MIL-HDBK-205A
15 JULY 1985
SUPERSEDING
MIL-HDBK-205
11 JUNE 1957

MILITARY HANDBOOK

PHOSPHATE AND BLACK OXIDE COATING
OF
FERROUS METALS

DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

No deliverable data required by this document.

AREA MFFP

DEPARTMENT OF DEFENSE
WASHINGTON, DC 20301

Phosphate and Black Oxide Coating
of Ferrous Metals

MIL-HDBK-205A

1. This Military Handbook is approved for use by all Departments and Agencies of the Department of Defense.

2. Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Director, Army Materials and Mechanics Research Center, ATTN: AMXMR-SMS, Watertown, Massachusetts 02172-0001, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

FOREWORD

This handbook provides a working knowledge of phosphate and black oxide coatings of ferrous metals as used by the Department of Defense for equipment and ordnance. It is not intended to be an exhaustive treatise on the subject, but rather to furnish detailed information on phosphate and black oxide coatings that have proved satisfactory in service. It is intended to supplement, but not replace, various specifications and standards covering these coatings.

A survey of military users of phosphate and black oxide coatings was conducted. Consequently, the information contained in this handbook describes processing procedures, chemical control methods, cleaning operations and equipment used by the military.

GENERAL REFERENCES

Federal and Military specifications and standards are government publications and are available from the Naval Publication and Forms Center, 5801 Tabor Avenue, Philadelphia, PA 19120.

Aerospace Material Specifications are available from the Society of Automotive Engineers, Inc., 400 Commonwealth Drive, Warrendale, PA 15096.

ASTM specifications and standards may be obtained from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

List of Figures

1. INTRODUCTION

1.1 General. Protective coatings composed of insoluble phosphate crystals or iron oxides are applied to ferrous metal parts by a number of component processes in which varying types of chemical solutions are used. (The iron oxide coatings are commonly known as black oxide coatings.) The following three stages are normally used to apply the coatings. These are:

Cleaning and pretreatment
Coating
Preservation Treatment

The objective of the coating process is to provide an economical base for subsequent treatment which will protect parts from corrosion resulting from abrasion or exposure to moisture and perspiration.

The zinc or manganese phosphate coatings are formed on the parts by dipping the iron or steel parts in a solution of zinc or manganese dihydrogen phosphate containing an oxidizing agent such as nitrate. The pH of the solution ranges from 2.0 to 2.5. As iron is dissolved from the part by the acidic solution, the pH of the solution adjacent to the part increases until the insoluble phosphate coating is deposited on the part. In the spray operation the reactions are similar and occur at the interface between the solution and the surface of the parts being treated.

The insoluble phosphates involved in the phosphate processes are of three types. An insoluble phosphate consisting of zinc, manganese or iron monohydrogen phosphate is precipitated at a pH of about 4. This material is found in the sludge in the bottom of the tanks and in the scale on heating surfaces and tank walls. The monohydrogen phosphate salts are soluble in an excess of phosphoric acid and serve as a buffer to prevent the accumulation of excess phosphoric acid in the processing bath. The phosphate coatings, normal phosphate salts, are formed at a PH of approximately 5.8 and are not easily dissolved in phosphoric acid even when exposed to an excess of that acid.

The zinc base phosphate coatings consist primarily of two crystals [$Zn_2Fe(PO_4)_2{:}4H_2O$ and $Zn_3(PO_4)_2{:}4H_2O$]. The proportions of the two crystals vary depending upon many factors. These factors include: The composition of the phosphating bath, the temperature of the phosphating bath, and the surface preparation which determines the number of sites on which the crystals form.

The manganese base phosphate coatings have not been as well characterized as the zinc base phosphate coatings but it is believed that the crystal composition is similar.

Water of Crystallization will be lost when the phosphate coating is exposed to elevated temperatures. This loss results in a non-adherent powdery coating and a subsequent decrease in corrosion resistance. Exposure of no more than 15 minutes to temperatures in air of 225°F (107°C) will not adversely affect a zinc phosphate coating Corresponding temperature for manganese phosphate coatings is 375°F (190°C). Exposure at these temperatures for longer times or for shorter times at higher temperatures will cause a decrease in corrosion resistance.

The black oxide coatings are formed by immersing the iron or steel parts in a solution where the iron or steel surface is converted to an oxide, generally believed to be Fe_3O_4. The bath for Class 1 treatments is a concentrated solution of sodium hydroxide and sodium nitrate. The bath for class 3 treatments is a molten dichromate salt, usually potassium dichromate. The bath for class 4 treatments is a concentrated solution of sodium hydroxide and proprietary sulfur compounds which form an oxide-sulfide coating.

The phosphate coatings are intended to provide supplementary resistance by holding a corrosion resistant finish such as an oil in the voids of the crystalline coating. Recent work has demonstrated that the phosphate coating itself provides some temporary corrosion resistance independent of the oil.

To obtain coatings (phosphate or black oxide) with the maximum corrosion resistance, it is necessary to remove all foreign matter from the part and process the part in a properly controlled chemical bath. On parts to be phosphated the surface must be conditioned to ensure that the crystalline coating has the desired structure. The preferred system is to remove all grease and oil, clean with abrasive blasting and process in a properly controlled bath.

Phosphate coatings meeting TT-C-490 are commonly suggested as the base for a paint specified by the procuring agency. The presence of the phosphate coating under the paint film aids in preventing underfilm corrosion and increases the durability of the paint film.

The black oxide coatings are commonly finished with a corrosion resistant oil. Both phosphate and black oxide coatings are used on a variety of military parts. Some examples of applications are listed in the Appendix.

Any of these protective coatings will be ineffective if their continuity is broken by surface defects that serve as points of entry for corrosive substances. Such imperfections are unavoidable unless the metal surface is completely free of dust, grit, oil, acid and alkaline residues, rust, and other contaminants before the protective coating is applied.

1.2 Cleaning. Thorough cleaning of the metal surface is of prime importance in the application of any of the coatings described in this handbook. With few exceptions, the methods followed for the removal of specific contaminants are similar in all systems. Thus, the cleaning methods described in this handbook apply to all the protective coatings described.

1.3 Conditioning. Some cleaning methods which are used to remove certain types of soil will cause the formation of coarse crystalline phosphate coatings which give inferior corrosion resistance. The use of these cleaners is required to remove the soil. The use of a grain refinement treatmemt chemical will change the surface and will result in a corrosion resistant crystalline structure. The material commonly used for this purpose ahead of zinc phosphate treatments is sodium monohydrogen phosphate containing titanium phosphate. The material commonly used prior to manganese phosphate treatments is a manganese phosphate. In order for these chemicals to have the desired affect on the coating formation, they are specially treated during manufacture. Conditioning salts increase the number of sites at which the phosphate coating is formed, thus producing a fine uniform coating rather than a coarse crystalline coating.

1.4 Phosphate coatings.

1.4.1 Manganese base phosphate coating, DOD-P-16232, type M. This phosphate protective coating, which ranges in color from gray to black depending upon the alloy being treated with high carbon alloys being darker, is used on iron and steel. The manganese base phosphate coating, although more resistant to heat than the zinc base phosphate coating, decomposes between 375°F (190°C) and 425°F (216°C). The coating may be applied to all clean ferrous metal parts with the exception of springs having a wire diameter less than one-eighth inch (3mm) and barrel bores, Patent No. 4194929, "Technique for Passivating Stainless Steel", describes a procedure for phosphating stainless steel. This phosphate coating is commonly used with a petroleum base, supplementary finish on articles or sections of articles not receiving paint. If the phosphate coated item is to be painted, no petroleum or wax based finish should be used prior to the application of the paint, as the petroleum or wax will interfere with the adhesion of the paint to the part. Manganese phosphate coatings are also used to improve the wear resistance of sliding surfaces which are under heavy load such as gear teeth. These coatings should not be used on roller or ball bearings.

1.4.2 Zinc base phosphate coating, DOD-P-16232, type Z. This phosphate protective coating, which ranges in color from gray to black depending upon the alloy, is used on iron and steel. It is suitable for application to parts where contact with alkaline materials or exposure to temperature in excess of 225°F (105°C) is not expected. The maintenance of the equipment is easier with the zinc based phosphate than with the manganese based phosphate. Also, zinc phosphate coatings normally provide greater corrosion resistance than manganese phosphate coatings, with or without supplemental coatings.

1.4.3 Phosphate coating for paint base, TT-C-490, type I. This coating process consists of a chemical treatment which produces a uniform, adherent, crystalline, phosphate coating on iron and steel surfaces. The color of the coating ranges from gray to black depending upon the alloy. The coating inhibits corrosion, retards the progress of filiform and underfilm corrosion, increases adhesion, and results in greater durability of applied paint finishes. The surface to be treated must be clean and free of rust, scale, dirt, paint or similar contaminant. The coatings used for TT-C-490, Type I normally are much lower in coating weight than those meeting DOD-P-16232.

1.5 Black Oxide Coatings.

1.5.1 Applications. These coatings are particularly suited for use on moving parts (sliding or bearing surfaces) which cannot tolerate the dimensional build-up of the more rust-resistant coatings. They are not recommended for weapons going into long-term storage because of their poor corrosion resistance.

1.5.2 Alkaline oxidizing process (for wrought iron, plain carbon, and low alloy steels), MIL-C-13924 class 1. This coating is applied by immersing the clean ferrous metal parts in an aqueous alkaline oxidizing bath at temperatures in the range of 285° to 290°F (140° to 143°C). The parts are then rinsed in water, dipped in a chromate rinse solution and dried. This coating is applicable to plain carbon steel, most low alloy steels cast and malleable irons.

1.5.3 Fused salt oxidizing process (for corrosion resistant steel alloys which are heated to 900°F (428°C) or higher MIL-C-13924, Class 3. This coating is applied by immersing the clean parts in molten dichromate salts at temperatures ranging from 825°F (440°C) to 850°F (455°C). Tempering can be done in conjunction with the blackening at temperatures up to 900°F (482°C) and is applicable to chromium stainless steels with draw temperatures above 900°F (482°C).

1.5.4 Alkaline oxidizing process (for 300 series corrosion resistant alloys), MIL-C-13924, Class 4. This coating is applied by immersing the clean parts in the aqueous alkaline oxidizing bath at temperatures in the 250° to 260°F (121° to 127°C) range.

2. CLEANING

2.1 Cleaning methods.

2.1.1 General. Surface preparation is one of the most important factors affecting the performance of the protective coating. The selection of an appropriate cleaning method for ferrous metals depends on three important factors:

The type and quantity of the grease, oil, and other soil
The equipment available, and
The residual effect of the cleaner on the coating produced
CAUTION: Protection from solvent splashing and projected particles is required. Goggles are the minimum protection and must be worn. Also, face shields, rubber aprons, rubber gloves, rubber boots, etc., must be used if needed.

Secondary, but very practical considerations include cost, quantities of parts involved, etc.

In general, there are three types of surface contaminants which must be removed to obtain adhesion of the protective coating. They are:

Grease, oil, drawing compounds, and dust from rolling, forming, extruding, machining, handling, etc.
Rust and mill scale, and
Salts or other chemicals which may or may not be visible but which serve as nuclei for rust formation.

No single cleaning process removes all of the surface contaminants encountered. Therefore, proper selection as well as the order of application of any combination of cleaning processes must be made. The best way to understand how a cleaning method or methods is selected is through knowledge of the properties and limitations of the various cleaning materials available commercially. Therefore, in this chapter the various mechanical and chemical surface cleaning methods and equipment presently in use will be outlined. It should be noted that abrasive blasting is recommended (and for some items required) as a final cleaning process prior to heavy phosphate coating (DOD-P-16232).

2.1.2 Solvent cleaning. Before adopting any solvent cleaning procedure, an investigation of the hazards involved and the regulations issued by the EPA and/or OSHA pertaining to the use of the solvents being considered should be completed.

Solvent cleaning is one of the oldest methods used for the removal of soil from a metal surface. The solvents employed cover a wide class of chemicals including mineral spirits, chlorinated hydrocarbons, etc. All solvents are potentially hazardous and should be used under such conditions that their concentration in the air being breathed by the workmen is within safe limits. Benzene, gasoline, and carbon tetrachloride should be avoided because of their toxicity or flammability. Solvents readily remove oils and greases, are easily applied, and the necessary equipment occupies a minimum of space. Unfortunately there are some serious disadvantages inherent in solvent cleaning which impose limitations on its use. These disadvantages include:

> Both solvent and applicator are soon contaminated and therefore instead of removing oil completely, only redistribute it.
>
> Solvent cleaning is expensive if carried out properly. Effective solvents have a high initial cost, distillation for re-use is expensive, and losses may be expected.
>
> Only oils and greases are removed. No rust or scale is removed. Rust stimulators, soaps, and salts may not be removed by some solvents in which case they must be removed or neutralized by other means.
>
> The fumes from some of the best solvents are toxic or represent long or short term health hazards in many instances. This includes most chlorinated solvents and aromatics.
>
> Some chlorinated solvents are decomposed by heat in contact with water and metal, forming hydrochloric acid which attacks the equipment and stimulates corrosion of clean parts.

The methods generally used in solvent cleaning are outlined in paragraphs 2.1.2.1 and 2.1.2.2.

2.1.2.1 Dipping. In dipping operations, parts are immersed in either cold or warm solvent. Usually two or more tanks are used for preliminary cleaning with the remainder used for rinsing. When the solvent in the first tank becomes contaminated, it should be discarded. The next tank should then be used for the preliminary cleaning and the clean solvent used for the final rinse.

2.1.2.2 Vapor degreasing. Cleaning materials by vapor degreasing consists of removing oils and greases from the part by suspending it in the vapor of chlorinated solvents. The vapors condense on the relatively cold metal surface and the condensate dissolves and rinses off the grease and other soils soluble in the solvent.

Equipment for vapor degreasing is specially engineered by the equipment manufacturers for proper heat input to control the solvent liquid and vapors. Machines are built with one or more compartments as required by the process. For continuous production, units are conveyorized and normally enclosed. Equipment for this type of cleaning is described briefly in section 2.2.2 and must be designed and assembled to enable the user to comply with all EPA and OSHA regulations. Vapor degreasing equipment is available meeting OSHA and EPA requirements.

2.1.3 Alkali cleaning. Alkali cleaning is usually more efficient, cheaper, and less hazardous than solvent cleaning. Alkaline cleaner chemicals, which are formulated to perform a variety of cleaning and pretreatment functions, are soluble in water and used at elevated temperatures. These formulations clean by saponifying certain oils and greases while their surface active additive components wash away other types of contaminants. Soil removal is accomplished through detergency or saponification, rather than solvency. Soil is removed mainly by displacement from the surface rather than by direct solution, as in solvent cleaning. One of the desirable characteristics of an alkaline cleaner is its ability to maintain reasonably high alkalinity despite the introduction of acidic soils or consumption of the alkali in the saponification of oils. Since no single alkaline salt has all the necessary properties (i.e., high pH, buffering action, rinsability, wetting and emulsifying action, detergent properties, etc.), blended alkaline cleaners are almost exclusively used today. These blends will differ depending on the cleaning problem of any given material, the kind of soil to be removed, and the equipment available.

Temperature is an important consideration in the application of any alkaline cleaner. Heat enhances the activity of the cleaner and improves the effectiveness of the alkaline cleaner components. Soaps formed by saponification of fatty acids are soluble in water and are readily removed by rinsing with water. Alkalies are less effective than solvents for removing heavy or carbonized oils, rust inhibitive oils, etc. Alkaline cleaners can be formulated to remove rust by immersion or electrolytic methods. (See MIL-C-14460.) Removal of heavy rust will require electrolytic action. The methods used in alkaline cleaning are outlined in paragraphs 2.1.3.1 to 2.1.3.3.

2.1.3.1 Dipping. In dipping operations, the contaminated parts are immersed in hot alkaline solutions contained in tanks. The use of two tanks is recommended. Some mechanical agitation is desirable to increase the effectiveness of this method of alkaline cleaning. One simple method of supplying this agitation is to maintain the cleaner at a rolling boil. Alkaline cleaners in a dip process are usually used at concentrations of 4 to 10 ounces per gallon (30 to 75 grams per liter), and at temperatures ranging from 180°F (82°C) to a rolling boil. Tanks should be equipped with an overflow weir so that oil and other floating contamination can be skimmed or overflowed periodically. See section 2.1.8.3 concerning disposal of the skimmings from the alkaline cleaner solutions.

2.1.3.2 Pressure spraying. In the spray process the contaminated parts are sprayed with the alkaline cleaning solution, usually in a mechanical system. The alkaline cleaning solution is pumped from a heated reservoir and applied to the metal under pressure through an array of nozzles. Alkaline spray cleaners are generally formulated with low foaming surface active agents to eliminate excessive foaming. Alkali concentrations used in power spraying are, in general, considerably lower than those used in other methods. One-quarter to 2 ounces per gallon (2 to 15 grams per liter) is the usual concentration range recommended. Recommended temperatures range from 160°F to 180°F (70° to 80°C), and cleaning time ranges from 30 to 75 seconds.

2.1.3.3 Electrolytic cleaning. Electrolytic cleaning is seldom used ahead of phosphate treatments due to the tendency for this type of cleaning to condition the metal surface such that non-uniform coatings are produced (phosphate coatings consisting of large crystals separated by uncoated areas). When electrolytic cleaning is used ahead of phosphate treatments, it is necessary to follow it with conditioning treatments as described in Section 3 which ensure the formation of the desired coating crystal structure. Electrolytic alkaline cleaning generates large quantities of gas close to the soil and is, consequently, very effective in providing a high level of mechanical agitation. The gas can be generated at the anode or cathode depending on the system employed. While a greater volume of gas is evolved at the cathode, there is a tendency to deposit small quantities of impurities. The trend has recently developed to combine cathodic and anodic cycles although straight anodic cleaning has been effectively used. High conductivity is important so electrolytic cleaners usually contain caustic soda. The electrolytic cleaners are used at higher concentrations than other alkaline cleaning methods. Recommended concentrations range from 6 to 14 ounces per gallon (45 to 105 grams per liter) and temperatures range from 180°F (82°C) to a rolling boil. In this method of cleaning, a reasonable amount of foam is desirable to hold down the mist that is generated by electrolysis.

2.1.4 Emulsion cleaning. Emulsion cleaning methods are designed to bring a soil into contact with both an organic solvent and water solution of surface active agents, so that the water and solvent soluble soils may be dissolved, and the soils dispersed in a water medium prior to being flushed away by a water rinse. In general, these cleaners leave a thin residue of an oily nature. When a protective coating is to be applied to the parts, this film must be removed by an additional cleaning operation. In other instances, it is desirable to have this light film of oily material to provide some rust protection during in-plant storage.

Because of the nature of the emulsions, there are no convenient methods for the control of the concentration of these cleaners other than performance checks.

While these cleaners are more effective in spray equipment, they have been used in dipping tanks. In dipping installations, the emulsion cleaners show some effectiveness at dilutions close to 1 to 10, and at temperatures of 160° to 200°F (71° to 93°C). In spray cleaning, the tank may be 140° to 180°F (60° to 83°C). Above these temperatures, solvent evaporation becomes a problem. A hot water rinse is recommended following emulsion cleaning.

In emulsion cleaners the solvent is present in the form of very fine droplets dispersed in the water solution and stabilized by surface active agents. In general, the solvents used are of the hydrocarbon type so that flammability becomes a problem but in emulsion cleaning the solvent is so well dispersed in water that a moderate flash point solvent can be used at temperatures as high as 180°F (83°C) without much danger. This cleaner concentrate consists of emulsifying agents, surface active agents, organic solvents, and, in some formulations, water. These formulations emulsify when mixed with water. Emulsion cleaners are used at concentrations ranging from 1 part of concentrate to 10 to 200 parts of water.

2.1.5 Steam cleaning. Steam cleaning is quite often used to remove soil when the parts to be cleaned do not lend themselves to soak or spray cleaning and the improved quality of cleaning over hand cleaning is desired. In steam cleaning, steam or hot water under pressure, along with detergents, is directed against the work to be cleaned through a hose fitted with an appropriate nozzle. The detergent used can be caustic enough to remove all oil paint as well as dirt, grease, smudge, soot, etc. The surface to be cleaned should be wetted to allow the cleaning compound to loosen foreign matter which is later removed by a cleaning pass. In applying the cleaning compound, the speed of spraying should be comparable to that used for spray painting. Several rapid passes are better than one very slow pass. Since large amounts of steam and chemicals are consumed in this type of cleaning, the cost may be several times that of immersion or spray cleaning.

CAUTION: The operators of steam cleaning equipment must wear protective clothing as well as face and eye protection to avoid burns from the steam, the hot equipment, and/or the caustic solutions.

