United States Patent Office 3,007,817
Patented Nov. 7, 1961

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3,007,817

COLD CLEANING AND COLD PHOSPHATE COATING PROCESS

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No Drawing. Filed Nov. 29, 1957, Ser. No. 699,469
7 Claims. (Cl. 148—6.15)

The present invention relates to a process of phosphate coating which enables the surface preparation of the metal and the phosphate coating steps to be accomplished at temperatures below about 100° F.

In preparing metallic surfaces for the reception of a phosphate coating, one or more cleaning operations are normally employed and these cleaning operations may comprise the use of molten alkali cleaners, vapor degreasers, aqueous acidic pickling solutions, aqueous alkaline cleaners, etc. In order to insure satisfactory cleaning in a short time such cleaners have usually been used under raised temperature conditions, that is at temperatures above about 140° F. and extending to the boiling point of the particular solution involved. Maintaining such cleaners at elevated conditions involves considerable expense and it has long been recognized that it would be desirable to precondition and clean metallic surfaces under lower temperatures. However, conventional cleaning compositions applied by conventional methods of application have not been found to be satisfactory when operated at such lower temperatures.

It is therefore the primary object of this invention to provide an improved method for preconditioning a metal surface and applying to that preconditioned surface a fine-grained adherent phosphate coating and in which both the preconditioning and coating steps are accomplished at temperatures below about 100° F.

A further object of this invention is to provide a cold cleaning composition which functions both to clean the metallic surface and precondition that surface so that it is in a condition to receive a fine-grained adherent phosphate coating, which phosphate coating is characterized by fine grain size, good adherence and is particularly useful as a base for paint, as a lubrication aid in deformation operations, as a coating in wear-resistant applications, etc.

A still further object of this invention is to provide a cold cleaning and cold phosphate coating process which is adapted to operate on a continuous line basis at speeds which are conventional in high production operations such as those encountered in automobile parts and hard goods manufacturing lines, etc.

Broadly stated, the method of this invention comprises the steps of forcefully spraying an aqueous alkaline cleaning solution on the surface to be cleaned and thereafter contacting that cleaned surface with an aqueous acidic phosphate coating solution where the temperature of both the cleaning and coating solution is below about 100° F. As used in this specification and in the appended claims, the expression "cold cleaning" is intended to mean the cleaning of a metallic surface with an aqueous alkaline cleaning solution having a temperature between about 60° F. and 100° F. The expression "cold phosphate coating" as used in this specification and in the appended claims, is intended to mean the application to a metallic surface of an aqueous acidic phosphate coating solution having a temperature between about 50° F. and 110° F.

In accordance with this invention it has been found that high quality cleaning and surface preconditioning results are obtained on the surfaces of iron, steel, zinc, alulminum, copper, etc. by the forceful impingement of

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an aqueous alkaline cleaning solution on the surface to be cleaned, that forceful impingement being in the form of a spray. Aqueous alkaline cleaning solutions are well-known, and the use of soaps and synthetic surface-active agents in such cleaning solutions has often been proposed. The removal of fingerprints, grease, dirt, oil and drawing lubricants from such surfaces by immersing or contacting the soiled surface with a conventional aqueous alkaline cleaning composition containing any of a wide variety of compatible surface-active agents is unsatisfactory, and such cleaning methods fail to produce uniform cleaning so that subsequently applied phasphate coatings are defective in containing uncoated portions, spots and the like. It was further found that when such aqueous alkaline cleaning solutions were modified with a variety of high detergency surface-active agents and applied by spraying that the solutions produced excessive quantities of foam. The problem of foaming is serious in the method of this invention because of the requirement that the cleaning solution be forcefully applied to the surface in order to obtain satisfactory cleaning results and only a limited number of surface-active agents have been found to be both compatible with the other ingredients in the cleaning solution and capable of continuous operation without over-foaming when forcefully applied.

