during the low temperature dispersion stage, 10%, 5% and 1%, respectively, were added and the remainder of the total amount added during the higher temperature aging treatment:

EXAMPLE 4

3.2 gms. commercial titanyl sulphate
3.0 gms. disodium phosphate (initial addition)
27.0 gms. disodium phosphate
60.0 ml. water

EXAMPLE 5

3.2 gms. commercial titanyl sulphate
1.5 gms. disodium phosphate (initial addition)
28.5 gms. disodium phosphate
60.0 ml. water

EXAMPLE 6

3.2 gms. commercial titanyl sulphate
0.3 gms. disodium phosphate (initial addition)
29.7 gms. disodium phosphate
60.0 ml. water

EXAMPLE 7

A slurry was prepared employing monosodium phosphate in lieu of disodium phosphate. The resulting pH of the slurry was outside the critical range.

3.2 gms. commercial titanyl sulphate
29.0 gms. monosodium phosphate
60.0 ml. water

EXAMPLE 8

A slurry was prepared in which only 5% of the required disodium phosphate was used.

3.2 gms. commercial titanyl sulphate
1.5 gms. disodium phosphate
60.0 ml. water

The pH of the slurry was not recorded for this example, but it was obviously outside the critical range as evident from the pH of the resulting pretreatment solution.

The following example illustrates the importance of attaining the desired pH in the slurry primarily through the use of phosphate ion and sodium ion only, as otherwise such compounds will not be present in their required amounts.

EXAMPLE 9

To a slurry prepared as in Example 8 was added 1.5 gms. of sodium carbonate to raise the pH to that of a normal slurry.

EXAMPLE 10

A slurry prepared as in Example 1 was tested for activating or conditioning ability without proceeding with the step of drying and forming a dried activating composition.

In the following four examples, approximately 25% and 50% of the amount of disodium phosphate normally added during the low temperature mixing treatment was replaced by monosodium and trisodium phosphate, respectively:

EXAMPLE 11

19.2 gms. commercial titanyl sulphate
27.0 gms. disodium phosphate (initial addition)
9.0 gms. monosodium phosphate (initial addition)
144.0 gms. disodium phosphate
360.0 ml. water

EXAMPLE 12

19.2 gms. commercial titanyl sulphate
18.0 gms. disodium phosphate (initial addition)
18.0 gms. monosodium phosphate (initial addition)
144.0 gms. disodium phosphate
360.0 ml. water

EXAMPLE 13

19.2 gms. commercial titanyl sulphate
27.0 gms. disodium phosphate (initial addition)
11.5 gms. trisodium phosphate (initial addition)
144.0 gms. disodium phosphate
360.0 ml. water

EXAMPLE 14

19.2 gms. commercial titanyl sulphate
18 gms. disodium phosphate (initial addition)
23 gms. trisodium phosphate (initial addition)
144 gms. disodium phosphate
360 ml. water

In the following first four examples, approximately 25%, 50%, 75% and 100% of the amount of disodium phosphate normally added during the higher temperature aging treatment was replaced by monosodium phosphate. In the fifth example, immediately following 25% of the amount of disodium phosphate normally added during the higher temperature aging treatment was replaced by trisodium phosphate. Greater replacements by trisodium phosphate during this stage acted in identical manner, i. e., resulted in no conditioning ability in the dried activating composition. Disodium phosphate was added during the low temperature mixing treatment in the normal manner in all of the five examples immediately following.

EXAMPLE 15

19.2 gms. commercial titanyl sulphate
36 gms. disodium phosphate
36 gms. monosodium phosphate (final addition)
108 gms. disodium phosphate (final addition)
360 ml. water

EXAMPLE 16

19.2 gms. commercial titanyl sulphate
36 gms. disodium phosphate
72 gms. monosodium phosphate (final addition)
72 gms. disodium phosphate (final addition)
360 ml. water

EXAMPLE 17

19.2 gms. commercial titanyl sulphate
36 gms. disodium phosphate
108 gms. monosodium phosphate (final addition)
36 gms. disodium phosphate (final addition)
360 ml. water

EXAMPLE 18

19.2 gms. commercial titanyl sulphate
36 gms. disodium phosphate
144 gms. monosodium phosphate (final addition)
360 ml. water