2.1.6 Phosphoric Acid Cleaning.

2.1.6.1 Brush cleaning. The wash-off type material is commonly applied by hand using brushes or sponges when; production is small or infrequent, the area to be treated is large, and the most economical and practical application is by hand.

The use of the brush-on method requires cleaning of the metal before using the phosphoric acid if a heavy coating of grease or drawing compounds are present. For mild rust, a concentration of 1 volume of acid cleaner to 1 or 2 volumes of water should be used. Experience will indicate the most effective concentration to use. The diluted cleaner is applied with a brush or sponge and the surface thoroughly scrubbed. More than one application may be necessary. Before the cleaning solution dries, it is rinsed with clean water in a tank or with running water from a hose.

CAUTION: For safety reasons, the operators must use face shields, rubber gloves, rubber aprons, and rubber boots when using these materials. Care must be taken to protect adjacent equipment.

2.1.6.2 Spray application. The nonfoaming type solutions are applied by spraying a solution of the chemical on the parts. The operating solution is prepared by diluting the concentrate with water. The normal dilution is 1 volume of concentrate to 3 volumes of water. However, experience may indicate that greater or smaller dilutions should be used. The solution is applied at temperatures of about 150°F (65°C). This type of application is normally use in a spray tunnel in which the parts are transferred from stage to stage by a conveyor. These stages consist of a spray alkali cleaning, a water rinse, a phosphoric acid pickle, another water rinse, a conditioning compound treatment (Section III), a zinc phosphate treatment, another water rinse followed by a chromate rinse. After the chromate rinse the part is dried. It should be noted that some of these stages are omitted at times.

2.1.6.3 Immersion cleaning. Immersion tank type solutions are recommended for parts with medium to large production which can be conveniently treated in immersion tanks. The recommended dilution is three volumes of water per each volume of the concentrate. However, experience may indicate that greater or less dilution is preferred.

CAUTION: For safety reasons, the operators must wear face shields, rubber gloves, and rubber boots when using these chemicals.

2.1.7 Acid pickling. Acid cleaning is not recommended as a method of cleaning if any other method will remove the soils. When metal dissolves in acid, atomic hydrogen is released and a portion of this is absorbed or dissolved in the metal. Any resulting embrittlement of the metal, known as hydrogen embrittlement, can result in breakage of steel under stress unless the hydrogen is removed. Hydrogen removal is usually accomplished with heat. The temperature and times required to remove the hydrogen absorbed during pickling may also destroy the corrosion resistance of the phosphate coatings. For this reason, pickling should never be employed before a phosphating operation which is used to meet DOD-P-16232 without permission of the procuring agency. The higher temperatures used in the black oxide treatments will normally drive off the absorbed hydrogen from most hydrochloric acid pickles. This acid is frequently used prior to black oxide treatments to remove all traces of corrosion.

Special provisions shall be required to handle embrittlement when treating steel parts with an ultimate tensile strength of 200,000 psi (1379 MPa) or above. See 5.1.5.

In acid pickling, metals are immersed in acid solutions for the purpose of removing oxides and/or scale. The various acids used in commercial pickling are sulfuric, hydrochloric (muriatic), nitric, phosphoric, and mixtures of these acids. Sulfuric acid, because of its low cost, high boiling point, availability, and general suitability, is used widely in the pickling of mild and low carbon steels. Pickling is usually carried out by immersing the work in suitable pickle baths. However, the same factors apply if the pickling solution is sprayed or flowed over the work or if the work is pulled through baths of acid as in the continuous pickling of strip steel. Acids suitable for pickling not only remove scale from the base metal but also attack and pit it. When this occurs, metal and acid are wasted, and more smut develops which must be removed before subsequent coating treatment. To prevent the formation of smut, inhibitors, such as dibutylthiourea or proprietary materials are frequently recommended. When inhibitors are used, care must be taken to prevent the inhibitor from being carried into the coating treatment bath (phosphate or black oxide). Careful control of the amount of metal removed by controlling the acid concentration, time in the acid, and the temperature, is preferred as the means of avoiding excess pickling of the parts but when some areas are heavily rusted or scaled and other areas are not, the use of an inhibitor may be necessary.

Before pickling, oils, grease, and surface contaminants should be removed by solvent or alkali cleaning. After pickling, the work should be thoroughly rinsed. Then the metal should be treated to give a surface suitable for the treatments which are to follow.

When acid pickling is used, provision for safe handling of these hazardous materials must be provided. Workmen must wear eye protection, face shields, acid resistant clothing, gloves, and boots. Provision for the removal of the fumes released must be provided. Copies of the applicable EPA and OSHA regulations should be obtained and provision made to comply with them.

The rate at which acid solution approaches saturation with iron varies depending upon production conditions. Eventually it becomes necessary to discard the spent pickle solution. Local regulations vary as to the treatment required. Provision must be made to comply with these regulations.

2.1.8 Abrasive blasting. Blast cleaning consists of cutting, chipping, or abrading the surface through the high velocity impact of abrasive particles against the surface. Ordinarily, no other cleaning is necessary on pieces that have been blast cleaned. Rust, mill scale, and old paint, are removed. On parts which are contaminated with grease or oil, degreasing is required before blast cleaning.

There are three methods that can be used to accelerate and discharge the abrasive from the equipment:

Discharging the abrasive in a stream of high pressure gas such as air,

Discharging the abrasive in a stream of high pressure liquid such as water,

Discharging the abrasive centrifugally from the periphery of a rotating paddle wheel traveling at a high peripheral speed.

In blast cleaning operations, the impact velocity of the abrasive against the metal should correspond to its most effective abrasion level which depends upon the particle size, shape, hardness and its breakdown rate. The key to obtaining economical blast cleaning rates lies in the proper selection and use of the abrasive. The abrasive used may be metallic, siliceous (containing free silica), or nonmetallic synthetic (containing no free silica). When aluminum oxide abrasives are used, care must be taken to remove all abrasives and abrasive dusts from the parts before they are immersed in the phosphate solution. The aluminum can dissolve in the phosphate bath and inhibit the coating formation. Abrasives may be any one of three shapes (shot, grit, or semishape abrasive) or may consist of a mixture of shapes.

Some of the important factors which help to determine the abrasives to be used are:

Type of metal to be cleaned
Shape of the part
Kind of material to be removed
Loss of abrasive
Breakdown rate of the abrasive
Cost of reclaiming the abrasive
Hazards associated with use of the abrasive

CAUTION: Any abrasive cleaning system should be designed to protect the workers from the dust. This is particularly important if silica containing abrasives are used.

All mill scale, rust, rust scale, paint or any other foreign matter should be removed and the surface appear as a grayish metallic white, very uniform in color and slightly roughened. Abrasive blasting is required as the final cleaning before heavy coatings (DOD-P-16232) are applied.

2.1.8.1 Nozzle blast cleaning. Nozzle blast cleaning utilizes a fluid medium to transport the abrasive. The fluid medium may be air or water. Three types of nozzle blast cleaning units are in general use.

2.1.8.1.1 Direct pressure type. A compartment or tank is held under constant pressure during the blasting operation. Abrasive is fed under pressure from the bottom outlet where the blasting stream of air meets the abrasive and carries it to the blast nozzle. This system offers many advantages over the gravity feed and suction feed units.

2.1.8.1.2 Suction Feed Type. The abrasive is drawn to the blast gun through an induction chamber. In the induction chamber the abrasive is fed to the blast gun by a small jet of compressed air. The expanded air and abrasive are passed through a large nozzle and directed at the work. This system is seldom employed in large applications.

2.1.8.1.3 Gravity Feed Type. The feed flows from a hopper at an elevation above the blast gun through the induction chamber behind the larger nozzle of the suction blast gun similar to the one described in 2.1.9.1.2.

2.1.8.2 Wheel Blast Cleaning. Lowest costs are achieved by use of a wheel blast cleaning system. The many advantages of wheel blast cleaning over air or nozzle blast cleaning are sufficiently great to warrant the installation of extensive wheel blast machines where feasible. One of the big advantages of using wheel blast cleaning equipment is the elimination of air compressors and pipelines and attendant labor. Other advantages are in the compactness and self-sufficiency of the unit as well as the ease of starting, the simplicity of the power supply, etc. The principle disadvantages of this type of equipment are the high initial cost, the high maintenance cost and shut down time for repair and maintenance. Where the equipment is used a high percentage of the time, it will furnish low cost cleaning.

Two types of wheels are used, the batter type and the slide type. In the batter type, the abrasive is propelled by impact when it comes in contact with the edge of the vanes. In the commonly used slide type, the abrasive is charged through the hub of the wheel and slides on the vanes to the edge of the wheel where it is projected at high velocity towards the work. The type of abrasive used with the wheel blast cleaning equipment is usually metallic.

2.1.8.3 Disposal of spent cleaning media. Consideration must be given to the proper disposal of spent cleaning media and the soil removed when selecting a cleaning method. Most cleaning procedures suspend the soils removed in the cleaning media and it is necessary to discard the mixture periodically in order to continue to remove soil. Selection of the disposal method will depend upon the local waste disposal regulations, the cleaning method used, and the soils being removed. Discussion of the disposal procedures and instructions is outside the scope of this handbook.

2.2 *Cleaning Equipment*

2.2.1 General. Only the major equipment required for each method of cleaning is outlined in this section. Further information concerning such equipment or any accessories needed may be obtained from current literature or from manufacturers. The necessity to comply with EPA and OSHA regulations and to allow for treatment of the spent cleaning media for proper disposal should be considered in the design and layout of any equipment.

2.2.2 Solvent Cleaning Equipment. Two or more solvent tanks are necessary for immersion solvent cleaning. For vapor degreasing, equipment which is specially engineered for proper heat input and control of solvent liquid and vapor is required. Machines are built with one to three or occasionally more compartments. Figure 1 illustrates a conventional degreaser with one compartment. For all solvent cleaning, equipment for reclaiming or recycling the solvent is needed, otherwise this method of cleaning is prohibitively expensive.

2.2.3 Alkali Cleaning Equipment. For immersion cleaning, tanks for the solution and equipment for heating the solution are required. Tanks equipped with electrodes or tumbling barrels with electrodes (very effective for small parts where electrolytic and mechanical action are combined) and accessories are required for electrolytic cleaning.

There are two general methods of applying cleaning solutions by spray. The most widely used method requires two banks of nozzles mounted on opposite sides of a conveyor. The nozzles may be mounted in vertical banks and directed at the work being conveyed between them with the solution returning to the heated reservoir. A variation of this system has the banks of nozzles mounted horizontally above and below a belt type conveyor. The second method is described in section 2.2.5 and, in this case, only one nozzle is used and the cleaner is not reused.

2.2.4 Emulsion Cleaning Equipment. Emulsion type cleaners are used by both immersion and by spray. The equipment used is similar to that used in alkali cleaning (Section 2.2.3).

2.2.5 Steam Cleaning Equipment. Equipment for steam cleaning usually consists of a small flash type boiler, a motor driven pump, and a water supply. The unit is normally mounted on wheels so that it can be easily moved to the part to be cleaned. Various types of nozzles are available depending on the type of cleaning problem.

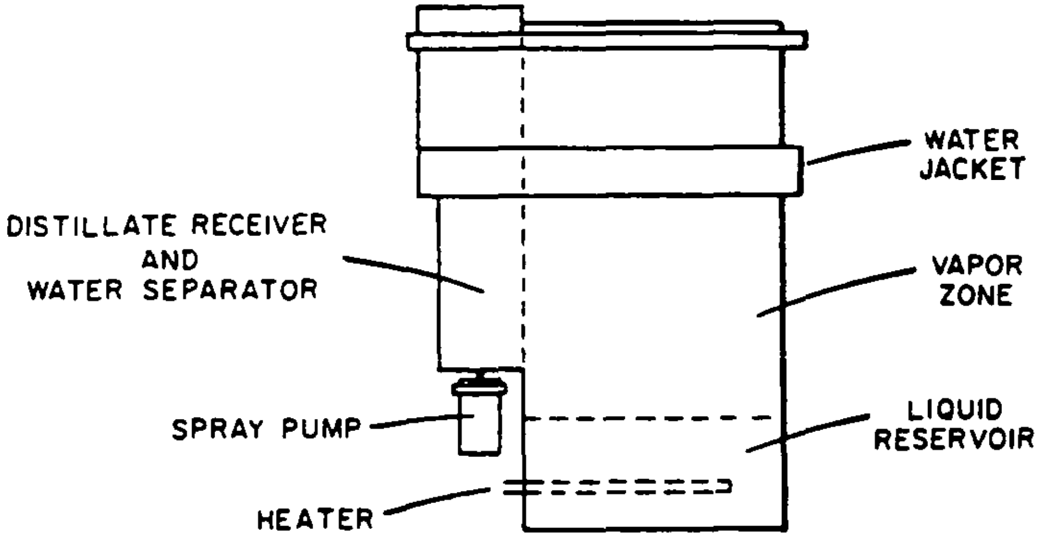


FIGURE 1: VAPOR DEGREASER

2.2.6 Acid-pickling Equipment. The materials of construction for the pickle tank, the rinse tank, and the heat exchanger must be resistant to the acid and temperature used.

2.2.7 Abrasive Blasting Equipment

2.2.7.1 Direct Pressure Type Equipment. In general, the equipment for direct pressure blast cleaning consists of a tank in which the abrasive is stored under pressure. The pressure on the abrasive forces it from the bottom of the tank into a mixing chamber. In the mixing chamber a stream of air picks up the abrasive and carries it to the nozzle. The design of direct pressure blast cleaning equipment is a specialized field. The services of manufacturers should be drawn upon for installation of this type of equipment. Their advice is particularly valuable in selecting abrasive lines, hoses, mixing chambers, valves, nozzles and reclamation, separation and ventilation equipment.

2.2.7.2 Suction Feed Type Equipment. The construction and design of suction feed type equipment is very simple. Operation of the equipment is based on a vacuum created by compressed air passing through a small jet. The vacuum draws the abrasive into an induction chamber where it is picked up by air from a larger nozzle. The mixture of air and abrasive is directed against the work through the blast gun.

2.2.7.3 Gravity Feed Type Equipment. Gravity feed equipment relies upon the flow of abrasive from a hopper to the nozzle by gravity alone. The conventional suction feed type equipment may be used for gravity feed abrasive blasting by raising the abrasive supply to a level above the gun. A feed control may be necessary to prevent blocking of the feed line because of the excessive amount of abrasive.

2.2.7.4 Wet Blast Cleaning Equipment. For some types of wet blast cleaning, special equipment must be used. For other types, standard dry blast units can be employed. Specially designed wet blast equipment is generally suitable for dry blasting. On the other hand, standard dry blasting equipment is usually not suitable for wet blasting.

2.2.7.5 Wheel Blast Equipment. The equipment for this type of cleaning consists of an abrasive feeding mechanism, a vaned wheel which supplies the final velocity of the abrasive, the drive assembly, and the wheel housing. Directional control of the stream is secured by varying the point at which the abrasive is fed to the vanes. Figure 2 illustrates an abrasive throwing wheel.

3. CONDITIONING PRIOR TO PHOSPHATE COATING

3.1 General. The phosphate coatings consist of many small crystals which are formed on and adhere firmly to the metal surface. Each crystal grows from a single point (a cathode) on the metal surface and continues to grow until it contacts a neighboring crystal. If there are few cathodes on the surface, few crystals will be formed. Thus, large crystals are formed which are easily broken and much of the surface is uncoated. If many cathodic sites are present when the parts are introduced into the phosphating bath many small crystals are formed. The coatings formed under these conditions are less easily broken (more resistant to abrasion). There is less uncoated surface, therefore, better corrosion resistance results.

3.2 Cleaning systems which leave many cathodic sites on the metal surface. Solvent cleaning, (with the exception of vapor degreasing), emulsion cleaning and abrasive blasting all appear to leave many cathodic sites on the surface. The phosphate coatings produced following these cleaning procedures consist of small dense crystals and are capable of meeting the required tests.

3.3 Cleaning systems which leave few cathodic sites on the metal surface. Strong caustic cleaners, electrolytic alkaline cleaners, pickles, and vapor degreasing appear to leave few cathodic sites on the metal surface. Phosphate coatings produced on these surfaces tend to be "sparse" in that there are uncoated areas between large crystals. These coatings frequently are not capable of meeting the required tests.

3.3.1 The use of conditioning agents. The surfaces referred to in Section 3.3 can be modified to produce the desired fine grain coatings by rubbing the surface with a damp rag or by the use of proprietary "conditioning" agents. A titanium-disodium phosphate complex (U.S. Patent 2,310,239-Jernstedt) is effective with zinc phosphate processes and can be obtained from many of the suppliers of phosphate coating chemicals. A proprietary chemical which produces a similar affect when used before manganese phosphate coating chemicals is also available.

4. PHOSPHATE COATINGS

4.1 Introduction

4.1.1 Characteristics. Phosphate coatings consist of crystalline, non-reflective, water insoluble metal phosphates which are very adherent to the base metal. The manganese and zinc phosphate coatings of DOD-P-16232 are impregnated with a rust-inhibiting oil, a solvent cut-back preservative, or other specified finish. The Type I phosphate coating of TT-C-490 is not oiled, since this coating is used as a base for paint.

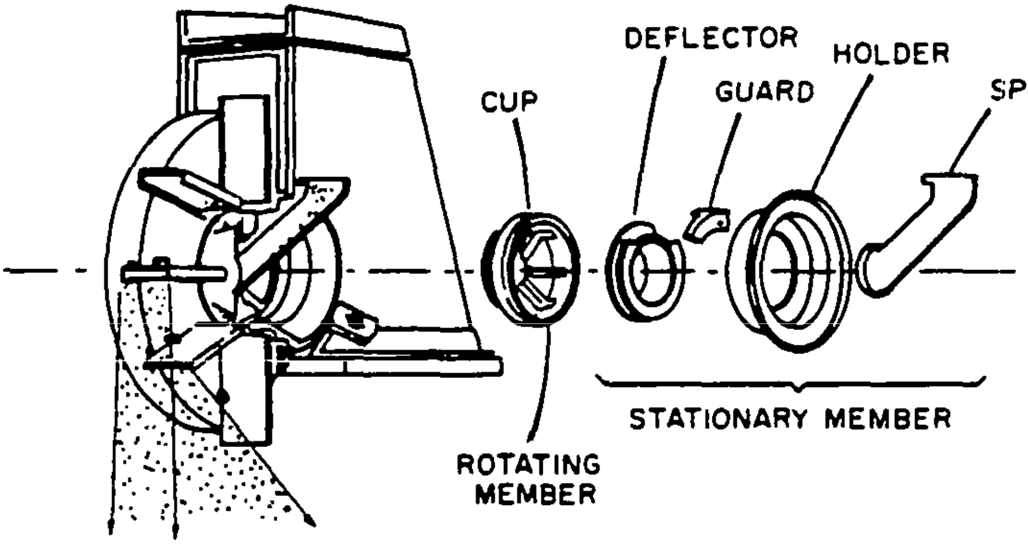


FIGURE 2: ABRASIVE THROWING WHEEL

The manganese based phosphate coatings are more resistant than the zinc based phosphate coatings to high temperatures but should not be exposed for long times to temperatures above 350°F (175°C). Zinc based phosphate coatings should not be exposed for long times to temperatures above 200°F (95°C). The maintenance of the heat exchangers is much easier with zinc based phosphate processes than with the manganese based phosphate processes.

The coatings meeting DOD-P-16232 are particularly effective in resisting corrosion between mating metal surfaces, such as encountered in fasteners and metallic belt links. These coatings reduce the tendency for parts to "freeze". Neither of these coatings is recommended for alkaline environments.

The color of the phosphate coatings ranges from gray to black depending upon the alloy and the dimensional buildup varies from 0.0001 to 0.0005 inch (0.0025 to 0.0125 millimeters). When the parts require close fit for proper functioning, no allowance should be made for this buildup as the crystals are easily broken and the parts quickly return to their original uncoated dimensions.

WARNING: When working with phosphating solutions and salts, goggles, face shields, impervous rubber aprons, boots and gloves must be worn.

4.1.2 Adaptability. Phosphate coatings may be applied to all ferrous metal parts used in military material by normal processing procedure with the exceptions noted in 4.1.2.1 through 4.1.2.6 below.

4.1.2.1 Springs. Springs, primarily those having a small diameter, are apt to become brittle during the phosphating process. This applies also to leaf springs and other parts of small cross section that take spring loads. Certain assemblies that contain springs which cannot be disassembled without damaging the parts may be phosphated without disassembling.

Any springs which are phosphatized should be relieved of hydrogen embrittlement by holding them at room temperature for 120 hours or heating them for eight hours at temperatures of 210° to 220°F (100° to 104°C).