The basic aqueous alkaline cleaning solution is not particularly critical in so far as the ingredients which can be employed in its formulation are concerned. Any of the alkali metal ortho phosphates and borates can be used satisfactorily, the sodium ortho phosphates and sodium borates being particularly desirable because of their availability and low cost. As a combination cleaner and pre-conditioner for fine-grained zinc phosphate coatings, the polyphosphates should be avoided. For example it is undesirable to replace the ortho phosphates with polyphosphates, metaphosphates, or pyrophosphates as illustrated specifically by tetrasodium pyrophosphate, sodium tetrameta phosphate, etc. The important aspects of the alkaline cleaning solution, per se, are its alkalinity and the type and amount of surface active agent incorporated therein.

The aqueous alkaline cleaning solution functions satisfactorily when the total alkalinity is in the range of about 2 to about 36 points, and the free alkalinity is in the range of about 1.0 to about 18 points when the ratio of free alkalinity to total alkalinity is in the range of about 0.05 to about 0.5, and preferably in the range of about 0.25 to about 0.5. The term "point," as used in this specification and in the appended claims refers to the number of ml. of N/10 sulfuric acid which is required to titrate a 10 ml. sample of the aqueous solution to a phenolphthalein endpoint to thus determine the points of free alkalinity, and to a brom-cresol green end-point to thus determine the points of total alkalinity.

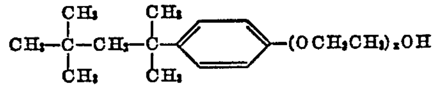
The alkyl-aryl polyether alcohols containing not more than eight oxyethylene groups have been found to be particularly effective in the above described aqueous alkaline cleaning compositions, as discussed in detail hereinafter.

In accordance with the method of this invention, the surface of the metal to be pre-conditioned for receiving a zinc phosphate coating is forcefully sprayed with a solution of the above described type, the solution having a temperature between about 60° F. and about 100° F., preferably between about 70° F. and 95° F., for a time of contact between the surface and the cleaning solution in the range of about ½ to about 1½ minutes. The pressure with which the cleaning solution is applied and the distance of the spray nozzle from the surface being cleaned is important to the attainment of uniformly good cleaning results, from piece to piece and batch to batch, particularly where the surfaces are covered with varying quantities of oil, grease, drawing lubricants and the like. In order to obtain such uniform results, the cleaning solution should be forcefully applied to the work as a spray. As used in this specification and in the appended claims, the expression "forcefully sprayed (ing)" is intended to mean that the sprayed solution has a velocity at the moment of impact with the surface being sprayed equivalent to that which is obtained from spraying water through a V-nozzle under a pressure of between about 15 p.s.i. and 50 p.s.i. gauge, when the nozzle is about 12 inches to about 30 inches from the surface being sprayed, and the orifice in the nozzle is about $^{11}/_{64}$ of an inch in diameter.

In some cases the degree of grain refinement in the subsequently applied zinc phosphate coating is enhanced by the modification of the alkaline cleaning solution to include a small amount of the titanium ion when added in the form specified below. The concentration of the titanium ion in the operating cleaning solution should be in the range of about 0.0004% to about 0.05% weight/volume. The preferred form of the titanium material for incorporation in the cleaning solutions of this invention is the titanium-containing compound produced by the method of United States Patent 2,874,081, issued February 17, 1959, since this material has been found to give the best over-all results. It is also feasible to apply this titanium-containing aqueous phosphate solution as a separate treatment step or as a modification of the water rinse step following the foreceful spray cleaning step by either spray or immersion application and for this purpose other conventional titanium-containing compositions may also be employed, such as, for example, the composition and method of U.S. Patent No. 2,310,239. In this latter case the treating solution would be an aqueous solution containing 0.1% to 2% disodium phosphate and 0.005% to 0.05% titanium ions therein.