EXAMPLE 19

19.2 gms. commercial titanyl sulphate
36 gms. disodium phosphate
46 gms. trisodium phosphate (final addition)
108 gms. disodium phosphate (final addition)
360 ml. water

Table I

Example	pH Slurry	pH Pretreatment solution	Minimum concentration of dried activated composition, gms./liter
1	7.5	7.5	0.16.
2	6.7	6.9	0.32.
3		7.35	0.63.
4	7.45	7.52	0.32.
5	7.55	7.51	0.32.
6	7.45	7.55	0.16.
7	2.99	3.77	No conditioning.
8		2.40	Do.
9	7.45	7.60	Do.
10	7.5		Do.
11	7.2	7.18	0.32.
12	7.1	7.18	0.32.
13	7.5	7.35	0.08.
14	7.6	7.75	2.5.
15	6.8	7.0	0.32.
16	6.4	6.63	0.32.
17	5.9	6.15	0.63.
18	5.0	5.70	No conditioning.
19	8.0	7.9	Do.

EXAMPLE 20

Batches of dried activating compositions were prepared by the present conventional method for comparison with activating compositions prepared in accordance with the present invention. In accordance with the present conventional method, for each batch 900 lbs. of disodium phosphate was dissolved in hot water at a temperature of 180° F. 97 lbs. of commercial titanyl sulphate, together with a slight amount of caustic soda was added to the solution of disodium phosphate at the elevated temperature. The pH of the slurry was maintained at 8.5 and subsequently dried on a rotary drum to produce a dried activating composition. The dried activating composition from each batch was dissolved in water to form pretreatment solutions of different concentrations. Out of 277 batches tested, 91 batches gave no conditioning at a concentration of dried activating composition of 5 grams/liter of solution. 124 batches gave conditioning at 5 grams/liter. 45 batches gave conditioning at 2.5 grams/liter. 14 batches gave conditioning at 1.25 grams/liter and 2 gave conditioning at 0.15 gram/liter.

In contrast, production batches were made in accordance with the present invention by dissolving 200 lbs. of disodium phosphate in cold water at a temperature less than 70° F. Separately 97 lbs. of commercial titanyl sulphate was dispersed in hot water at 160° F. and cooled down to 65° F. before admixture of this dispersion with the disodium phosphate solution. The dispersion of titanyl sulphate was mixed with the cold solution of disodium phosphate at a temperature below 70° F. The pH of the resulting slurry was maintained at 7.3 and the slurry was mixed for 45 minutes. Thereafter, the temperature of the mixture was raised to 140° F. and the remainder of the required amount of disodium phosphate, viz., 700 lbs., was added. The mixture was aged for a period of one hour at 175° F. The slurry was then run onto a rotary drum drier and a dried activating composition was produced. The dried activating composition from each batch was dissolved in water. When the above procedure was followed, essentially all of the resulting pretreatment solutions gave conditioning at a concentration of 0.63 gram of dried activating composition per liter of solution. Substantially all of the batches could have produced conditioning at even lower concentrations, but the lowest concentration was not determined for these batches.

What is claimed is:

1. A method of forming a dried activating composition which comprises the steps of forming an aqueous slurry consisting essentially of a titanium-containing compound and a phosphate of sodium compound, said titanium-containing compound and said phosphate of sodium compound being present in such proportions as to produce a pH of said slurry in the range of about 5.7 to about 7.8, mixing the slurry at a temperature below about 75° F.

and thereafter raising the temperature of the mixed slurry for a period of time and at a temperature sufficiently elevated to age the slurry so that a dried activating composition can be evolved therefrom which when dissolved in aqueous solution is capable of activating metal surfaces for subsequent reaction with phosphate coating solutions, and thereafter drying the aged slurry to produce a dried activated composition containing at least 0.005% titanium based on the combined weight of said titanium-containing compound and said phosphate of sodium compound in said dried activating composition.

2. A method of forming a dried activated composition which comprises the steps of forming an aqueous slurry consisting essentially of a titanium-containing compound and a phosphate of sodium compound, said titanium-containing compound and said phosphate of sodium compound being present in such proportions as to produce a pH of said slurry in the range of about 5.7 to about 7.8, said slurry being formed below a maximum temperature of about 75° F., mixing the slurry at said temperature and thereafter raising the temperature of the mixed slurry between 165° F. and 190° F. to age the slurry, drying the aged slurry to produce a dried activating composition containing at least 0.005% titanium based on the combined weight of said titanium-containing compound and phosphate of sodium compound in said dried activating composition.