4.1.2.2 Nonferrous Metals. The phosphate coatings described in this handbook cannot be applied to brass and copper. However, nonferrous metal parts such as brass bushings, which are permanently assembled to iron or steel components, will not normally be seriously damaged during processing. A small amount of copper will be dissolved in a normal operating phosphating bath and large amounts may be dissolved if the free acid is high. The dissolved copper will cause the coatings produced to be less resistant to corrosion than they would have been in the absence of copper in the bath. Brass, bronze, or other nonferrous metal holding fixtures or baskets should not be used to hold pieces of work while in the phosphating tank.

To remove copper from the phosphate bath, process batches of degreased steel wool or clean scrap iron for approximately 5 minutes. The steel wool or scrap iron should be removed as the copper plates out on the metal.

4.1.2.3 Stainless Steel. This material cannot be successfully treated with any known phosphate treatment. However, stainless steel is "activated" by blasting the metal surface with cast iron grit or cut steel blasting abrasive. Particles of ferrous metal abrasive are embedded in the corrosion resistant steel surface, causing a passive coating to form in a conventional phosphatng or oxalating solution. This may be desirable to make the stainless steel surface non-reflective and more corrosion resistant.

4.1.2.4 Gun Barrels. The barrels of all weapons must be plugged before phosphating. For this purpose, silicone plugs, tapered wooden plugs, rubber stoppers, or straight or tapered cork stoppers may be used. New corks should be soaked for 15 minutes at 200°F (95°C) in a dilute solution of soda ash and water to remove tannic acid, which may cause discoloration of the barrel.

4.1.2.5 Gas Ports. Gas ports on automatic rifles must be plugged before phosphating.

4.1.2.6 Reprocessing Phosphated Parts. Abrasive blasting is a process for cleaning and finishing of materials by propelling an abrasive media in a dry condition or suspended in a water slurry. As a cleaning tool it has the ability to remove phosphate coatings when required and will prepare that surface for additional treatment. It is highly recommended that abrassive blasting be used for these operations.

4.1.3 Cleaning of Phosphate Coatings. After this type of finish has been applied, it should be cleaned only with hot water and a surfactant or with solvent-type cleaners such as dry-cleaning solvent, mineral spirits, or degreasing solvent.

Phosphate coatings are soluble in alkali. Therefore, caustic soda, soda ash, trisodium phosphate, and all other strong alkali materials must be avoided, since they will destroy the phosphate finish.

4.1.4 Exercise of Assembled Weapons. Refinished weapons should be operated by hand until the moving parts work smoothly without binding or undue effort.

4.2 Processing Tanks and Equipment

4.2.1 General. The cleaning and other pretreatment operations preceeding the application of the phosphate coating have been described. This section covers the tanks and equipment used after the pretreatment operations are completed and includes those required for:

Phosphating,
Water rinsing,
Chromate rinsing, and
The application of the supplementary preservative coating

4.2.2 Phosphating Tank

4.2.2.1 Materials of Construction. Since the phosphating solution will corrode mild steel, the tank should be constructed of stainless steel (types 304, 316, 321, or 347), or plastic which is resistant to both the chemicals and the temperature used in the process. If plastic is used, the material should be checked to be sure that no plasticizers are present which can leach out and inhibit the phosphating reactions. A piece of the plastic, representative in composition, can be immersed in the phosphating solution at operating concentration and temperature for 48 hours. The volume of the phosphating solution and the size of the plastic part should be close to the relative volume and area that will exist in the operating tank. Test pieces should be run in this phosphate solution after it has been cooled, mixed thoroughly with the sludge formed, and reheated to be sure that the coatings produced are satisfactory. Mild steel may be used to construct the tank but the life of the tank will probably not exceed one year.

4.2.2.2 Construction. The tank should be double-wall construction with suitable insulation installed between the walls to conserve heat (Figure 3). The tank should be provided with a cover to conserve heat. Drains are not recommended in the phosphate processing tanks due to the tendency of the sludge to interfere with closing of the valves which leads to loss of solution.

The dimensions of the tank are governed by the number and size of the parts to be processed. Provisions should be made for at least 6 inches (15 centimeters) of sludge to accumulate on the bottom without contacting the work being processed. If a perforated processing barrel (Figures 4 and 5) is to be used in the processing system, the tank should be sized to accommodate the perforated barrel and its drive system.

4.2.2.3 Tank heating. Under no circumstances should any phosphating tank be heated from the bottom. If bottom heating is used, steam pockets will form under the sludge. These pockets can erupt violently, throwing hot solution on personnel in the vicinity.

Heating with entrance and exit pipes welded into the tank walls is objectionable for two reasons. The stresses due to temperature and differential expansion of the metal can cause leaks to develop. The removal of scale and sludge from the heating surfaces can be done only after the processing solution has been removed from the tank.

Excellent results have been obtained when the temperature differential between heating surface and the operating bath does not exceed 50°F (10°C). Higher temperature differentials have adverse affects on the phosphate bath and may cause distortion of portions of the tank and/or the heater.

Mixed results have been obtained when the heat is supplied through the tank walls by means of either a jacketed tank or by attaching electric strip heaters to the outside of the tank. The electric heaters produce local areas with a high temperature differential between the tank wall and the solution. Excellent results have been obtained when the heat is supplied by a heating medium circulating in a jacket around the tank as long as the temperature differential is less than 50°F (10°C). However, poor results have been obtained with higher heat differentials.

The use of electric immersion-type heaters should be avoided as the heating surfaces are normally at high temperatures and the high heat differential is harmful to the phosphating solution.

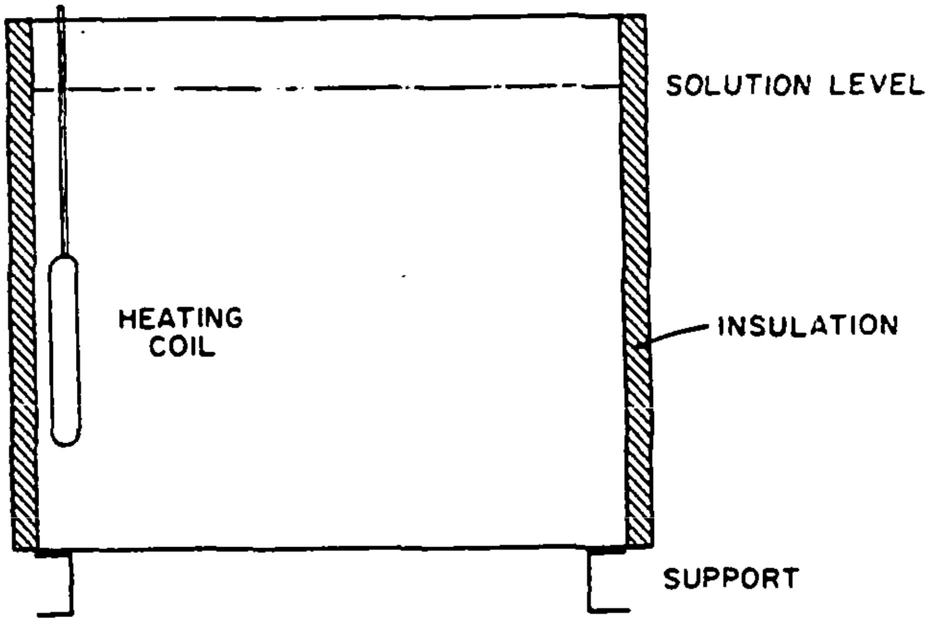


FIGURE 3 : PHOSPHATE TANK (CROSS SECTION)

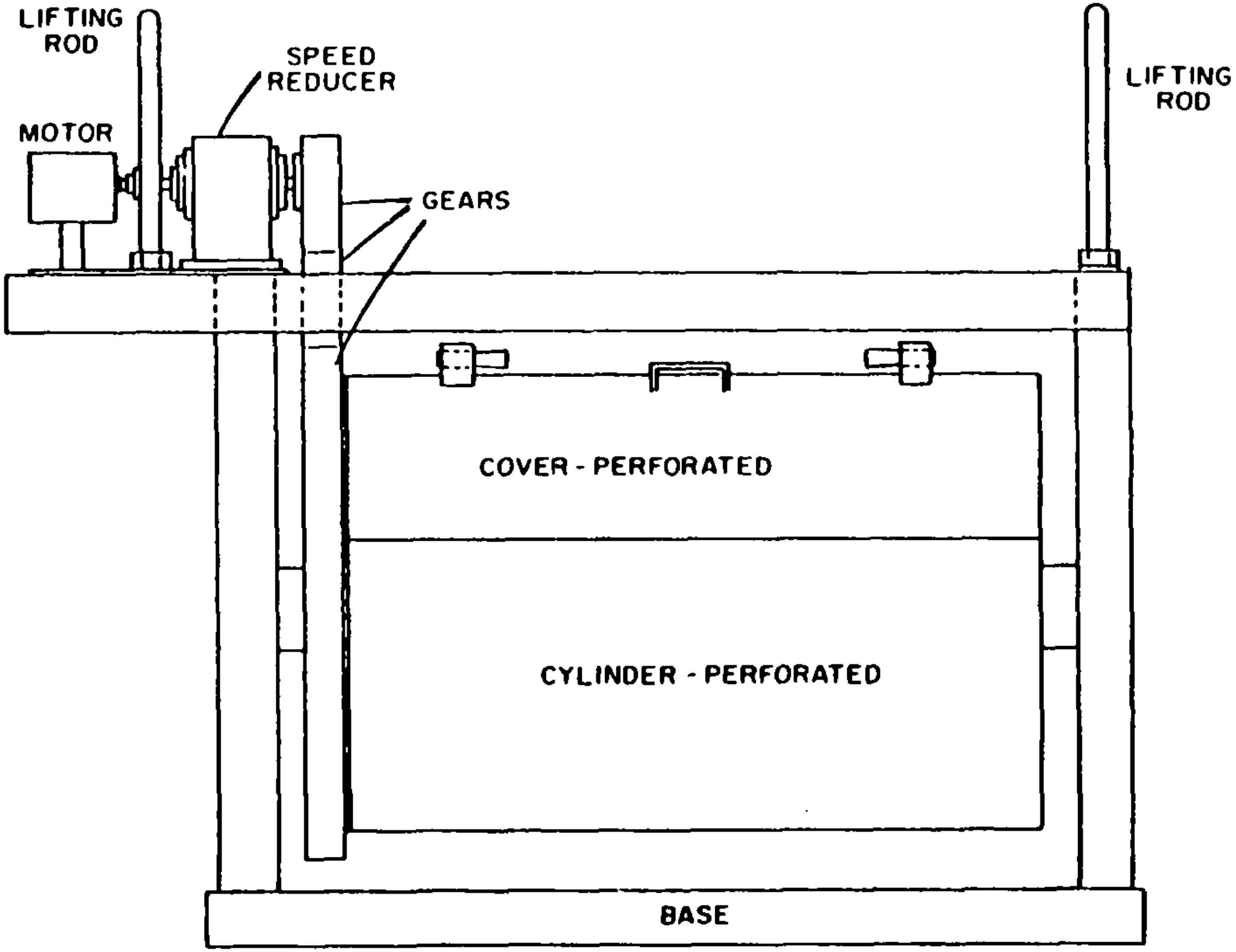


FIGURE 4: TUMBLING BARRELL (SIDE VIEW)

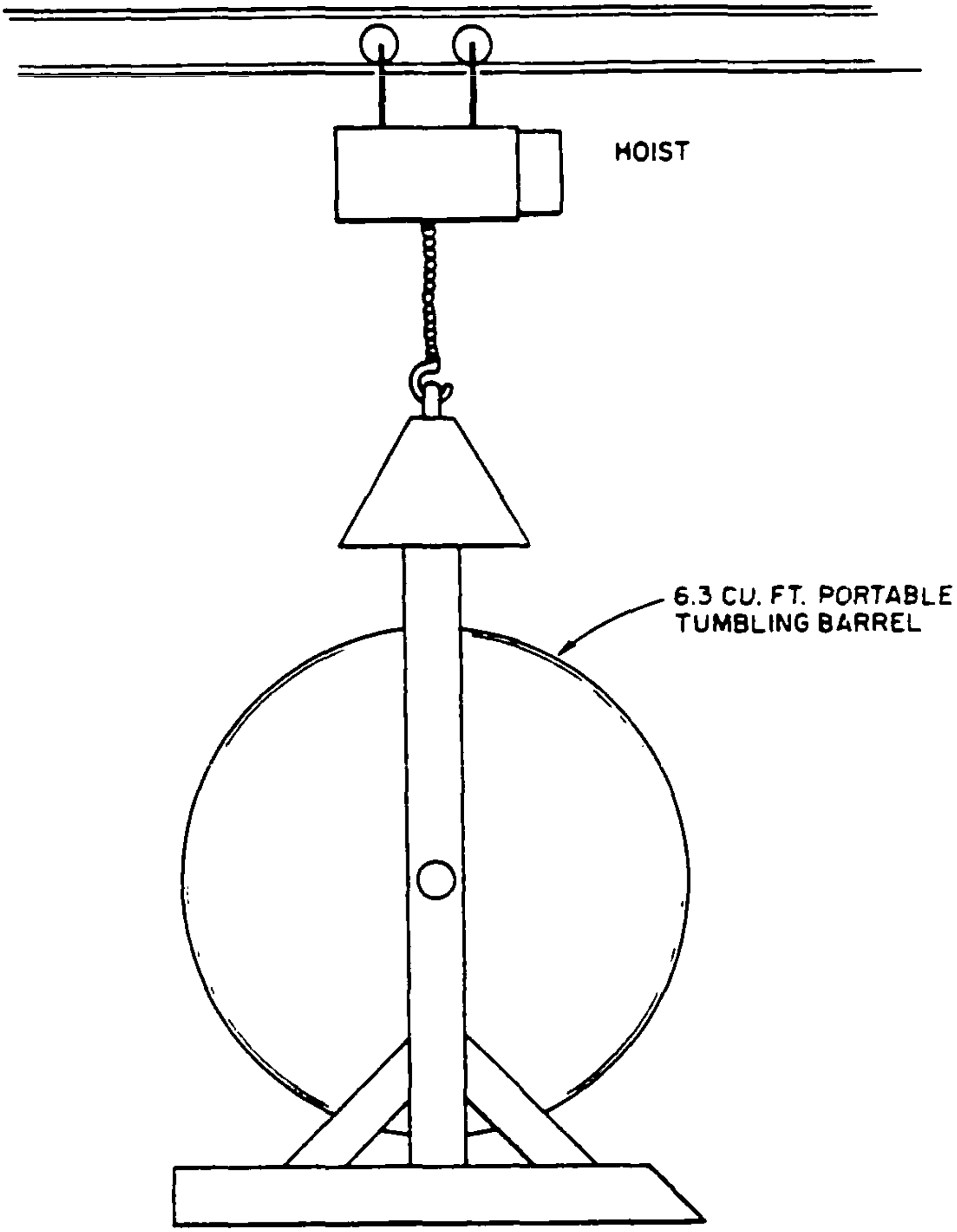


FIGURE 5 : TUMBLING BARRELL (END VIEW)

Steam at 30 psi (2.1 kg/sq cm) or less is the most desirable source of heat for a phosphating process. Downdraft gas heating units have been used successfully where steam was not available. Unfortunately, there is a high heat differential between the heating tube and the phosphate bath and adverse affects occur in the phosphate solution. In addition, the removal of scale and sludge is more difficult. Both the steam and the gas heating elements must be so installed that they can be easily removed from the tank for the removal of accumulated scale. The heating coil may be suspended on strap iron hangers hooked over the tank edge and equipped with a lifting lug to facilitate its removal from the solution. The coil should not be installed on the tank bottom nor should steam return nipples be cut through the tank wall. A steam trap should be placed in the return line at floor level to free the coil of water. At least two sets of coils should be provided for each phosphating tank to ensure continuous operation, and these should preferably be constructed of stainless steel to minimize scaling.

Effective steam heat exchangers are commercially available. These exchangers consist of steel plates welded together with passages between the plates through which the steam flows. These heat exchangers are light, easy to clean, and occupy less space than pipe coils. Heat exchangers of this type, constructed of mild steel or of stainless steel, are available. One type consists of two sheets embossed to form a tube similar to a pipe coil when the two sheets are joined. Another type is manufactured by welding the edges of the flat plates together, intermittently spot welding the two sheets, and inflating the sheets with hydraulic pressure to form "pillows" through which the steam flows. Both of these heat exchangers are light, easy to clean, and occupy less space than the pipe coils.

Immersion-type downdraft gas heating equipment can be used for heating the phosphatizing solution. The piping layout in this heating system is similar to that used for steam, but the ducts are much larger than the steam pipes. They are removable for removal of scale and sludge.

4.2.3 Processing Barrel. When the parts to be treated are small, it is frequently expensive to place them individually on racks. A common solution to this problem is to place the parts in a perforated barrel such as that shown in Figures 4 and 5. The parts are cleaned, rinsed, processed and, occasionally, finished without removal from the perforated barrel. The barrel is rotated while immersed in the cleaning and processing solutions. Rinsing is best accomplished by immersing the barrel in the rinse solution, and then removing it to allow the contaminated rinse solution to drain. This may be repeated 2 or 3 times for improved rinsing. To minimize abration of the coating during processing it is suggested that the barrel be filled completely.

The design shown in Figures 4 and 5 combines the rack to support the barrel and the mechanism to rotate the barrel in a single unit. An older design, still used in many places, uses a frame mounted in the tank. The shafts at each end of the barrel rest in bearings in the frame permitting the barrel to be rotated. A driving mechanism is mounted on the rear of the tank. The barrel is placed in the frame and the rotating mechanism engages the ratchet at the end of the barrel so the barrel can be rotated. This design requires that a frame and driving mechanism be present in each tank where the barrel is to be rotated. The speed of rotation is normally one revolution every 3-5 minutes in the phosphating baths used to produce coatings meeting DOD-P-16232.

4.2.4 Ventilating System. Steam and fumes rising from heated tanks containing corrosive liquids must be removed from the vicinity of operating personnel. The required ventilation is effectively accomplished with built-in exhaust equipment. The recommended type of exhaust system has a slot-type opening on the rear of the tanks, air is fed across the surface from the front and provision is made to scrub the fumes exhausted from the rear. The fan capacity for these units is based on 200 cubic feet of air per minute for each square foot of tank surface (18.6 cubic meters of air for each square meter of surface).

4.2.5 Cold Water Rinse Tank

4.2.5.1 Construction. The cold water rinse tank is constructed of mild steel, is provided with a bottom drain nipple, and has a weir type overflow with discharge nipple.

4.2.5.2 Location. The tank should be located as close as possible to the phosphatizing tank, thus reducing the time required to transfer the work from the phosphating solution to the rinse.

4.2.5.3 Water Supply. The water supply to the cold water rinse tank should enter the tank on the side of the tank opposite the overflow. The water should be delivered close to the bottom of the tank using a vacuum breaker or other means to prevent siphoning of water from the rinse tank into the water line. Heating coils need not be installed.

4.2.6 Chromate Rinse Tank. The chromate rinse tank is constructed of mild steel with double walls and insulated sides and ends. It has a heating coil mounted on one side of the tank and a bottom drain. A water inlet for replacement of water lost by evaporation is installed at the top of the tank. This tank should be located adjacent to the cold water rinse tank.

4.2.7 Compressed Air Outlet. It may be advisable to use compressed air to remove excess moisture from parts after the chromate rinse or to remove dust left on grit or sand blasted parts. If compressed air is to be used, an outlet should be provided near the area where the air will be used The air must be free of oil, moisture, and other contaminants. This can be accomplished by installing a moisture trap and particulate filter before the point of use.

4.2.8 Preservative Oil Tank. The tank holding the preservative oil can be constructed of mild steel. The oil being used may require specific features which would be unnecessary with other oils. When a water displacing oil is used, a bottom drain may be required to remove displaced water. Some oil in water emulsion type oils work best when recirculated continuously with the emulsion overflowing into a sump from where it is pumped back into the tank. Some oil in water emulsions are used at elevated temperatures to help dry the parts. In these cases heat must be supplied to the tank.

4.2.9 Automated Immersion Lines

4.2.9.1 General. The preceeding discussion has covered batch type operations in which the immersion of the parts to be cleaned, rinsed, or processed was controlled by an operator. In most cases he uses a hoist to handle the heavy loads but controls the treatment time and sequences. Many types of equipment are available in which the parts are transferred from operation to operation without operator dependence.

4.2.9.2 Types of Automated Equipment. There are many different designs for accomplishing the desired results. The most commonly used are of three general types.

Tumbling barrels automatically transferred from one station to the next station

Rotating or oscillating open perforated drums, automatically transferred from station to station

Horizontal rotating drum with an internal screw which advances the parts through the drum where they are immersed in the different solutions

4.2.9.2.1 Automated tumbling barrels. The tumbling barrels are basically the same as those described in Section 4.2.3. The barrel, loaded with parts, is placed on the automated system where it is transferred to the processing stages in the correct order and left in each stage for the proper time before transfer to the next stage. The results are comparable to a manually controlled system.