The titanium-containing material, according to United States Patent 2,874,081, is typically prepared by admixing disodium ortho-phosphate or sodium tripolyphosphate and titanyl sulfate for about 10–60 minutes to form an aqueous slurry having a pH in the range of 5.7 to 7.8 at a temperature not exceeding 75° F., with the quantity of titanium sulfate being selected so as to produce a titanium concentration in the dried final product between about 1% and about 4%. The slurry is then aged at a temperature of 160° F.–190° F. for about 30 minutes or more and after this aging treatment is dried to a powder. This dried powder can be added as such to the cleaning composition of this invention either in its concentrated or dilute form to produce the above given concentrations of titanium in the operating solutions. A typical composition, so formed, that is satisfactorily added is a slurry containing 3.2 grams titanyl sulfate, 16 grams sodium tripolyphosphate and 60 ml. water.

The alkyl-aryl polyether alcohol surface-active agents which have been found to be unusually satisfactory are prepared by reacting t-octylphenol with ethylene oxide to produce octylphenoxy ethanols having controlled numbers of polyoxyethylene groups. These materials have the general formula:



where x equals 5–8. The best over-all results, that is, best cleaning and preconditioning for receiving the finest grain, most adherent phosphate coatings have been obtained from the use of octylphenoxy-ethanols containing an average of 7–8 ($—OCH_2CH_2—$) groups. When the $—OCH_2CH_2—$ group content exceeds 8, excessive foaming is encountered on forceful spraying.

A concentrated make-up material suitable for use in making up the aqueous cleaning solutions of this invention may contain the following ingredients in the range of relative proportions shown:

MAKE-UP MATERIAL

	Parts by weight
Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	15–30
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	25–40
Sodium nitrite	0–12
Octylphenoxy ethanol (5–8 $—OCH_2CH_2—$	1–5
groups)	1–5
Pine oil	0–25

As shown, sodium nitrite and pine oil are not necessary ingredients, but their inclusion is preferred. When titanium is desired, the above make-up material may include 0.28–0.6 part of titanium added in the form above described. Operating or spray solutions may be made by using 0.1 oz. to 10 ozs. per gallon of water of the above make-up material, thus producing operating solutions having the following composition:

OPERATING SOLUTION

	Percent weight/volume
Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	0.01–4
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	0.02–5.35
Sodium nitrite	0–1.7
Octylphenoxy ethanol (5–8 $—OCH_2CH_2—$ groups)	.007–0.83
Pine oil	0–2.84

For surfaces having the usual soil on the surface to be removed, that is, fingerprints, oil, grease and drawing lubricants from conventional sheet steel or zinc processing operations, from about 1 ounce to about 1½ ounces/gallon is satisfactory.

After the surface has been cleaned, as above described, and rinsed, it is ready to receive a phosphate coating. The phosphate coating solution is preferably an aqueous acidic zinc phosphate solution of the type which is formed from zinc dihydrogen phosphate or its chemical equivalent, and which operates at a pH range between about 1.5 and 3.5. Such solutions may be conventional in all respects except that they should contain an oxidizing agent which is capable of accelerating the rate of metal attack so that a uniform phosphate coating can be obtained in a relatively short period of time, for example, about one to about two minutes. Nitrite is the preferred accelerating agent for use in these zinc dihydrogen phosphate solutions when they are applied after the above cleaning step. In certain applications it is satisfactory to employ other oxidizing agents such as bromates, sulfites and nitro-organic compounds including m-nitrobenzene sulfonate and picric acid, particularly where low coating weights are satisfactory. The use of oxidizing agents other than nitrite may even be employed where heavier coating weights are desired by including in the solution a small proportion of an acetic amino acid such as sodium ethylene diamine tetra-acetate. The phosphate coating solutions may satisfactorily have a total acid of about 10–50 points and contain about 0.5% to 2.5% PO_4, sufficient zinc to form the dihydrogen phosphate, .002%–.15% nitrite, or .03%–0.5% bromate, or .02%–.15% sulfite, or .03%–0.5% sodium meta nitrobenzene sulfonate, or .01%–.3% picric acid or nitrate in combination with one of these agents, particularly nitrite. Where sodium ethylene diamine tetra-acetate is used it should be present in an amount of at least about 0.01%. These solutions are preferably applied by spraying, but may be applied in other conventional ways, at temperatures between about 70° F. and about 110° F. The application of the cleaning solution and the phosphate coating solution at temperatures which approximate room temperature conditions saves all of the applied heat which is normally used in phosphate coating similar surfaces in each of the steps, and this saving is obviously an important commercial advantage. So far as is known, the method of this invention represents the first time in this art that it has been considered feasible to obtain cold clean and cold phosphate coat metallic surfaces on a production line basis.