3. A method of forming a dried activating composition which comprises the steps of forming an aqueous slurry consisting essentially of a titanium-containing compound and a phosphate of sodium compound, said titanium-containing compound and said phosphate of sodium compound being present in such proportions as to produce a pH of said slurry in the range of about 5.7 to about 7.8, said slurry being formed at a temperature between about 60° F and 75° F., mixing the slurry at said temperature and thereafter raising the temperature of the mixed slurry between 165° F. and 190° F. to age the slurry, drying the aged slurry to produce a dried activating composition containing from about 0.005% to 4% titanium based on the combined weight of said titanium-containing compound and phosphate of sodium compound in said dried activating composition.

4. A dried activating composition capable of activating metallic surfaces for subsequent reaction with phosphate coating solutions consisting essentially of a titanium-containing compound and a phosphate of sodium compound in such proportions to yield from about 0.005% to 4% titanium based on the combined weight of said titanium-containing compound and said phosphate of sodium compound, said composition being the product of claim 3.

5. A pretreatment solution for activating metal surfaces for subsequent reaction with phosphate coating solutions comprising an aqueous solution consisting essentially of titanium-containing compound in an amount sufficient to yield between about 0.0004% to 0.05% titanium ion and from 0.01% to 2% of a phosphate of sodium compound, said pretreatment solution being the product of dissolving the composition of claim 4 in aqueous medium.

6. In a method of treating a metal surface to produce phosphate coatings thereon, the step comprising contacting said surface with the pretreatment solution of claim 5.

7. A method of treating metal surfaces to produce phosphate coatings thereon comprising contacting said surface with the pretreatment solution of claim 5 and thereafter contacting said surface with an aqueous acidic solution of a phosphate to form a protective phosphate coating thereon.

8. A method of forming a dried activating composition which comprises the steps of forming an aqueous slurry consisting essentially of a titanium-containing compound and a phosphate of sodium compound selected from the group consisting of disodium phosphate, sodium tripolyphosphate, and tetrasodium pyrophosphate, said titanium-containing compound and said phosphate of sodium compound being present in such proportions as to produce a pH of said slurry in the range of 5.7 to 7.8, said slurry being formed at a temperature below a maximum temperature of about 75° F., mixing the slurry at said temperature and maintaining the pH within said range during the mixing step and thereafter raising the temperature of the mixed slurry between 165° F. and 190° F. to age the slurry, drying the aged slurry to produce a dried activating composition containing at least 0.005% titanium based on the combined weight of said titanium-containing compound and phosphate of sodium compound in said dried activating composition.

9. A method according to claim 8 wherein between about 1% and 20% of the required amount of said phosphate of sodium compound is added during the low temperature mixing treatment and the remainder of said required amount is added during the higher temperature aging treatment.

10. A method according to claim 9 wherein said phosphate of sodium compound is disodium phosphate.

11. A method according to claim 8 wherein the phosphate of sodium compound is a mixture of disodium phosphate and a phosphate of sodium selected from the group consisting of monosodium phosphate and trisodium phosphate.

12. A method of forming a dried activating composition which when dissolved in water is capable of activating metal surfaces for subsequent reaction with phosphate coating solutions which comprises mixing a titanium-containing compound and sodium tripolyphosphate in an aqueous medium to form a slurry, drying the slurry to produce a dried activating composition, the proportion of said titanium-containing compound and said sodium tripolyphosphate used to form said slurry being selected to produce at least 0.005% titanium based on the combined weight of said titanium-containing compound and said sodium tripolyphosphate in said dried activating composition.

13. A dried activating composition capable of activating metal surfaces for subsequent reaction with phosphate coating solutions which comprises a titanium-containing compound and sodium tripolyphosphate in an amount sufficient to yield at least 0.005% titanium based on the combined weight of said titanium-containing compound and sodium tripolyphosphate.

14. A pretreatment solution for activating metal surfaces for subsequent reaction with phosphate coatings comprising an aqueous solution of titanium-containing compound and sodium tripolyphosphate, said solution containing between about 0.0004%–0.05% titanium ion and from about 0.01% to 2% of said sodium tripolyphosphate.

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