4.2.9.2.2 Open rotating or oscillating drums. These systems use drums which are open at the top making loading and unloading rapid and simple but the loosely loaded parts are subjected to more abrasion than when in a closed, completely filled barrel. Heavy parts with sharp edges may be severely abraded. To minimize abrasion, parts should be tumbled as little as possible when not immersed in liquid.

4.2.9.2.3 Horizontal drum with internal screw. An example of this type of unit is shown in Figures 6 and 7. Parts are fed into the rotating drum at the entrance and are moved forward as the drum rotates. The exterior shell of the drum is solid in the processing and rinse stages. Scoops on the drum pick up solution from the tank and transfer it to the drum where the parts are kept immersed for the designated time. The shell is perforated in the sections following the processing and rinse stages permitting the solution to return to the tank.

Parts are particularly subject to abrasion when being advanced by the screw in drain areas where no solution cushions the parts as they are tumbled. The weight and design of the parts contribute to the severity of the abrasion.

4.2.10 Spray Process Systems. The spray method for application of phosphate coatings may be used when applying coatings meeting TT-C-490 but never for coatings meeting DOD-P-16232. The spray method is normally used in a conveyorized system.

The construction of the equipment for this type of application is complex and expensive. It is recommended that an experienced equipment builder be consulted or contracted to build the equipment to avoid costly mistakes.

4.3 Phosphate Coating Process

4.3.1 Cleaning and Conditioning Before Phosphating. All parts must be completely free of oil, grease, rust, residues, and other contaminants before treatment with the phosphating solution. The methods used for the removal of such substances depend on the equipment and facilities available, the type of ferrous metal of which the parts are made, and their service application. See Section 2.

Each cleaning medium and each cleaning method, such as wiping, brushing, abrasive blasting, pickling, etc. have different and distinctive effects on the depth and design of the metal etching and the crystalline structure of the phosphate coating. This leads to the variations in the corrosion resistance of the phosphate coatings. Therefore, the conditioning procedures used for specific parts must be either based on experience or determined by trial. See Section 3. Several variations in the conditioning processes that can be used are illustrated in Figure 8. The conditioning procedure which includes a pickle shown in Figure 8 must not be used prior to heavy phosphate coatings (DOD-P-16232) without authorization from the purchasing facility.

The application of a phosphate finish with maximum corrosion resistant qualities depends not only on the accurate control of the phosphating solutions, but, particularly, on the cleaning and conditioning operations that precede the application of this coating. Therefore, the conditioning procedures described below must be observed if the desired results are to be obtained.

4.3.1.1 For phosphate coatings meeting the requirement of DOD-P-16232, abrasive blasting of all work is necessary to obtain the best results. Abrasive blasting provides the most satisfactory surface for receiving the phosphate coating and, if properly used, will not change the dimensions of most parts. Thin cross-sections and surface smoothness may require special consideration during processing.

4.3.1.1.1 Dust on abrasive blasted work should be removed with compressed air. It must not be removed by wiping with a cloth or by brushing.

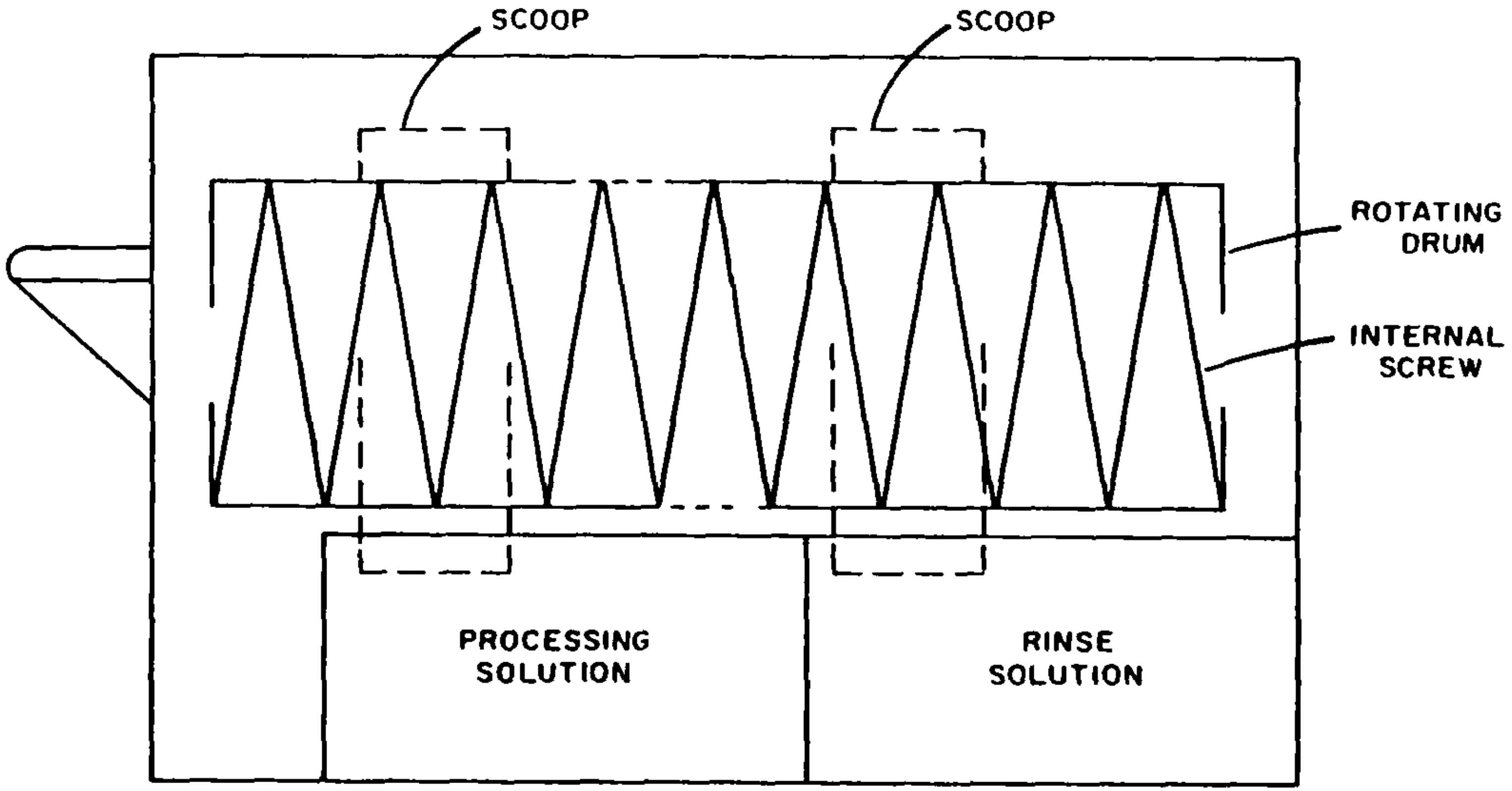


FIGURE 6: ROTATING DRUM WITH INTERNAL SCREW (SIDE VIEW)

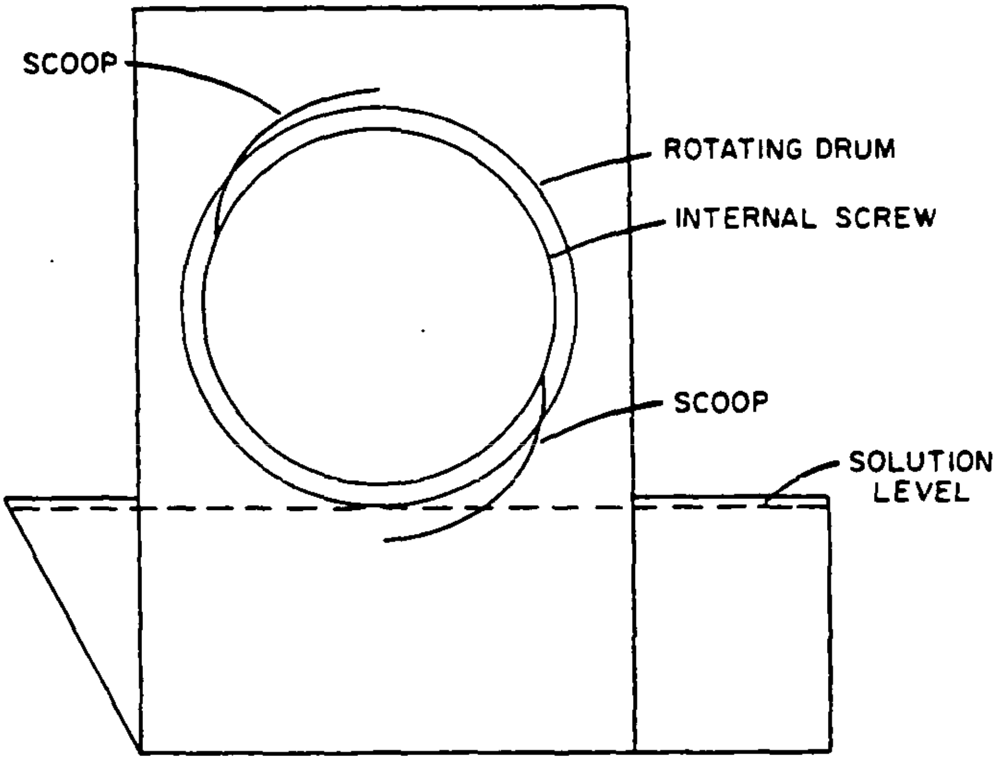


FIGURE 7 : ROTATING DRUM WITH INTERNAL SCREW (END VIEW)

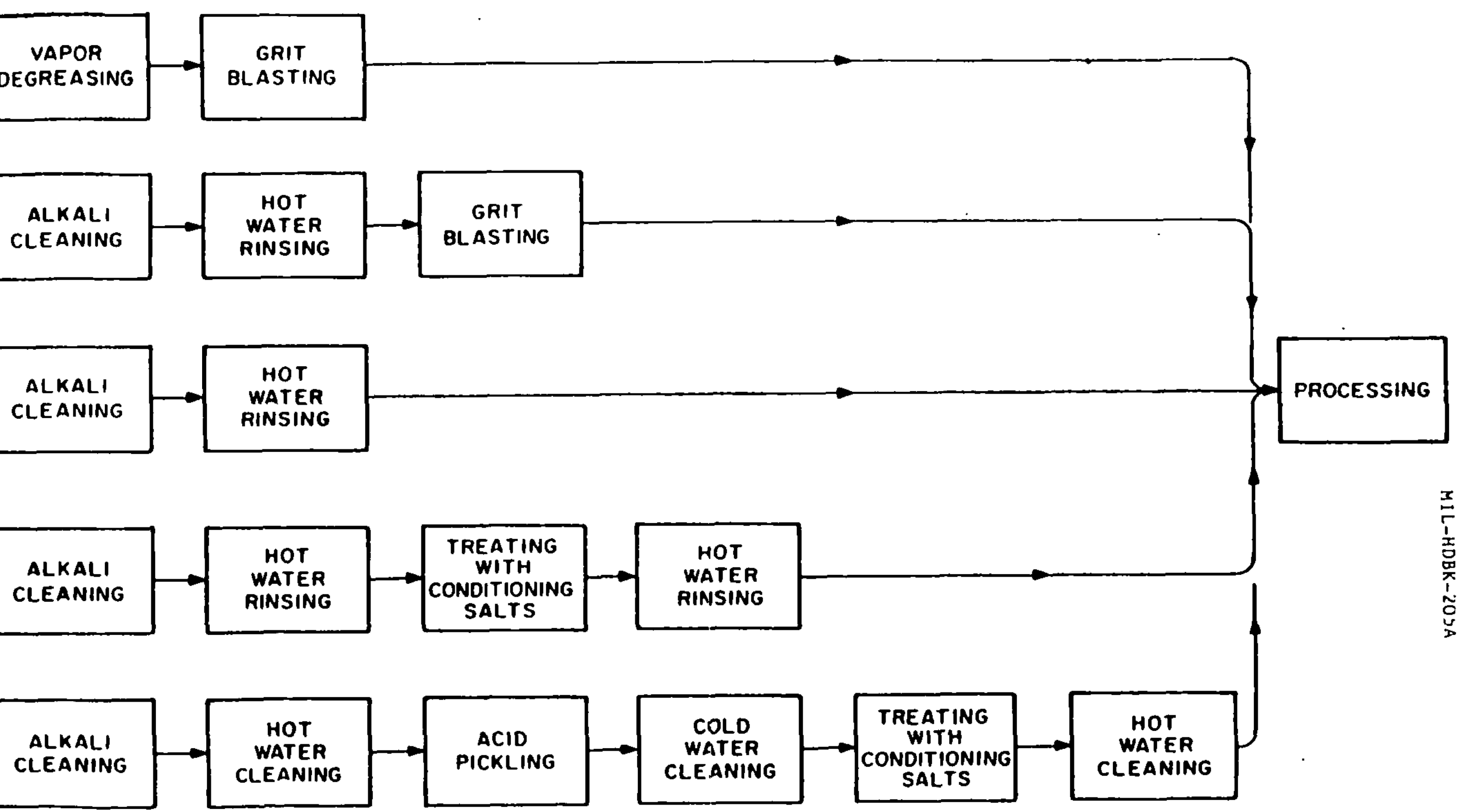


FIGURE 8 : PHOSPHATING UNIT CLEANING OPTIONS

4.3.1.1.2 Abrasive blasted work must not be touched by bare hands. Clean cotton or rubber gloves should be used when parts are turned on the blast table or placed in baskets or racks used for processing.

4.3.1.1.3 Abrasive blasted work must not be deburred or exposed in any manner to oil or any substance that will require removal by washing or rinsing before phosphating.

4.3.1.2 In most instances, oil and grease are removed from the work by vapor degreasing. However, some soaps with rust preventatives and greases contain substances that are insoluble in the solvents used. These substances are not removed by vapor degreasing. If these soils are present, other cleaning procedures have to be used. Vapor degreasing may still be included in the cleaning sequence to remove the oil and grease.

4.3.3 Processing Sequence. Cleaning materials, cleaning procedures, conditioning and cleaning equipment have been described in Sections 2 and 3. This section covers the operations that follow the cleaning and conditioning processes and includes phosphating, water rinsing, chromate rinsing, and the application of the supplementary preservative coating (Figure 9).

4.3.4 Phosphating Process

4.3.4.1 Materials. Phosphating materials may be either a manganese-base or a zinc-base phosphate chemical. The chemicals can be obtained by specifying the desired chemical meeting MIL-P-50002 or from commercial sources which supply chemicals capable of producing coatings meeting the requirements of the specification called for in the drawing.

4.3.4.2 Preparation of the Phosphating Solution

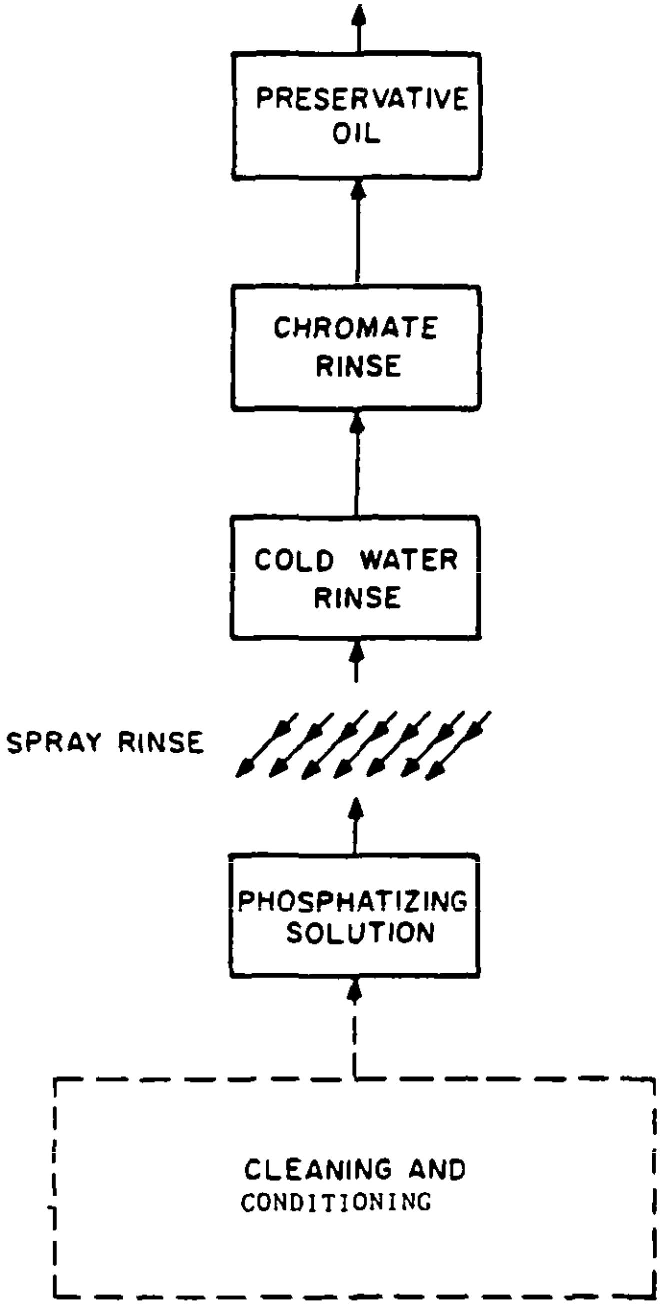
4.3.4.2.1 Type M and Z coatings (DOD-P-16232). Proper adherence to the procedures listed in (a) through (g), for preparation of the phosphating solution is necessary in order to prevent serious difficulty in the initial stages of use of the phosphating solution.

(a) Fill the tank with water to within 6 inches (15 centimeters) of the level at which it will ultimately be operated.

(b) Heat the water to 160°F (71°C). Do not exceed this temperature during the preparation of the solution. This is particularly important with the zinc-based chemicals as the nitrate content is higher in these chemicals than in the manganese-based chemicals. The nitrate may be reduced to nitrite while the ferrous iron content is low.

(c) Add the proper amount of phosphating chemical for the desired solution as shown in Table I or as recommended by the supplier of the chemical.

(d) Add the required amount of iron to the bath using any of the procedures given in 4.4.2.4.1.



NOTE: THE TYPE I TT-C-490 FINISH IS NOT TO BE OILED. THIS FINISH WILL BE THOROUGHLY DRIED AFTER THE CHROMIC ACID RINSE, AND THEN PAINTED OR COATED WITH THE REQUIRED FINISH.

FIGURE 9 : PHOSPHATING SEQUENCE

(e) Add water to the operating level, stir thoroughly, and remove a sample of the solution for analysis. See 4.4.2 for manganese-base and zinc-base baths.

(f) At this point, it is desirable to continue to use every means at hand to raise the iron content of the solution to within the range of 0.2 to 0.4% for the manganese-type solution and 0.2 to 0.45% for the zinc-type solution. When the iron content of the solution has reached the lower figure in the concentration range indicated above and the total acid has been adjusted as indicated in paragraph 4.4.2.1, the solution is ready for use.

(g) The thermostat may then be set between 190°F (88°C) and 210°F (99°C) and the phosphating process may begin.

(h) To maintain the concentration of iron in the solution within the designated percentage, the steam or other heat source should be shut off when the solution is not being used to process parts. In the hot solution ferrous iron is oxidized by air to the ferric form which forms insoluble ferric phosphate and drops out as sludge.

TABLE 1.

Coating Specification	Material Specification	Quantity Required*
Type M DOD-P-16232	Type M Composition B MIL-P-50002	62 (16.4)
Type Z DOD-P-16232	Type Z MIL-P-50002	40 (4.8)

*in pounds per 100 gallons (kg per 100 liters)

The oxidation of the ferrous iron is accompanied by an increase in the free acid content of the bath because for every unit of iron oxidized, one unit of phosphoric acid is released into solution. When work is being processed, the free acid is normally consumed by the dissolving iron as rapidly as it is formed. Under these conditions, there is no significant change in the free acid content and the ferrous iron may tend to increase. If the solution is kept hot when no work is being processed, the ferrous iron may decrease and the free acid increase. When the use of the phosphating solution is to be discontinued, for overnight or a longer period, and the heat has been shut off, water should be added to the solution until the surface of the solution is 3 to 5 inches (7.5 to 12.5 centimeters) above normal. This reduces the rates of oxidation by cooling the solution and, at the same time, prevents excessive loss of water by evaporation which normally occurs during longer periods of cooling.

4.3.4.2.2 Type I coating (TT-C-490). Preparation of the phosphating bath is accomplished by following steps (a) through (g).

(a) Fill tank to within 6 inches (15 centimeters) of the operating level.

(b) Add the proper amount of phosphating material for the desired solution as recommended by the supplier of the chemical.

(c) Add water to the operating level.

(d) Add any additional chemicals according to the supplier's instructions.