After the phosphate coating has been formed on the metal surface, additional resistance to corrosion is obtained by rinsing the coating in a conventional dilute aqueous chromic acid solution, e.g., an aqueous solution containing about 2 to about 4 ounces of CrO_3 per 100 gallons of water.

The examples given below set forth typical compositions and typical operating conditions for utilizing the method of this invention and these examples are to be understood to be merely illustrative only and not to represent the defining limits of this invention.

Example I

A plurality of aqueous alkaline cleaners were prepared containing specific quantities of ingredients within the small range of variation shown, in percent by weight:

	Percent
Sodium nitrite	10–11
Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)	20–22
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	30–32
Octyl phenoxyethanol (Triton X–114)[1]	2.5–4.5
Sodium bicarbonate	31–33.5
Pine oil	1.4–1.6

[1] Octyl phenoxyethanol having an average polyoxyethylene chain length of 7–8 —OCH_2CH_2 groups.

Specific aqueous operating baths were made by using 1 to 1½ ounces of the above materials per gallon of water. These solutions were sprayed on mild steel automobile body parts at a temperature of about 90° F. from 11/64" diameter V nozzles located 12"–14" from the parts at a line pressure of 20 p.s.i. so that the contact time between the solution and the surface being preconditioned was between 1 to 1½ minutes. These solutions were used as the preconditioner and cleaning solution for commercial scale quantities of parts prior to the phosphate coating of those parts with a variety of phosphate coating solutions. One phosphate coating solution which was used for treating such preconditioned parts contained in percent by weight: 0.18% NO_3, 0.22% zinc, 0.66% PO_4, 0.007% nitrite, 0.047% sodium, balance water. This solution had a total acidity of about 10 points and a free acidity of 0.3–0.9.

Another phosphate coating solution used after preconditioning with the above solution contained 0.18% NO_3, 0.23% Zn, 0.59% PO_4, 0.03% Ni, 0.018% sodium and 0.007% NO_2, balance water. This solution had a total acidity of about 9.5–12.5 points and a free acid of 0.3–1.0 points. Both of these phosphate solutions were spray applied, at a temperature of 100° F.–110° F., and an inspection of the coatings obtained showed that the surfaces were uniformly coated with a fine grain, adherent, typically appearing zinc phosphate coating.

Other zinc phosphate solution formulations that are satisfactory for use after the cold preconditioning step of this invention are set forth in Examples II and III.

Example II

	Percent (weight/volume)
Zinc	0.46
PO_4	1.04
NO_3	1.43
Ca	0.38
NO_2	0.005
F.A.	4.8
T.A.	26.4

Example III

Zinc	0.18
PO_4	0.68
NO_3	2.30
Calcium	0.51
NO_2	0.003
F.A.	1.8
T.A.	16.0

Example IV

A commercial installation was provided with the cold cleaner composition set forth above in Example I and used for spraying mild steel automobile body parts including bumper guards, body trim and the like under the same conditions of application with respect to temperature of the solution, nozzle type and location and line pressure as set forth in Example I. The cleaned parts after water rinse were then spray coated with an aqueous acidic zinc phosphate solution containing 0.26% zinc, 0.78% PO_4, 1.07% NO_3, balance water. An analysis of this solution showed that it had a free acid of 0.3 point and a total acid of 11.5 points. The phosphate solution was maintained at a temperature between 100° F. and 110° F. and was sprayed on the cleaned part surfaces so that the contact time of the solution and the surface was an average of about 1¼ minutes. An inspection of the parts emerging from the phosphate coating step showed that the surfaces were uniformly coated with a fine grained, medium gray color, adherent phosphate coating. By periodically replenishing the zinc, the phosphate and the nitrate portions of the coating bath and continuously adding a dilute aqueous solution of sodium nitrite to maintain the concentration of NO_2 in the bath between about 0.005% and 0.01%, approximately two and one-fourth million square feet of work was processed and the quality of the coating was relatively uniform, fine grained and satisfactory throughout the run.