(e) Heat the solution to operating temperature. The recommended temperature for immersion processing is 180°F to 190°F (82°C to 88°C) and for spray processing is 130°F to 175°F (55°C to 79°C).

(f) Stir thoroughly and take samples for analysis. See 4.4.3.

(g) Sodium nitrite accelerator. When specified in the operation of the bath, add one ounce per 100 gallons (7.5 grams per 100 liters) of sodium nitrite for immersion processing and two ounces per 100 gallons (15 grams per 100 liters) of sodium nitrite for spray processing immediately before processing work.

Some phosphating processes make use of accelerators other than sodium nitrite. The most commonly used of these is sodium chlorate. This material is stable in the concentrated phosphate chemical while sodium nitrite is not. The fact that no external accelerator is required simplifies the control of the bath but the coating weights tend to be below the weights required to meet TT-C-490.

4.3.4.3 Processing Procedures

4.3.4.3.1 Type M Coating (DOD-P-16232).

(a) The work should be completely immersed in the phosphatizing bath and should be kept between 200° and 210°F (93° to 99°C) for approximately 45 minutes. The chemical reactions involved in the formation of the coatings release hydrogen gas. The visible evolution of gas normally ceases within 15 minutes but the parts should be left in the processing solution for 45 minutes to produce coatings with the maximum corrosion resistance.

(b) Unless previous experience with parts of like composition and pretreatment indicate otherwise, a continuation of visible gassing beyond a period of 15 minutes may be an indication of high acidity, high iron content, or poor cleaning. In such cases, the parts should be removed from the bath, thoroughly rinsed, and prepared for reprocessing as outlined in paragraph 4.1.2.6.

(c) Work loads should be as large as possible and the interval between the removal of one load from the solution and the introduction of the next load should be as short as possible. It is much more advantageous, from the standpoint of solution control, to operate the solution steadily for one day, than to spread one day's work over two days.

(d) Evaporation losses should be replaced at least twice during the processing of each load of work if no provisions for automatic level control are available. The electronic level controller is superior to the mechanical float type in the phosphating solution, because layers of phosphate scale form on the floats and other mechanical parts of these devices. Water should be added in frequent small quantities rather than in infrequent large quantities.

(e) Shaking the work at intervals during processing minimizes contact marks. It also ensures the escape of gas, which might collect in blind holes or cavities and cause a poor or spotty finish.

4.3.4.3.2 Type Z coating (DOD-P-16232).

(a) The temperature of this solution should be maintained at 190° to 205°F (88° to 96°C). It is best to establish a temperature and maintain it so that less than a 5°F (3°C) variation will occur. The solution should not be allowed to boil.

(b) The clean work is completely immersed in the solution for approximately 30 minutes. Shorter immersion periods produce coatings with a suitable appearance but such coatings usually have substandard corrosion resistance. Longer immersion in the phosphating solution will not provide a significant improvement in corrosion resistance.

(c) The processing is continued as in paragraph 4.3.4.3.1 (c) through (e).

4.3.4.3.3 Type I coating (TT-C-490).

(a) Metals being prepared for this coating should be cleaned by vapor degreasing, emulsion cleaning, or alkaline cleaning. In some instances it may be desirable to clean with phosphoric acid in accordance with Method VI of TT-C-490, using phosphoric acid solution complying with MIL-M-10578. After cleaning, the metal must be rinsed with water to remove any solution on the surfaces. Carrying cleaning solution into the processing solution will destroy the chemical balance of the solution. This can result in excessive use of chemical and/or loss of the ability of the solution to produce a satisfactory coating. If a strong alkaline cleaner or phosphoric acid is used in the cleaning sequence, a conditioning agent (Section 3) should be used following the water rinse. It should be noted that baths have been developed that operate at relatively low temperatures, e.g. 100°F, for energy conservation.

(b) When treating parts by immersion, the properly cleaned parts should be immersed for a minimum of three minutes in the phosphating solution. The temperature at which the processing solution is operated should not be allowed to vary more than 5°F (3°C). This temperature is established for each installation and may vary from 130° to 165°F (55° to 75°C) in spray installations and from 180° to 190°F (82° to 88°C) in immersion installations. Fluctuations of more than 5°F (3°C) will tend to produce unsatisfactory results.

4.3.5 Water Rinsing

4.3.5.1 Immersion Water Rinsing. The water in the immersion rinse tank is unheated and immersion time should be about one minute. Agitation of the work in the rinse water is more effective than additional time for thorough rinsing. The most effective rinsing is obtained by raising the parts out of the rinse water and reimmersing them two or three times. The rinse water must overflow continuously while being used. The tank should be completely drained daily and filled with clean water. Use of double counter flow rinses should be considered for reduction of water consumption and more effective waste treatment of smaller volume rinse effluents.

4.3.5.2 Spray Water Rinsing on Immersion Processing Lines. The time lag in the transfer of work from the phosphating tank to the immersion rinse tank should be as short as possible to prevent the phosphating solution from drying and "setting up" on the surface of the work. This "setting up" is most effectively prevented if a cold water rinse is applied immediately after the work is lifted out of the phosphating solution by either of the methods described below:

(a) Install a system of spray nozzles positioned along the front and rear edges of the phosphating tank. These nozzles should be approximately two feet (60 centimeters) above the top of the tank and so directed that the cone of the spray will fall within the confines of the tank. The sprays should be controlled by a foot operated valve positioned such that it and the power hoist used to lift the work from the tank can be operated simultaneously by one man. After being phosphated for the required time, the work is slowly raised from the solution through the cold water spray and then transferred to the immersion rinse tank.

(b) If a permanently installed tank spray system is not avaialble, the work can be hand sprayed by means of a hose and attached nozzle.

(c) It is desirable to spray the parts until they are cool but the volume of water required may cause the phosphate solution to overflow. By using nozzles with the minimum flow rate which gives complete coverage, the phosphate solution on the parts can be removed so that no "setting up" of phosphating chemicals occurs even when the part is still hot when the sprays are shut off.

4.3.6 Chromate Rinse

4.3.6.1 Rinses Controlled by Free Acid. The chromate rinse plays a very important role in the corrosion resistance of the phosphate coatings. This rinse can be prepared by dissolving 8 ounces of chromic acid (CrO_3) or 4 ounces of chromic acid and 4 ounces (by weight) of 75% phosphoric acid (H_3PO_4) in 100 gallons (60 grams of chromic acid or 30 grams of chromic acid and 30 grams of 75% phosphoric acid per 100 liters) of water. These baths are normally controlled by titrating the free acid (see paragraph 4.6.2.3). A constant free acid concentration is maintained by additions of chromic acid or equal parts by weight of chromic acid and 75% phosphoric acid. The corrosion resistance offered by rinses prepared in this manner vary from plant to plant. Hexavalent chromium is the major contributor to the corrosion protection provided by the rinse which will vary with the amount of hexavalent chromium present in the rinse. The alkalinity of the water available varies widely. Larger amounts of acid, and thus the hexavalent chromium, are required where the alkalinity of the water is high in order to obtain the same free acid.

4.3.6.2 Rinses with Controlled Chromate. The problem of varying hexavalent chromium levels can be solved by the use of commercially available solutions. These are used to build up and maintain a constant chromate concentration in waters with varying alkalinities by means of two solutions. One is a solution of chromic acid and the other a solution of a dichromate salt (usually a calcium salt). The control procedures will be furnished by the supplier of the chemicals and should include a test for hexavalent chromium and pH or free acid.

4.3.6.3 Rinses Containing Trivalent Chromium. Rinses containing trivalent chromium (U.S. Patent Nos. 3,222,226 and 3,279,958) are available which may or may not contain hexavalent chromium. These rinses, when properly controlled, can be followed by a water rinse (deionized water is preferred) without reducing the benefits provided by the chromate rinse. This makes possible the removal of any soluble salts which can cause problems under paint. See 4.8.4.2. This type of rinse is normally used with processes meeting TT-C-490.

4.3.6.4 Chromium Free Rinses. Proprietary rinses which contain no chromate are available for use over phosphate coatings meeting TT-C-490. These are used where there are no provisions for disposing of the chromate salts and where anodic or cathodic paints, which can be harmed by the chromate salts, are being used.

4.3.6.5 Temperature. The temperature at which the chromate rinse is operated can vary widely and is frequently selected on the basis of what is needed to obtain dry parts. Many parts are sufficiently massive to retain enough heat from a hot chromate rinse to cause the parts to dry with no further treatment other than to remove any chromate solution from recessed areas. In these cases the chromate rinse is maintained at the temperature required to obtain dry parts. When the parts are made of thin sheet metal an additional drying stage may be required in which case the temperature of the chromate rinse is not important but temperatures below 130°F (55°C) are seldom used.

4.3.7 Drying. After the work is removed from the chromate rinse, it must be thoroughly dried before the final finish is applied unless a water displacing oil is used. Even when the latter type of oil is used, most of the moisture should be removed from the parts before they are placed in the oil. Parts being finished with a Type I finish (TT-C-490) must not be oiled. Heavy parts which retain heat will dry spontaneously when removed from a hot chromate rinse. Thinner metal parts may require a heated dry off. However, the temperature of the dry off should not exceed 225°F (107°C) with DOD-P-16232 Type Z coatings or 375°F (190°C) with DOD-P-16232 Type M coatings. Small parts phosphated in tumbling barrel units may be dried conveniently by centrifuge, preferably equipped with heated air circulation. The last traces of moisture can be removed from parts which are to be oiled by dipping them in a water displacing oil.

4.3.8 Preservative Oil Dip. The preservative oil dip is used only on parts coated to meet DOD-P-16232. The parts should be oiled as soon as possible after phosphating. The parts should be dried before oiling. However, the degree of dryness required varies with the type of oil used.

Water displacing oils can be used on parts with damp areas where the dry-off has not removed all traces of moisture. For the best corrosion resistance the water displacing oil should be followed by a rust preventative oil.

Other oils require that the parts be thoroughly dry before dipping in the oil.

4.3.9 Finish for TT-C-490 Type I Coatings. Parts given a Type I (TT-C-490) coating are to receive an organic coating and must not be oiled. Parts to be painted after assembly or to be held for a period of time should be given a prime coat of paint immediately after phosphating.

4.4 Maintenance of the Phosphating Tank and Chemical Control of the Phosphating Solution

4.4.1 Maintenance of the Phosphating Tank

4.4.1.1 Sludge Removal. In the normal operation of the phosphating process, a quantity of sludge is formed. This sludge consists primarily of ferric phosphate. However, in the operation of the process, partially soluble iron and zinc or manganese phosphates are also formed. These compounds act as buffers in stabilization of the iron, zinc, and free acid of the solution. Complete removal of these compounds from the solution permits large fluctuations in the concentration of the constituents of the solution. Therefore, sludge should not be completely removed from the tank. A satisfactory method consists of removing a small portion with a hoe each day. This prevents drastic changes in the solution and disturbance of work schedules. In addition, the sludge should be stirred into the cold solution before turning on the heat when starting production.

4.4.1.2 Level Control, Thermo-regulator Bulbs and Temperature Regulators. Level controls, thermo-regulator bulbs and temperature regulators must be removed periodically and all scale removed from the surfaces exposed to the solutions. In no instance should any regulator or other device constructed of lead, copper or its zinc and tin alloys be used in the phosphate solution. Only stainless steel or glass equipment should be used.

4.4.1.3 Coils. Scale on the coils may be removed by the use of a tool or with the aid of chemicals. Scale may be removed quickly by means of a tool shaped to the contour of the coil and a 5 pound air hammer.

CAUTION: Eye protection should be worn when removing scale in this manner.

The scale on coils can be removed more easily if the scale is heated before removal is attempted. A simple way of heating the scale is to run steam through the coil while it is not immersed in the solution. (If the tank is emptied, the coil can be heated in place.)

Heating coils for the zinc-base phosphating solutions may be cleaned chemically as indicated in (a) through (d) below:

(a) Remove the coil from the phosphating solution and place it in a narrow mild-steel tank just large enough to accommodate the coil with about three inches (7.6 cm) of clearance on all sides.

(b) Attach the coil to a steam line.

(c) Fill the tank with a solution of the following composition:

Rochelle Salts	15 pounds (6.82 K_g)
Caustic soda	150 pounds (68.18 K_g)
Water	100 pounds (45.45 K_g)

(d) The steam in the coil must be regulated so that the solution is maintained just below the boiling point. An automatic temperature control is required to avoid hazardous boiling of the highly caustic solution. The heat transfer efficiency of the coil increases as the scale is dissolved and adequate manual control is nearly impossible.

Immediately after being cleaned, the coils should be rinsed with a hose, followed by immersion in a water rinse tank. The cleaning solution will gradually lose its strength and a heavy sludge will accumulate on the bottom of the tank. When this interferes with the coil cleaning, the solution should be discarded. The cleaning solution, when ready for disposal, contains a large amount of caustic soda and phosphates of iron and zinc plus the Rochelle salts. The disposal of the solution must comply with all government, state and local regulations concerning waste disposal.

CAUTION: Protective clothing and face and eye protection must be used by operators working with this material.

4.4.2 Control of Phosphating Solutions. The manganese - base phosphate solution is used in producing heavy manganese phosphate coatings and the zinc-base phosphate solution is used in producing heavy zinc phosphate coatings. These coatings meet the requirements of DoD-P-16232, Type M and Type Z respectively. The phosphating baths should be operated in the concentration ranges recommended in Table 2. The control measure for adjusting the concentrations are given in the following paragraphs:

TABLE 2

Recommended Concentration Ranges

	Phosphating Solution	
	Manganese-Base	Zinc-Base
Free Acid, points[a], maximum	5.0	5.5
Total Acid, points[a]	26 to 30.0	26 to 30.0
Free Acid to Total Acid Ratio		
Minimum	1 to 5.5	1 to 5.5
Optimum	1 to 6.0	1 to 6.0
Iron (ferrous), percent	0.2 to 0.4	0.2 to 0.4

(a) One point equals 1 ml of 0.1 N NaOH per 10 ml sample.

4.4.2.1 Total Acid. The total acidity of the phosphating solution is maintained as follows:

Manganese - base phosphate solution - add a solution of manganese phosphate, manganese nitrate and phosphoric acid.

Zinc - base phosphate solution - add a solution of zinc phosphate, zinc nitrate and phosphoric acid.

The total acidity of these baths is maintained within the limits shown in Table 2. Small deviations are maintained by frequent small additions of the above solutions. The amount of chemical required to increase the total acid one point is 2.1 pounds per 100 gallons for the manganese - base phosphate solution when using the chemical conforming to MIL-P-50002 Type M, Composition B, and 1.5 pounds per 100 gallons for zinc - base phosphate solution when using the chenical meeting MIL-P-5002 Type Z. When material not covered by specification is used, this information may be obtained from the supplier. It is advisable to add the phosphating chemical in small frequent additions rather than larger infrequent additions. The bath should be stirred thorougly after the addition of chemical.

4.4.2.2. Free Acid. Maintenance of the free acidity of the solution is of great importance in the reactions involved in the coating formation. The free acidity which tends to rise due to dissociation of the dihydrogen phosphate salts in water, reaches a point where excessive etching of the work may occur. This condition is generally accompanied by inability to produce a complete coating within the normal processing period. Severe hydrogen embrittlement may be encountered as a result of the large amount of hydrogen formed when this condition arises. High free acidity is caused by the following:

(a) Prolonged idle periods during which the bath is heated but no work is processed.
(b) Overheating the solution.
(c) Processing small loads of work in a relatively large volume of solution.

Should the free acidity rise above the range designated, corrections should be made. The method used will depend upon the concentration of the ferrous iron as described in the two methods below.

4.4.2.2.1 If the iron content is near or approaching the upper limits, add 8 ounces per 100 gallons (60 grams per 100 liters) of manganese carbonate (manganese - base phosphate) or 8 ounces of zinc carbonate (zinc - base phosphate)for every point of free acid above the desired level. Manganese carbonate (for manganese-base phosphate solution) or zinc carbonate (for zinc-base phosphate solution) should be weighed, placed in a bucket, water added and mixed thoroughly. The resulting slurry should be stirred well and distributed over the solution surface. This treatment will reduce the free acidity but it may have to be repeated several times before the free acid remains within the desired range.

4.4.2.2.2 If the iron content of the solution is in the lower part of the recommended range or below, the free acid can be reduced by processing iron as described in 4.4.2.4.1.

4.4.2.3 Total Acid to Free Acid Ratio. The ratio of total acid to free acid should be maintained above the limit of 5.5 parts total acid (i.e., free acid plus combined acid) to one part free acid. The ratio, for most rapid coating action and best corrosion resistance, should be held at approximately 6 parts total acid to 1 part free acid. Should the free acidity tend to drop, the cause is usually contamination of the bath with alkaline cleaning salts. The source of the contamination must be located and eliminated. If the low free acid is causing poor coatings, it may be necessary to discard the contaminated phosphate bath and begin again with a new phosphate solution.

4.4.2.4 Ferrous Iron

4.4.2.4.1 Low ferrous iron. Ferrous iron can be introduced into the phosphating solution to build up a new solution or to raise the concentration in an existing bath by dissolving iron in the processing solution. The source of the iron is not important and the most readily available and cheapest source can be used providing it is clean or can be cleaned before it is immersed in the processing solution. Rusty metal should be pickled and thoroughly rinsed before being used. Steel wool, cast iron chips, scrap steel, and steel shavings can be placed in baskets and immersed until vigorous gassing ceases. No harm is done by leaving the iron in the phosphate solution after gassing ceases, but little iron will be dissolved after this point is reached. Iron powder and steel dust are best added by placing a cloth across the top of the tank so that it is 2 to 3 inches (5 to 7.5 centimeters) below the solution surface and scattering the powder or fine grit onto the solution surface. Additions should be at a rate which maintains vigorous gassing. When finished, remove the cloth and discard any material remaining on it. One pound of iron dissolved in 100 gallons (120 grams per 100 liters) will raise the ferrous iron content 0.12%. When introducing iron into a newly prepared phosphating solution, the instructions for temperature given in 4.3.4.2.1 should be observed.

4.4.2.4.2 High ferrous iron. While processing work, the iron which is dissolved during the coating action may cause the concentration of the ferrous iron to increase and eventually exceed the maximum level shown in Table 2. The concentration of the ferrous iron should be reduced before the maximum is reached. The ferrous iron content can be lowered by the addition of an oxidizing agent such as hydrogen peroxide. If the ferrous iron content is lowered in this manner it is essential that manganese carbonate (for manganese - base phosphate solution) or zinc carbonate (for zinc - base phosphate solution) be added to neutralize the phosphoric acid when ferrous phosphate is oxidized to form insoluble ferric phosphate. The addition of 0.5 pounds of 35% hydrogen peroxide to 100 gallons of processing solution (60 grams per 100 liters) will lower the ferrous iron 0.05%.

CAUTION: 35% hydrogen peroxide is a hazardous material and the precautions given by the supplier must be observed.

The hydrogen peroxide should be diluted with water before being added to the phosphating solution. For every added unit of weight of 35% hydrogen peroxide, two units by weight of manganese carbonate (for manganese - base phosphate solution) or two units by weight of zinc carbonate (for zinc - base phophate solution) should be added. The manganese carbonate or zinc carbonate should be separately mixed with water to form a slurry before addition to the phosphating solution. (Do not mix the hydrogen peroxide with either the manganese or the zinc carbonate.) No more than 0.05% ferrous iron should be removed at one time using this procedure.

An alternative method to lower the ferrous iron concentration consists of discarding a portion of the bath, and restoring the bath to the proper total acid following restoration of the level of the bath with water that has been thoroughly mixed into the bath. This method requires proper treatment of the discarded solution prior to disposal.

4.4.2.4.3 Ferrous iron vs. nitrite accelerator. If a bath which is thought to contain ferrous iron is milky in appearance or a sharp end point is not achieved when testing with potassium permanganate, the bath may contain nitrite instead of iron.

4.4.3 Control of Paint Base Zinc Phosphate Baths (TT-C-490 Type I). Zinc-based phosphate baths designed to produce coatings used as a base for paint (TT-C-490 Type I) are used in immersion applications and by spraying the solution on the work which is enclosed in a tunnel. With few exceptions these baths operate with nitrite as an accelerator and with no ferrous iron in the baths. The fact that the sodium nitrite is converted to volatile gasses in the phosphate solutions requires substantial differences in the control of immersion and spray processes and the instructions for their control will be given separately. See sections 4.4.4.1 and 4.4.4.2.

The zinc phosphate baths which do not use nitrite as the accelerator are seldom used on items being procured by the military and their control will not be covered in this manual. If these processes are being used, the control procedures will be furnished by the supplier.

4.4.3.1 Control of Immersion Type Processes. As work is processed in the solution, metallic acid phosphates, nitrates, and free phosphoric acid are consumed in the formation of the coatings. The bath must be replenished from time to time with the phosphating chemical. Frequent small additions of the phosphate chemical will produce more uniform work than occasional large additions. Not more than one point variance should be allowed. The processes are controlled by the operating temperature, the absence of any ferrous iron, the total acid, and the free acid (in decreasing order of importance).

4.4.3.1.1 Temperature. Operation of these baths below 170°F (76°C) greatly increases the risk of ferrous iron accumulation in the bath. Operation above 190°F (88°C) is not harmful but increases the cost of operation. The temperature should not be permitted to vary more than 5°F (3°C).

4.4.3.1.2 Absence of ferrous iron and presence of nitrite. For proper operation of these baths, some nitrite and no ferrous iron must be present.

4.4.3.1.3 Total acid. The total acidity of the bath should be maintained at 19 to 21 points. The amount of phosphating chemicals to increase the total acid 1 point can be obtained from the supplier of the chemical.

4.4.3.1.4 Free acid

4.4.3.1.4.1 High free acid. Free acid values above 5.0 in a 20 point bath may cause poor coatings. They are normally caused by excessive loss of processing solution due to leaks or drag-out of solution on the parts being processed. The loss of solution should be corrected and the free acid lowered by adding sodium hydroxide (or soda ash). The free acid will be reduced 1.0 points by the addition of 5.4 ounces of sodium hydroxide or 7.6 ounces of soda ash per 100 gallons of solution (40 grams of sodium hydroxide or 56 grams of soda ash per 100 liters). The sodium hydroxide or soda ash must first be dissolved in water to form a dilute solution before being added to the phosphate solution.

Another source of high free acid which is occasionally encountered occurs when pickling solution is carried into the phosphate solution. The source of the contamination should be determined and corrected and the free acid adjusted with sodium hydroxide (or soda ash) as in the previous paragraph.

4.4.3.1.4.2 Low free acid. If the free acid drops below 2.5 in a 20 point bath, the most frequent cause is contamination by alkaline cleaner salts. Any contamination should be eliminated. Normally, the bath will restore itself to a proper free acid level after a few hours of operation and no further adjustments should be necessary. If the free acid drops below 2 it may be necessary to discard the bath and prepare a new solution. If the bath is discarded, make sure that all waste disposal compliance requirements are met.

4.4.3.2 Control of Spray Type Processes. As work is processed in the solution, metallic acid phosphates and free acid are consumed in the formation of the coatings as in the immersion treatment. Control of the spray type processes differs from that for the immersion type due to the necessity of continuously adding sodium nitrite to replace the nitrite which is volatilized as the solution is sprayed. Unless corrective steps are taken, the sodium accumulates in the bath and the zinc decreases if the total acid is maintained at a constant value. A satisfactory bath can be maintained based on the total acid control if one nitrate ion is added (nitrate is contained in the zinc phosphate chemical) for each sodium ion added as sodium nitrite. (U.S. Patent, 2,351,605-R.C. Gibson.) For best results, both the phosphate chemical and a solution of sodium nitrite are added by means of small pumps capable of feeding small measured amounts of chemical.

The spray type processes are controlled by the total acid, nitrite, the free acid and the temperature (in decreasing order of importance).

4.4.3.2.2 Total acid. The total acidity of the bath should be maintained at 14 to 16 points. The supplier of the chemical will advise as to the amount of chemical required to increase the total acid one point.

4.4.3.2.3 Accelerator (nitrite). Sodium nitrite accelerator must be added continuously while processing parts in a spray process. (Avoid operating the sprays and adding sodium nitrite when no work is being processed.) The concentration of the accelerator should be maintained at the lowest level which will produce a satisfactory coating. This level is normally between 0.5 and 2.0. If it is determined that concentrations above 2.0 are required, refer to the discussion below under free acid (4.4.3.2.4). The problems due to improper free acid (high or low) are frequently counteracted by increased accelerator concentrations at the expense of using needlessly large amounts of chemical.

4.4.3.2.4 Free acid. The factors which affect the free acid in immersion type processes also affect the free acid in spray type processes. In addition, in spray type processes, the continuous additions of sodium nitrite can cause high or low free acid depending upon the composition of the phosphating chemical and ratio of phosphating chemical to sodium nitrite being used.

Frequently it is observed that satisfactory coatings can be obtained by operating with the accelerator at a higher level. While this produces satisfactory coatings, it does so at the cost of excessive usage of chemical.

4.4.3.2.4.1 Low free acid. Low free acid in the processing bath will develop if fewer ions of nitrate are furnished by the phosphating chemical than are necessary to compensate for the sodium ions being added as sodium nitrite. Low free acid values may also occur if excess nitrite is present in the phosphating chemical in the form of zinc nitrate.

The correction of low free acid due to either of these problems requires formulation of the phosphate chemical concentration by the supplier.

4.4.3.2.4.2 High free acid. If the free acid is high enough to give an acid ratio lower than 1 to 10 (i.e., 1 to 8) it may be difficult or impossible to obtain a satisfactory coating. The free acid can be lowered with sodium hydroxide as discussed in 4.4.3.1.4.1.

The high free acid values are normally the result of one of two conditions. If processing solution is lost due to leaks or is dragged out on the parts being processed, the problem of high free acid and high consumption can be corrected by eliminating the solution losses. If the phosphate chemical concentrate contains excess nitrate as nitric acid, the problem can be corrected by the supplier of your chemical by reformulating the material.

4.4.3.2.4.4 Temperature. The spray type process will operate satisfactorily at temperatures ranging from 130°F to 160°F (55°C to 70°C). The solution must be kept at the established temperature within 5°F (3°C) in order to produce consistent coatings.

4.5 Maintenance of the Chromate Rinse. During operation of the chromate rinse, evaporation causes the salts present in the water to become more concentrated. In addition, chemicals dissolved from the coatings accumulate in the chromate solution. These salts will be present in the solution and can dry on the work as it is removed from the chromate rinse. If present in sufficient quantities, failure in performance can result.

4.5.1 Control of the Chromate Rinse. The chromate solutions are controlled with a free acid test combined, in some cases, with a test for hexavalent chromium. A total acid test may be used as a guide for discarding the bath as discussed above and in section 4.5.2. The use of both a free acid test and a hexavalent chromium test permits excellent control and consistent results but requires the use of two chromate concentrates with different acidities. These are available from most suppliers of phosphate chemicals.

4.5.1.1 Free Acid. The free acid concentration is normally maintained at about 0.5 point with values as low as 0.2 and as high as 1.0 being used occasionally.

4.5.1.2 Hexavalent Chromium. The test and optimum concentration will be supplied by the supplier of the chemical.

4.5.1.3 Total acid. The acid is used as an indicator as to when to discard the bath. For further information see the first paragraph of this section (4.5) and paragraph 4.6.3.

4.5.2 Disposal of Chromate Solutions

4.5.2.1 These solutions, due to evaporation, accumulate salts present in the water and a small amount of the dissolved coating. When excessive amounts of these contaminants are present, they can cause failure of the finished parts. To prevent failures, all rinses must be discarded whenever they become contaminated. The final rinse shall be checked at least weekly and shall be discarded when the total acid reading rises to more than 7 times the free acid reading.

4.5.2.2 Common methods for determining when to discard the chromate solution are based on the free and/or total acid values. Discarding is recommended when the total acid exceeds an established value or divided by the free acid exceeds an established value.

These methods of determining when to discard the solutions frequently require discarding solutions which are capable of producing satisfactory results.

4.5.2.3 The cost of the chemicals is small and the cost of preparing new solutions is relatively minor. However, since the spent solutions usually must be treated to comply with waste disposal regulations (see paragraph 4.5.2.4), the cost to accomplish compliance requires that the baths not be discarded more often than necessary. The best procedure to use with a particular bath is to extend the time of use one shift at a time while testing all work processed. When it has been determined that process failures begin to occur after a given period of use, then set up a schedule for discarding the solution before this failure point is reached.

4.5.2.4 Waste Disposal. The method of disposal of chromate solutions depends on the local waste disposal regulations and is beyond the scope of this handbook. Generally it will be necessary to reduce the hexavalent chromium to trivalent chromium, precipitate the trivalent chromium, separate the precipitate from the liquid, and adjust the liquid to the proper pH.

The liquid can, in most cases, be discharged into the sewer but the precipitated trivalent chromium is normally shipped to a land fill site.

4.6 Chemical Analyses of Phosphating and Chromate Rinsing Solutions

4.6.1 Analytical Reagents. It is recommended that reagents required in the analysis of phosphating compounds be requisitioned if available from chemical supply houses. These are already made up to the proper strength. If local laboratory facilities are available, solutions may be made up as outlined in (a) through (j) below.

(a) Methyl orange-xylene cyanole indicator: Dissolve 1 gram methyl orange and 0.14 gram xylene cyanole in one liter of deionized water.

(b) One percent phenolphthalein indicator: Dissolve 1 gram phenolphthalein in 100 ml of alcohol.

(c) One percent bromcresol green indicator: Dissolve 1 gram bromcresol green in 100 ml of alcohol.

(d) 0.4% bromphenol blue indicator: Dissolve 0.4 gram of bromphenol blue in 6 ml of 0.1N sodium hydroxide diluted with 8 ml of deionized water. When completely dissolved, dilute to 1000 ml with deionized water.

(e) Sulfuric acid, H_2SO_4, 6 Normal: Sulfuric acid 6 N is made by adding 1 part by volume of concentrated sulfuric acid to 5 parts by volume of water.

> CAUTION: Always add the acid to the water. Heat is generated when the acid mixes with water and protective clothing and eye and face protection should be worn when making this material.

(f) Sodium hydroxide, 0.1 Normal: Dissolve 4.0 grams of C.P. sodium hydroxide in deionized water and dilute to one liter. Standardize by titrating equal volumes of 0.1 N potassium acid phthalate, $KHC_8H_4O_4$, and the sodium hydroxide, using phenolphthalein indicator to a pink end point. The solution of sodium hydroxide must be diluted with deionized water or strengthened by adding a concentrated solution of sodium hydroxide, until the concentration is adjusted to 0.1 Normal.

(g) Potassium acid phthalate, 0.1 Normal: Weigh exactly 10.2 grams of carefully dried, chemically pure potassium acid phthalate (National Bureau of Standard Sample No. 84d) and transfer to a 500 milliliter volumetric flask. Dissolve the salt in the flask, dilute to 500 ml, and mix thoroughly. The resulting solution may be considered as being 0.1 Normal.

(h) Potassium permanganate solution, $KMnO_4$, 0.18 Normal: Weigh 5.66 grams potassium permanganate and dissolve in deionized water and dilute to a total volume of 1 liter. Mix well and allow to stand in a dark bottle for a week. Siphon off the clear solution (or filter through an asbestos filter) and standardize against known samples of pure iron wire, previously weighed and dissolved in sulfuric acid, in absence of air. Titrate the sample of iron solution with the $KMnO_4$ solution to a pink end point, and record the number of mls used. Calculate as follows:

Grams of pure iron in sample x

purity of iron divided

= Normality of $KMnO_4$

by Mls of $KMnO_4$ x 0.0558

Store in absence of light.

(i) Potassium permanganate solution, $KMnO_4$, 0.042 Normal: Prepare as above using 1.32 grams of potassium permanganate or dilute 233 ml of the 0.18 N $KMnO_4$ solution to 1 liter with deionized water and mix thoroughly. Store in the absence of light.

(j) 4,4' bipyridine paper: Dissolve 1 gram of 4,4' bipyridine in 100 ml of ethanol. Wet pieces of filter paper and allow the paper to dry. Cut the paper into convenient size strips and store in a closed glass jar.

4.6.2 Free Acid. The proper procedure for determining the free acid depends upon the solution being tested. Select the proper procedure as described below.

4.6.2.1 Free Acid in Phosphate Baths Containing Ferrous Iron. Using a 10 ml volumetric pipette, transfer a 10 ml sample of the solution to an Erlenmeyer flask or beaker. Add 3 drops of methyl orange-xylene cyanole indicator. Titrate with 0.1 N sodium hydroxide. The end point is a gray to greenish-gray color. Record the number of mls of 0.1 N sodium hydroxide used. This number is the number of points of free acid in the solution.

4.6.2.2 Free Acid in Phosphate Baths Containing Nitrite. Using a 10 ml volumetric pipette transfer a 10 ml sample of the solution to an Erlenmeyer flask or beaker. Add 5 drops of bromphenol blue indicator. Titrate with 0.1 N sodium hydroxide. The end point is reached when the yellow just changes to bluish-green by daylight or blue-violet by incandescent light. Record the number of mls of 0.1 N sodium hydroxide used. This number is the number of points of free acid in the solution.

4.6.2.3 Free Acid in Chromate Rinse Solutions. Using a 25 ml volumetric pipette transfer a 25 ml sample of the solution to an Erlenmeyer flask or beaker. Add 4 drops of bromcresol green indicator. The solution should remain yellow. If it turns green or blue there is no free acid present, and additional chemical is required. When the solution remains yellow, titrate with 0.1 N sodium hydroxide. The end point is the appearance of a permanent green color. Record the number of mls of 0.1 N sodium hydroxide used. This number is the number of free acid points in the solution.

4.6.3 Total acid. The procedure for determining the total acid depends upon the solution being tested. Select the proper procedure as described below.

4.6.3.1 Total Acid in Phosphate Baths. Using a 10 ml volumetric pipette transfer a 10 ml sample of the solution to an Erlenmeyer flask or beaker. Add 5 drops of phenolphthalein indicator. Titrate with 0.1 N sodium hydroxide. The end point is a permanent pink color. Record the number of mls of 0.1 N sodium hydroxide used. This number is the number of points of total acid in the solution.

4.6.3.2 Total Acid in Chromate Solutions. Using a 25 ml volumetric pipette transfer a 25 ml sample of the solution to an Erlenmeyer flask or beaker. Add 5 drops of phenolphthalein indicator. Titrate with 0.1 N sodium hydroxide. The end point is the appearance of a red or purple color. Record the number of mls of 0.1 N sodium hydroxide used. This number is the number of points of total acid in the solution.

4.6.4 Determination of Nitrite and Ferrous Iron. Both nitrite and ferrous iron react with potassium permanganate in an acidic solution and either may be present in a phosphate solution. This is seldom a problem in the manganese phosphate type baths as nitrite seldom develops in these baths. In the zinc phosphate type baths (and particularly those used to meet the requirements of TT-C-490), either material may be present and the potassium permanganate titration does not indicate which one is present. Therefore, a positive test for one or the other is desirable. The presence of ferrous iron can be determined by wetting a strip of paper impregnated with 4,4' bipyridine (see paragraph 4.6.1) with the phosphate solution. Ferrous iron is present if the paper turns pink or red. If the paper does not change color, and the acidified sample reacts with potassium permanganate, nitrite can be assumed to be present. There is no simple test for the positive identification of nitrite but under the above conditions, it can be assumed that it is present in a phosphate solution.

4.6.4.1 Ferrous Iron. Check for the presence of ferrous iron with paper immersed with 4,4' bipyridine. If the paper does not change color see paragraph 4.6.4.3. If the paper turns pink or red use a 10 ml volumetric pipette to transfer a 10 ml sample of the phosphate solution into an Erlenmeyer flask or beaker and add 10 ml of 6 N sulfuric acid. Titrate with 0.18 N potassium permanganate. The end point is a permanent pink color. Record the number of mls of 0.18 N potassium permanganate used. Divide this number by 10 to determine the percent of ferrous iron present.

4.6.4.2 Nitrite. Check for the presence of ferrous iron with paper impregnated with 4,4' bipyridine. If the paper turns pink or red, it indicates that ferrous iron is present and the ferrous iron must be removed in order to operate with nitrite present. See paragraph 4.6.4.4 for procedures for removing the ferrous iron. When the paper does not change color, use a 25 ml volumetric pipette to transfer a 25 ml sample of the phosphate solution into an Erlenmeyer flask or beaker and add 50 ml of 6 N sulfuric acid. Titrate with 0.042 N potassium permanganate. The end point occurs when one drop of potassium permanganate produces a pink color which persists for 10 seconds. Record the number of mls of 0.042 N potassium permanganate used. This number represents the concentration of the nitrite.

4.6.4.3 Destruction of Unwanted Nitrite. When iron is processed in a hot immersion type phosphate bath containing nitrite, the result is normally the generation of additional nitrite. To develop ferrous iron in the bath, allow the bath to cool below 160°F (70°C) and allow the nitrite to escape either by standing overnight or by bubbling air through the bath. Load the bath with iron as described in paragraph 4.4.2.4.1. When the minimum concentration of ferrous iron is present, the temperature can be increased to the proper operating level and production resumed.

4.6.4.4 To Destroy Ferrous Iron and Develop Nitrite. If the bath is designed to operate with nitrite present it is necessary to make sure that no ferrous iron is present. Wet a strip of paper impregnated with 4,4' bipyridine with the phosphate solution. If the paper turns pink or red, ferrous iron is present and must be removed.

If the paper turns pink, the ferrous iron can be oxidized to insoluble ferric phosphate with sodium nitrite. Add 2 ounces of sodium nitrite dissolved in water for each 100 gallons (15 grams per 100 liters) of phosphating solution. Repeat if necessary until no test for ferrous iron is obtained.

CAUTION: When adding sodium nitrite to a phosphate bath containing ferrous iron, make sure that the ventilating system is operating.

If the paper turns red, the above procedure may produce large amounts of a brown gas which consists of toxic oxides of nitrogen. In addition, a large volume of sludge will be produced.

The recommended procedure is to discard the solution observing local waste disposal regulations. Prepare a fresh phosphate solution.

4.6.5 Hexavalent Chromium. The procedure for controlling hexavalent chromium can be obtained from the supplier of the chromate rinse chemicals. The supplier will advise as to whether or not such a procedure is necessary.

4.7 Inspection of Phosphated Parts

4.7.1 Visual Inspection. To ensure work of acceptable quality, all work should be visually inspected before being oiled or painted. Good work may range in color from gray to black depending upon the alloy being treated but should be uniform in color except where a portion of the part has been subjected to localized heat treatment. These areas may be lighter or darker in color. There should be no contact marks which show uncoated metal. The phosphate coating should show no white or greenish-white stains. These streaks are normally indications of inadequate rinsing of the processing solution from the surface of the work.

4.7.2 Corrosion Resistance of the Phosphate Coating

4.7.2.1 Salt Spray Test for Heavy Phosphate Coatings, DOD-P-16232. The phosphated parts should be subjected to a 5% salt-spray (fog) test as described in ASTM B-117. The phosphate coatings should meet the salt-spray requirements of specifications. Parts intended for dry (i.e., unoiled) salt-spray corrosion tests should be placed directly in test without rinsing, degreasing, or any treatment other than that which constitutes a part of the process. Should the surface have been contaminated in handling, the parts should be thoroughly degreased, rinsed in the chromate solution, dried and placed directly in test.

4.7.2.2 Salt-Spray Test for Type I, TT-C-490. The phosphated parts to be tested should be coated with the coating to be used on the finished products. These parts should satisfactorily pass the 5% salt-spray requirement for the specification of the final coating used.

4.7.3 Determination of Phosphate Coating Weight Per Unit Area

4.7.3.1 Removal of Phosphate Coatings. Manganese based coatings (Type M, DOD-P-16232), zinc based coatings (Type Z, DOD-P-16232), and zinc based coatings (Type I, TT-C-490), can all be removed to determine the weight of the phosphate coating or to examine the base metal by following steps (a) through (f) below. Steps (a) and (f) can be omitted if the only concern is the appearance of the base metal.

(a) Weigh a suitable phosphated part which is clean and free from oil. Calculate the entire surface area.

(b) Immerse for 15 minutes at 165°F (74°C) in a 5% solution of chromic acid in water. The chromic acid solution should be used only once.

(c) Rinse thoroughly in two separate rinses of clear deionized water.

(d) Rinse in alcohol.

(e) Dry in an oven or with clean compressed air.

(f) Weigh the stripped part.

4.7.3.2 Phosphate Coating Weight. The weight of the phosphate coatings can be calculated from the above data as follows:

$$\text{Phosphate Coating (in mg per sq meter)} = \frac{\text{Weight Loss (in mg)}}{\text{Area of Part (in sq. meters)}}$$

4.8 Common Difficulties Encountered in Phosphate Coating Processes

4.8.1 General. In all protective coating processes, a certain amount of difficulty may be encountered, due to unobserved errors in carrying out one or more of the operations that directly influence the quality of the work. This section is devoted to brief descriptions of commonly encountered difficulties and the recommended corrective measures.

4.8.2 Visual Defects. The appearance of the phosphate coatings may vary. Some of these differences indicate a problem exists but other variations do not reflect a difference in quality.

4.8.2.1 Color. The color of the coatings can vary from gray to black. Variation in color is, by itself, not a cause for rejection and no attempt should be made to match the color of the coatings.