Example V

The cold cleaner composition of Example I was reformulated except that the octylphenoxy ethanol containing an average of 7–8 oxyethylene groups was replaced with an octylphenoxy ethanol, in the same relative proportions, having an average of 5 oxyethylene groups. Another cleaning solution was prepared similar in every respect to the composition of Example I except that an octylphenoxy ethanol having an average of 3 oxyethylene groups was employed in the same concentration as that used for the same ingredient in Example I. A still further composition was prepared in all respects similar to the composition of Example I except that the octylphenoxy ethanol contained an average of 9–10 oxyethylene groups. Each of these cleaners was operated in the same manner described in Example I, and satisfactory cleaning and surface conditioning was obtained with the octylphenoxy ethanols containing an average of 5 oxyethylene groups, whereas the operation of the solution containing an average of 3 oxyethylene groups was unsatisfactory and the operation of the solution containing an average of 9–10 oxyethylene groups in the octyl phenoxy ethanol was found to produce an excessive quantity of foam so that re-circulation of the cleaner was ineffectual and operation on a continuous basis was unsatisfactory.

What is claimed is:

1. A method for cold cleaning and cold coating metallic surfaces which comprises the steps of forcefully spraying against said surface an aqueous alkaline solution consisting essentially of water, hydrated ortho phosphates and borates and having a total alkalinity between about 2 and about 36 points and a ratio of free alkalinity to total alkalinity in the range of about 0.05 to 0.5 and about 0.007% to about 0.83% of an octyl phenoxyethanol having 5-8 oxyethylene groups, and thereafter contacting said surface with an aqueous acidic zinc phosphate coating solution and maintaining said surface in contact with said phosphate solution until a phosphate coating is formed thereon, said cleaning solution having a temperature between about 60° F. and 100° F. and said phosphate coating solution having a temperature between about 50° F. and 110° F.

2. A method in accordance with claim 1 wherein said octyl phenoxyethanol contains 7–8 oxyethylene groups.

3. A method in accordance with claim 1 wherein said aqueous alkaline cleaning solution consists essentially of the solution resulting from incorporating 1/10 oz. to 10 ozs./gallon of water of a material consisting of, in parts by weight, up to 12 parts sodium nitrite, 15–30 parts trisodium phosphate, 25–40 parts borax, and 1–5 parts octyl phenoxyethanol having an average of 5–8 oxyethylene groups.

4. A method in accordance with claim 3 wherein said zinc phosphate coating solution contains the nitrite ion as an accelerator.

5. An aqueous cold cleaning solution for metallic surfaces comprising an aqueous alkaline solution consisting essentially of water, hydrated ortho phosphates and borates and having a total alkalinity in the range of about 2 to about 36 points and a ratio of free alkalinity to total alkalinity in the range of about 0.05 to about 0.5 and having incorporated therein about 0.007% to about 0.83% octyl phenoxyethanol having 5–8 —O—CH_2CH_2— groups.

6. A concentrated make-up material for a cold alkaline cleaner for metals consisting of, in parts by weight, 15–30 parts trisodium phosphate, 25–40 parts borax, up to 12 parts sodium nitrite, 1–5 parts octyl phenoxyethanol having 5-8 oxyethylene groups and up to 25 parts pine oil.

7. A concentrated make-up material for a cold alkaline cleaner for metals consisting of, in parts by weight, 15–30 parts trisodium phosphate, 25–40 parts borax, up to 12 parts sodium nitrite, and 1–5 parts octyl phenoxyethanol having 5–8 oxyethylene groups.

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