4.8.2.2 Rust Stained and Frozen Assemblies. Assemblies must not be phosphated as assemblies when the individual components can be treated separately. Where complete disassembly is impossible due to riveting or brazing, every precaution should be taken to prevent oil from remaining between the surfaces prior to phosphating. Special attention should be given to rinsing the solution from these areas. When treating parts to meet DOD-P-16232, a preservative compound of the water displacing type should be used after the phosphating.

4.8.2.3 Bare Areas on or Near Heated Areas (i.e. welds). These bare areas occur where oiled parts are subjected to enough heat to bake the oil but not enough to burn it off. This can be corrected by removing the oil before subjecting the part to heat or by removing the surface with the oil baked on by abrasive blasting.

4.8.2.4 Coarse Crystalline Coatings. Coarse crystalline coatings are not cause for rejection if the part meets all requirements of the specification. Unfortunately, these coatings frequently fail to give adequate corrosion protection and corrective steps are then necessary. These coatings are commonly the result of the cleaning procedure used. When alkaline cleaners are not thoroughly rinsed from the surface before phosphate treatment, a coarse crystalline coating may be produced, even when the alkaline cleaning stage is followed by abrasive blasting.

When parts are pickled prior to treatment with a phosphate process, coarse crystalline coatings may be produced even with good rinsing. (Acid pickling ahead of phosphate coating is not recommended and should never be used without the approval of the purchasing facility.)

Even with good rinsing, some cleaners result in the formation of phosphate coatings which are more crystalline than desired. There are proprietary pretreatments available which will help produce coatings with a fine crystal structure when such cleaners are used. These frequently are referred to as "conditioning salts".

4.8.2.5 White Powder on the Coating. This problem develops on parts processed by immersion but not on parts processed by spray. The phosphated work may have a white powder on the coating covering the upper surface of the work with the remaining surfaces of normal color and nature. This condition is the result of sludge from the bath depositing on the upper surfaces of the work during processing. While a light dusty deposit of sludge causes no serious difficulties, heavy deposits prevent adequate rinsing of the work surface. The most common causes for sludge depositing on the work are agitation of the sludge which has settled to the bottom of the tank due to boiling the solution or disturbing the sludge by movement of the work being processed. The first of these can be corrected with adequate temperature control and the second by removal of excess sludge (see paragraph 4.4.1.1.).

4.8.2.6 Streaks. The phosphated part may have streaks which appear to follow the flow of solution draining from the parts. These streaks may appear as rust streaks, as sandy material, or as green or gray-white material. This condition is generally the result of poor rinsing. If the water rinse following the phosphating bath is allowed to become contaminated with phosphating chemicals, streaks may occur. Streaks may also result if phosphating salts are trapped in recessed areas of the parts and allowed to drain out over the rinsed areas after removal from the rinse water.

This can be corrected in immersion processing by two methods or preferably by a combination of the two: namely, rotating the work in the rinse water to allow trapped solution to escape and/or removing the parts from the rinse water, rotating, and reimmersing. Streaks can also be formed when massive parts are being processed and the phosphate solution dries on the parts before they get into the rinse water. This can be corrected by the use of the spray rinse procedure described in paragraph 4.3.5.2.

When this problem occurs on parts processed by spray, the problem can be solved by adjusting the direction of the sprays in the water rinse and/or the use of a mist rinse of fresh water at the exit end of the spray zone.

4.8.2.7. Mottled Streaks. This problem develops on parts processed by immersion but not on parts processed by spray. The phosphated parts may have mottled streaks of extremely thin, light colored phosphate over part or all of the work surface. Streaks always are directed toward the uppermost portion of the piece as it is suspended in the phosphating solution. This difficulty is frequently encountered where alkaline cleaners are used and oil is allowed to collect on the surface of the cleaner. It is also encountered where heavy rust-preventive compounds are incompletely removed from recessed, blind or small holes, threaded parts, or between joining surfaces. The oil, grease, or rust-preventive compounds remain in these places through the abrasive blast treatment and flow out when the part is placed in the hot phosphating solution.

4.8.2.8 Scratches and Abrasions. This problem occurs primarily when treating parts to meet DOD-P-16232. When heavy parts are phosphated in a tumbling barrel or rotating screw unit, considerable battering, scratching, and abrading may occur. In such instances, every effort should be made to reduce the amount of tumbling but sufficient movement of the parts to avoid contact marks is essential. When closed tumbling barrels are used, the barrel should be filled as tightly as possible to reduce the movement of the parts during processing. It has been found that, regardless of how tightly the barrel is packed, enough movement of individual parts occurs to prevent the formation of harmful contact marks.

4.8.2.9 Fingerprints. This problem occurs primarily when treating parts to meet DOD-P-16232. Work that has been abrasive blasted in preparation for phosphating is very susceptible to fingerprints, which cause formation of very thin, light colored deposits. Even when clean cotton or rubber gloves are used, marks may be produced by the wiping action of sliding the fingers over the surface. This "wiping" action produces a thinner phosphate coating which will retain less preventive finish.

4.8.3 Failure to Meet Corrosion Resistance or Coating Weight Requirements of Specifications. When the coating appears to be uniform and shows none of the preceding faults, but fails to meet the specified requirements, the following possibilities should be investigated.

4.8.3.1 Is the bath being properly controlled as to temperature, total acid, ratio of free acid to total acid and ferrous iron (or nitrite accelerator)?

4.8.3.2 Has the bath been kept hot with little or no work being processed? If so, allow the bath to cool to below 110°F (44°C), stir thoroughly to mix the sludge with the solution, heat to operating temperature, and process freshly cleaned parts.

4.8.3.3 Has the chromate rinse been used too long a time? Prepare a fresh chromate rinse in a small container and compare the results obtained using the fresh rinse with those obtained using the production tank.

4.8.3.4 Is a silicate containing cleaner being used? Silicate containing alkaline cleaners are excellent in detergency, buffering, and ability to keep the removed solid in suspension. A problem can develop with these cleaners due to absorption of carbon dioxide from the air, burner exhausts, or acid introduced into the cleaner. A silicate containing cleaner contaminated in this manner may deposit a jell-like material which may not be visible on the surface of the parts, which is not removed in the rinse stage. The presence of this jell prevents the formation of a satisfactory phosphate coating. If this is suspected, it can be confirmed by taking a part which has been cleaned and rinsed, dipping the part in a solution containing approximately 5% by weight of sodium hydroxide in water for one minute, rinsing it in clean water, and finally processing it through the remainder of the phosphate system. If this corrects the problem, discard the cleaner solution (observing local waste disposal regulations) and prepare a fresh cleaner solution. Eliminate or reduce the input of carbon dioxide or other acidic material into the cleaner. If the problem continues, change to a silicate free cleaner.

4.8.3.5 Drawn or Pressed Parts. These parts, including metal stampings, are difficult to phosphate because of the nature of their surface. Such parts must be cleaned mechanically, preferably by abrasive blasting, in order to remove the surface stresses developed in their manufacture. Highly caustic alkaline cleaners and alkaline derusting must be followed by abrasive blasting, abrasive tumbling, treatment with a metal conditioner, or wiping to ensure a smooth phosphate coating.

4.8.3.6 Are the parts clean before entering the phosphating solution? A cleaning solution which has been satisfactorily removing the soil from the work may cease to do so. Two reasons for this are:

(a) A change in the soil present on the work and

(b) An accumulation of soil in the cleaner until it can no longer remove the soil from the work.

Try cleaning parts in a fresh cleaner solution. If this is successful, discard old solution. If the fresh solution does not remove the soil, other cleaning procedures should be investigated to find one which will remove the soil. The possibility of changing the soil to one which is more easily removed should also be investigated.

If it is necessary to discard a cleaner solution, make sure of compliance with all waste disposal regulations.

4.8.3.7 Low Coating Weights. Phosphate coating weights below the minimum specified can be caused by several conditions including those listed below:

(a) Excessive use of "conditioning salts" in or following the cleaner.

(b) Presence of surfactants or pickling inhibitors in the phosphating solution.

(c) When steam is used for heating, many plants use volatile inhibitors in the boiler water to protect the steam lines from corrosion. A loose connection or a leaking steam coil can allow these inhibitors to get into the cleaner, the water rinse (before the phosphate), or the phosphate solution. When present, the inhibitors can interfere with the formation of a satisfactory coating. The supplier of your boiler compound can provide chemicals which permit you to control the corrosion in the steam lines without the use of volatile inhibitors.

4.8.3.8 Determine if the poor corrosion resistance is due to poor corrosion resistance of the phosphate coating or poor corrosion resistance of the supplementary finish. Is the correct amount of finish being applied to the parts?

When treating parts to meet DOD-P-16232, the weight of the finish can be determined as follows: weigh a finished part, remove the finish with a solvent, dry, and reweigh the part. The difference in the two weights is the weight of the finish. If the specified amount of finish is present, compare parts finished with the material being used in production with parts finished with a freshly prepared finish. The finish may have been contaminated or may have lost some of its inhibitors.

When treating parts to meet TT-C-490, the paint should be checked for film thickness and the curing procedure should be checked. If the preceding appears to be correct, finish a part with a sample of paint known to give proper results.

4.8.3.9 Chromate Stains. Chromate stains have the general appearance of rust. These stains occur where the chromate solution is allowed to accumulate and dry on the part. They seldom cause any problem when the water used in the chromate rinse contains no dissolved salts. When the water does contain dissolved salts, these are also concentrated in the area of the chromate stain and can accelerate the formation of rust. This problem can be corrected by using deionized water to build up and replenish the chromate rinse solution or by removing any accumulation of the chromate rinse solution before it dries.

4.8.3.10 Effect of excessive heat on the corrosion resistance of the coating. This problem is related to coatings for DOD-P-16232. Zinc phosphate coatings should not be exposed to temperatures in exess of 225°F (105°C) for more than 15 minutes. Manganese phosphate coatings should not be exposed to temperatures in excess of 375°F (190°C) for more than 15 minutes. Longer exposures at these temperatures or shorter times at higher temperatures can lower the corrosion resistance of these coatings.

> NOTE: DOD-P-16232F (7 November 1978) allows parts with a zinc phosphate coating to be heated 8 hours at 207-225°F (97-107°C) to relieve hydrogen embrittlement, but it will also reduce the corrosion resistance of the coating. The alternative method of holding the parts for 120 hours at room temperature is the preferred method of relieving hydrogen embrittlement in phosphated parts.

4.8.3.11 Contaminated Grit Used for Abrasive Blasting. If the grit being used for abrasive blasting becomes contaminated with grease or oil, the oil and grease will be driven into the surface during blasting and satisfactory coatings will not be produced. Oil and grease can get into the grit if oily or greasy parts are blasted or through leaking seals in the equipment. If the grit has become contaminated, the source of the contamination must be eliminated and the grit replaced with clean material.

4.8.3.12 Lime Drawn Wire. This problem occurs primarily on parts being treated to meet DOD-P-16232. Many nuts and bolts are made from heavy wire or rod which has been drawn using lime as a lubricant. When parts made from such wire are cleaned, it is usually necessary to include a pickle in the cleaning system. If sulfuric acid is used, insoluble calcium sulfate deposits on the work and interferes with subsequent phosphating. These parts can be successfully cleaned if a hydrochloric acid pickle is used. The calcium chloride which is formed is soluble and readily removed in the rinse stages.

4.8.3.13 Case Hardened Parts. This problem also is one encountered on parts being treated to meet DOD-P-16232. The problem generally occurs when phosphate coatings are used to replace plating. The tempering operation in the heat treat is frequently omitted when the parts are to be plated as it is necessary to bake the parts after plating to relieve hydrogen embrittlement. If the tempering operation is omitted prior to the phosphating operation, the coatings produced will not provide the expected corrosion resistance. The tempering operation is necessary to give the required physical properties as well as to permit proper formation of the phosphate coatings.

4.8.3.14 Cast Iron and Alloys Which Are Difficult to Treat. This is a problem when treating parts to meet DOD-P-16232. Cast parts such as malleable, pearlitic malleable, or cast iron, cast steel and some alloys which are difficult to treat may fail to meet corrosion resistance requirements. Cast iron, steel, or pearlitic malleable iron has a burned-in and sand-cast surface or high silicon alloy cast surface, which must be given a very thorough blasting treatment to permit the phosphate coating to be formed. In addition, these metals may not completely phosphate in the time normally required to phosphate steel. In the treatment of these materials, a low free acid phosphating solution gives a considerable advantage. Superior corrosion resistance can be obtained on cast parts as well as other steel parts by using either Procedure A or Procedure B.

Procedure A

(a) Abrasive blast all parts.

(b) Plan work schedules so parts made of malleable or cast iron will be treated immediately after a period during which the phosphate solution is idle and has been allowed to cool to room temperature.

(c) Add to the solution, prior to the shut down period, 0.5 pound per 100 gallons (75 grams per 100 liters) of either zinc carbonate (for zinc-base solutions) or manganese carbonate (for manganese-base solutions) and stir thoroughly.

(d) Turn on the heat to the tank. When the solution temperature reaches 170°F (75°C), place the work in the solution and raise the temperature to 205°F (95°C) as quickly as possible. Allow the work to remain in the solution after reaching the operating temperature for at least 45 minutes.

Procedure B

(e) Abrasive blast all parts.

(f) Use zinc or manganese carbonate to raise the ratio of total acid to free acid to 7.5 to 1 or higher.

(g) Process a large load of parts (a large surface area).

(h) Process the critical parts.

4.8.3.15 Heat Treated Parts. Satisfactory phosphate coatings may not form on parts if oil was present when the parts were subjected to heat during the heat treatment. If oil is present or suspected of being present on parts which are to be heat treated, try removing the oil from some parts, heat treat these parts and follow them through the phosphating operation to determine whether there is an improvement in the coatings produced.

4.8.4 Paint failures - blistering and/or spotting paint adhesion. The paint adhesion failure referred to here occurs when the adhesion is checked with tape and the paint pulls away in spots. This type of failure is normally the result of a blister having formed under the paint film destroying the adhesion of the paint to the metal. To prevent this type of paint failure, it is necessary to avoid those conditions which cause blisters to form.

Blisters form under paint when water soluble salts are trapped under the paint film and the paint is exposed to humid conditions. Water vapor can pass through the paint film and, if a water soluble salt is present, a solution is formed which lifts the paint and forms a blister. When checked for adhesion the paint is lifted from these areas even if the blister is no longer evident.

To prevent this type of failure, it is necessary to make sure that no water soluble salts are on the surface.

4.8.4.1 Salts Left by Poor Rinsing. If the rinse solutions are allowed to become contaminated or trapped solutions are not completely removed, the residue remaining on the surface may contain water soluble salts which can cause blistering. For corrective measures see 4.8.2.6.

4.8.4.2 Contaminated Chromate Solutions. The chromate solution is normally dried on the surface of the phosphate coated parts. If the chromate solution is prepared with water containing soluble salts, these salts will accumulate as water is added to replace that lost by evaporation. The amount of water soluble material left on the parts will increase as these salts accumulate. In areas of the parts where the chromate solution collects in streaks, puddles, or beads, this blistering problem can be of major importance. Corrective steps are of three types:

(a) Avoid allowing streaks, puddles, or beads of chromate solution to dry on the parts.

(b) Use deionized water to build up and replenish the chromate rinse.

(c) Follow the chromate rinse with a rinse of deionized water. If this is done, it is necessary to use specially formulated chromate rinses. See 4.3.6.3.

4.8.4.3 Handling. Soluble salts can also be left on the parts when they are handled with bare hands or dirty gloves.

5. BLACK OXIDE COATINGS

5.1 Introduction

5.1.1. General. This type of coating is produced by converting the surface of iron and steel parts to black iron oxide (Fe_3O_4) with a thickness of less than 0.0001 inch (0.00025 cm) according to MIL-C-13924. This coating affords very limited corrosion protection. The alloys that are given MIL-C-13924 Class 3 and 4 coatings have little need of added corrosion protection. The metals that are given a MIL-C-13924 Class 1 coating can have the corrosion resistance improved by the application of a rust-preventive oil.

Due to the fact that these coatings show only a slight build-up on the parts, they are suitable for moving parts that cannot tolerate a heavier coating.

5.1.2 Characteristics. The coatings produced by all three classes of MIL-C-13924 are similar in composition and appearance. The three classes use different chemicals to treat the alloys.

5.1.2.1 Class 1. Class 1 coatings are formed in an alkaline oxidizing bath on wrought iron, plain carbon, low alloy steels and cast and malleable irons.

5.1.2.2 Class 3. Class 3 coatings are formed in a fused salt bath on corrosion resistance steel alloys which are tempered at 900°F (482°C) or higher.

5.1.2.3 Class 4. Class 4 coatings are formed in an alkaline oxidizing bath on 300 series corrosion resistant steel alloys.

5.1.3 Safety Precautions. The safe handling of these chemicals requires caution due to different hazards at different phases in their operation.

5.1.3.1 The baths are operated at temperatures ranging from 250°F (121°C) in Class 4 baths to 850°F (455°C) in Class 3 baths. Contact with these baths can cause severe burns. Moisture on parts being introduced into the operating baths can turn to steam and cause the hot chemicals to splash or erupt and anyone nearby can be burned. Operators should wear protective clothing and no other personnel should be allowed in the vicinity of the operating bath.

5.1.3.2 The salts in the baths can cause chemical burns as well as thermal burns. In case the hot salts are splashed on anyone, the area contacted by the chemical should be flushed immediately with water to remove the salts and the affected area should be kept in water or kept covered with wet compresses which are constantly changed until medical attention can be obtained. If anyone should contact the unheated salts, the area of contact should be washed with water immediately. If there is evidence of skin irritation, medical help should be obtained.

5.1.3.3 The baths can solidify when allowed to cool. When heat is applied to a solidified bath there is danger of an eruption of molten salt through the solid crust. Class 1 and Class 4 baths will normally not solidify at room temperature but may solidify at lower temperatures or if allowed to become more concentrated than normal. Class 3 baths will solidify at room temperature and can be expected to erupt through the crust when being heated. This type of eruption may also occur with the other baths if they have cooled enough to cause solidification.

5.1.3.4 When cold, the Class 3 salts must be handled as toxic hexavalent chromium compounds. The Class 1 and 4 compounds are caustic with oxidizing agents and should be handled according to the instructions and cautions furnished by the supplier.

5.1.4 Disposal. The processing baths may have to be discarded for various reasons such as equipment repair or discontinued operations. The chemicals must be treated before disposal and the rinse waters may contain amounts of salts which will require that they be treated in order to meet the local waste disposal regulations.

5.1.4.1 Disposal of the Operating Baths. The Class 1 and 4 baths are normally "slushy" at room temperature and should be diluted with at least an equal volume, and preferably three or four volumes, of water before being treated for disposal. Class 3 baths are solid at room temperature. These baths are best handled by ladling them out, while hot, into shallow trays and allowed to cool in thin enough layers that they can be broken up without tools. THE SOLID SALT SHOULD NEVER BE STRUCK WITH A TOOL TO BREAK IT OR FOR ANY OTHER PURPOSE. The small pieces can then be dissolved in water and the solution treated for disposal.

5.1.4.2 Treatment for Disposal, Classes 1 and 4. The alkaline portion of these baths will have to be treated to lower the pH to an acceptable range in all locations. The oxidizing portion of the baths may require treatment depending upon the oxidizing chemical used and the local regulations.

5.1.4.3 Treatment for Disposal, Class 3. The waste disposal regulations will normally require that the hexavalent chromium be reduced to trivalent chromium and that the trivalent chromium be precipitated and removed before discharging the solution to the sewer.

5.1.5 Embrittlement. Embrittlement is seldom a problem with the black oxide treatments but can become a problem with high strength steels.

5.1.5.1 High strength steel (Rockwell C 40 or greater hardness) may fail due to "caustic embrittlement" if the part is processed in the black oxide bath under internal or applied stress.

5.1.5.2 Treatment of High Strength Steel. When specifying the treatment of steel parts having an ultimate tensile strength of 200,000 psi (1379MPa) or above, the procuring agency may require that the parts be baked at 375° ± 25°F (190° ± 14°C) for three hours or more or given an equivalent embrittlement relief treatment after the application of the oxide coating and/or specify that the parts be tested for embrittlement. If an embrittlement relief bake is required, it shall follow the chromate rinse and precede the supplementary preservative treatment.

5.2 Equipment

5.2.1 Processing Tanks. The tanks used to contain the black oxide chemicals are heated by gas or by immersion electric heaters. The high cost of heating these tanks makes the use of thorough insulation imperative. They should be installed on a concrete slab and surrounded by a curb (or installed in a non-combustible tray) providing adequate area to catch any drippings and deep enough to contain the chemicals if a tank should fail.

5.2.1.1 Gas Heated Tanks. Heat is supplied to gas heated tanks by burners mounted beneath the tank (Figure 10). Greater heat efficiency can be obtained by conducting the products of combustion around the sides of the tank using a second wall surrounding the tank. The products of combustion are then vented to the flue. The tank should be surrounded by insulation to minimize heat loss.

5.2.1.2 Electrically Heated Tanks. The immersion electric heaters must have adequate capacity to heat the baths to operating temperature in a reasonable time. What is reasonable will vary with the production requirements. The heaters should be protected from mechanical damage by a protective grating.

5.2.2 Water Diffuser. This applies to Class 1 and 4 only as water is not added to Class 3 baths. The addition of water to Class 1 and 4 baths can cause spattering due to the rapid conversion of the water into steam by the hot bath. Water can be safely added by adding it through a pipe with small holes in it. The pipe should be mounted along the back side of the tank with the holes directed toward the back wall. This allows a thin film of water to flow down the back wall into the bath away from the operator.

5.2.3 Rinse Tanks

5.2.3.1 Mist Rinse. If the use of a mist rinse is found to be necessary (5.3.2.3.3), it can be supplied either from a hand held nozzle or from nozzles mounted a short distance above the bath surface. The nozzles used must supply only a small amount of water and must break up the water into extremely small droplets to prevent spattering of the hot bath.

5.2.3.2 Warm Water Rinse Tanks. The first rinse following the black oxide treatment is overflowed at a rate which permits removal of the salts but may allow the water to be warmed by the hot parts. The tanks should be equipped with drains to permit emptying when they become excessively contaminated. Provision for heating the rinse used after the Class 3 treatment is essential as this rinse must be at about 190°F (88°C) for proper removal of the salt. (If necessary to obtain the required temperature, the overflow can be discontinued temporarily.)

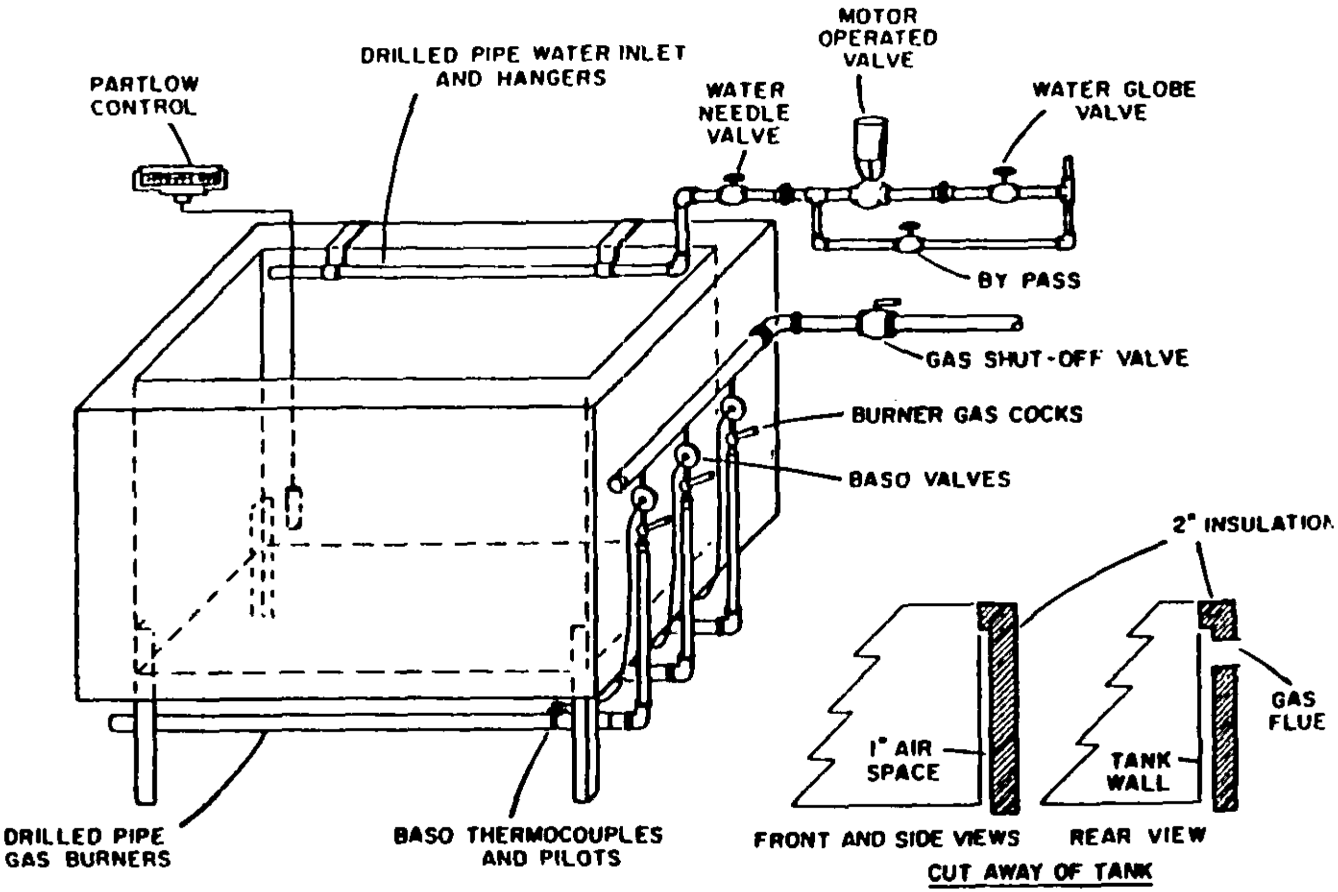


FIGURE 10: BLACK OXIDE TANK

5.2.3.3 Cold Overflowing Rinse Tanks. These tanks should be equipped with an overflow weir and a drain. The water supply to the tank should enter on the side opposite the overflow and should be delivered close to the bottom of the tank using a vacuum breaker or other means to prevent siphoning water from the rinse tank into the water line. Heating coils need not be installed in these tanks.

5.2.4 Chromate Rinse Tank. The chromate rinse tank is constructed of mild steel and can be heated by gas, electric heaters, or steam.

5.2.5 Thermometers and Thermocouples. The black oxide processing baths must be maintained at the specified temperature. It is recommended that a dial type thermometer be mounted where it can be readily seen and that the diameter be at least 5 inches (12.5 cm) for ease of reading. The thermocouple bulb should be mounted in a corner of the tank and kept away from the tank wall.

To relieve the operator, the thermocouple temperature control is connected to a motor-operated water valve which allows water to be fed automatically into the boiling solution whenever the control calls for it (i.e., whenever the temperature rises above the set operating temperature).

Because of the importance of close temperature control in the black oxide processes, particularly of Class 1, the accuracy of the indicating thermometer should be checked frequently. A reference thermometer should be available to check the indicating thermometers. A mercury thermometer can be used for this purpose in Class 1 and 4 baths but a thermocouple should be used in Class 3 baths.

5.2.6 Racks, Tumbling Barrels, and Baskets. The work being treated will usually be placed in a tumbling barrel, a rack, or an open mesh basket made of mild steel (do not use stainless steel). These should be constructed to allow good drainage. They must be welded, never soldered, and shall contain no tin, copper, zinc, lead or other non ferrous metals.

5.3 Processing

5.3.1 Processing Sequences. After the parts to be processed are cleaned of all soil, etc., rinsed and most or all water removed, they are immersed in the processing bath for the specified time. Following the blackening treatment they are given a warm or cool overflowing water rinse, except Class 3 which is given a hot water rinse prior to the cool rinse. The water rinse is followed by a chromate rinse and the parts are dried and, if specified, dipped in oil. See Figure 11.

5.3.2 Procedures for Class 1 and 4 Alkaline Oxidizing Processes

5.3.2.1 Preparation of the Solution. Determine the volume of solution necessary to fill the tank to the working level. This is normally about 6 inches (15 cm) below the top of the tank. More space may be required when processing long parts in a deep tank. Place one third of this volume of cold water in the tank. Slowly add about one third of the required amount (as recommended by the supplier of the chemical) of the black oxide chemical required for the volume at operating level while stirring vigorously to prevent caking.

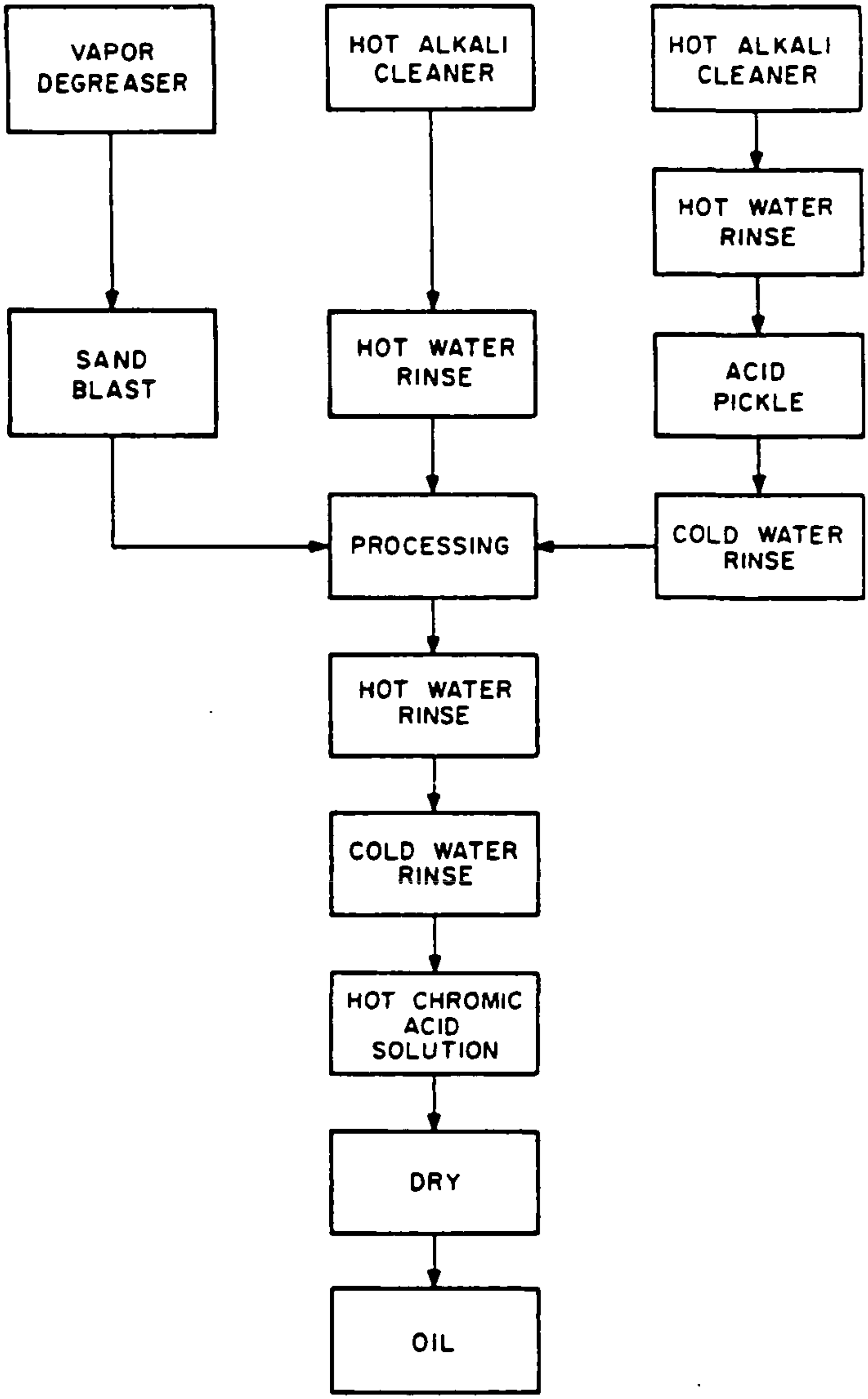


FIGURE 11 : BLACK OXIDE PROCESS

CAUTION: Wear goggles, rubber apron, rubber gloves and face shield. Avoid adding large amounts or lumps of chemical. Avoid causing the solution to splash or adding chemical rapidly enough to cause the temperature of the bath to exceed 200°F (93°C).

When the chemical is completely dissolved add an equivalent amount in the same water. Continue until the required amount has been added. Add cold water to bring the solution up to operating level. While stirring, heat the solution slowly to boiling and adjust to the specified operating temperature. See 5.3.2.2.1.

5.3.2.2 Processing. The clean work must be completely immersed for the specified time in the processing solution which is boiling at the correct temperature. The work should be lowered into the processed bath slowly to allow any water remaining on the parts to evaporate before contacting the hot bath. When processing in Class 3 baths, the parts must be completely dry. Any water contacting the hot bath will be transformed into steam and cause spattering of the hot chemical. While parts may be wet when introduced into Class 1 and 4 baths, special care must be used when immersing tubular parts so that the water inside the tubes does not erupt towards the operator.

5.3.2.2.1 Solution temperature control. The correct operating temperature may vary depending upon the chemical used and the metal being treated but Class 1 baths are normally operated at 285 to 290°F (140 to 143°C). Temperatures over 300°F (149°C) tend to build up red iron oxide in the bath and on the processed parts. To lower the boiling point, add water to the bath using a water diffuser such as that described in 5.2.2. To raise the boiling point, add more chemical by adding it slowly over the surface of the bath to avoid localized boiling and splattering of the solution.

CAUTION: Never dissolve the chemical in water to make additions. This will cause eruptions.

5.3.2.2.2 Ventilating system. A good system for removal of fumes is required with all three types of blackening baths. The recommended system for Class 1 and 4 baths is similar to that for phosphating baths (see 4.2.4). The Class 3 baths should be totally enclosed and good ventilation can be obtained with less air movement.

5.3.2.2.3 Excessive boiling and splashing. Excessive boiling and splattering may occur in a freshly prepared bath or when long parts are being processed in a deep tank. When the excessive boiling is caused by a newly prepared bath, the problem can be controlled by processing smaller loads less frequently until the boiling no longer is excessive. When the excessive boiling is caused by long parts in a deep tank, it will be necessary to allow more free board between the top of the tank and the solution level.

5.3.2.2.4 Sludge removal. Insoluble iron oxides will settle in the bottom of the processing tank as sludge. This sludge must not be allowed to accumulate. The common method for removing this sludge is to lift it out with a hoe or similar tool.

5.3.2.2.5 Smut on the work. The insoluble oxides will accumulate as a scum on the surface of the tank and if carried out on the work will appear as smut. This scum can be removed with a tool similar to a steel dust pan. Suspended sludge can also settle on the work and appear as smut. If this happens the sludge should be removed as described in 5.3.2.2.4.

5.3.2.2.6 Precautions. Non ferrous metals should not be introduced into these baths as they may contaminate the baths and interfere with the formation of the desired coating. Some metals will cause violent boiling of the processing solution which can result in injury to the operators and by-standers. If the baths become contaminated to a point where satisfactory coatings are not obtained, the chemical suppliers have proprietary chemicals which will restore the baths to operating condition in most cases.

5.3.2.3 Rinsing

5.3.2.3.1 Warm water rinsing. When the work is removed from the processing bath it should be transferred to the overflowing warm water rinse as quickly as possible and the parts should remain in the rinse long enough to lower their temperature sufficiently to prevent off-color (red) from developing. Rinsing is improved by agitation of the parts and/or the rinse water and raising the parts out of the water and reimmersing them.

5.3.2.3.2 Disposal of the warm water rinse. The warm water rinse must be discarded before it becomes too contaminated to adequately rinse the parts. The frequency of discarding will depend upon the amount of blackening salts carried into it. The contaminated rinse must be treated to meet the local waste disposal regulations before being discharged to the sewer. See 5.1.4.2 or 5.1.4.3.

5.3.2.3.3 Mist rinsing. If problems arise due to the processing solution drying on the parts before immersion in the warm water, the use of a fine mist of water sprayed on the parts can overcome this problem (see section 5.2.3.1). A very fine mist must be used to avoid drops of water causing steam eruptions at the bath surface and to avoid dilution of the bath which would lower the boiling point.

5.3.2.3.4 Cold water rinse. Following the warm water rinse the parts are rinsed in a cold, overflowing water rinse to remove the last traces of the blackening salts. Agitation of the part and/or the water and removal and reimmersion of the part will improve the rinsing.

5.3.2.4 Chromate Rinsing. After the cold water rinse the parts are immersed in a chromate rinse as described in section 4.5.

5.3.2.5 Drying. The chromate rinsed parts must be dried. The use of a hot chromate rinse makes it possible for many parts to dry spontaneously. If necessary the remaining beads of moisture can be removed with dry, clean compressed air, by heating in a air circulating oven or by dipping into a water-displacing oil.

5.3.3 Procedures for Class 3 Fused Salt Oxidizing Process

5.3.3.1 Preparation of the Bath. The required amount of salt will depend upon the size of the pot which should be no larger than necessary to hold the parts being treated and allow approximately 6 inches (15 cm) of free board between the bath surface and the top of the pot. The pot is initially charged by placing approximately one quarter of the required amount of potassium dichromate in the pot and heating it until it is liquid. Additions of similar amounts should be made until the desired operating level is reached by waiting until each addition has liquified before making the next addition.

The molten salt is then heated to the operating temperature of 825° to 850°F (440° to 455°C).

CAUTION: When reheating the solidified bath, the furnace door must remain closed until after the eruption of the liquid through the top crust of the bath. This will occur at approximately 450°F (232°C) The furnace door must not be opened except during the process of inserting or removing work. During these operations, an apron, long sleeved clothing, gloves, and a hood-type face shield must be worn. Every precaution should be taken to ensure that the work is dry before it is immersed in the molten salt.

5.3.3.2 Cleaning. All grease, oil, scale, and shop dirt must be removed before processing. The clean parts must be completely dry before introduction into the molten salt. The preferred method of ensuring a completely dry surface is to use abrasive blasting as the final cleaning step. Another method is to hold the parts near the pot for the time required to evaporate the last traces of moisture.

5.3.3.3 Processing. The clean dry parts are immersed in the molten salt bath for 30 minutes, removed from the pot, allowed to drain and air cool for 8 to 10 minutes.

CAUTION: Any moisture will create a hazardous spraying or splattering. Caution must be exercised to avoid the hazards of molten drippings when work is transferred from the furnace to the cooling fixture.

5.3.3.4 Hot Water Rinse. After cooling, the parts are rinsed in non-overflowing hot water at 190°F (88°C). Rinsing is improved by agitation of the parts and/or the water and by removal and reimmersion of the parts.

5.3.3.4.1 Disposal of the hot water. Potassium dichromate will accumulate in this rinse and eventually adequate removal of the salts will no longer be possible. The rinse should be discharged before this point is reached. Before discharging this solution to the sewer, it must be treated to meet the local waste disposal regulations. See 5.1.4.3.

5.3.3.5 Cold Water Rinse. To remove the final traces of the blackening salts, the parts are rinsed in a cold overflowing water rinse, after the hot water rinse. Rinsing is improved by agitation of the parts and/or the water and by raising the part out of the water and reimmersing it.

5.3.3.6 Chromate Rinse. After the cold water rinse the parts are immersed in a chromate rinse as described in 4.5.

5.3.3.7 Drying. See 5.3.2.5.

Custodians:

Army - MR
Navy - SH
Air Force - 20

Review activities:

Army - AR, AT, GL, ME,
Navy - AS, EC, OS, YD
Air Force - 99

Users:

Army - AR, AT
Navy -AS
Air Force - 12, 70, 82, 84

Preparing Activity:

Army - MR

Project No. MFFP-0010

WP ID #0637A/DISC 0028A (FOR AMMRC USE ONLY)

Bibliography

John Von Wazer	Phosphorous and Its Compounds Vol. 2 Interscience Publishers, New York, NY
Dale Cheever	"The Chemistry of Phosphate Coatings" Society of Automotive Engineers, May 1970
W. R. Cavanagh	"The Evaluation of Phosphate Coatings for Corrosion Protection and Appearance" Society of Automotive Engineers, May 1970
	"How Do Phosphate Coatings Reduce Wear on Moving Parts" Society of Automotive Engineers, Jan. 1967

Other Sources

Metals Handbook Vol. 2, 8th Edition
American Society of Metals
Metals Park, Ohio

Metal Finishing Annual Guidebook and Directory Issue
Metals and Plastics Publications
Hackensack, NJ

Industrial Finishing
Hitchcock Publishing Co.
Wheaton, IL

Index

Index (Continued)

Index (Continued)

Index (Continued)

Appendix

Examples of the use of Phosphate and Black Oxide Coatings on Military Parts.

Phophate Process:

M-16-A1	(Barrel Assembly, Trigger, Sear)
M-60	Machine Gun
M-203	Grenade Launcher
M-85	Machine Gun 50 Cal
M 2	Machine Gun 50 Cal
M-240	Machine Gun 7.62 MM
SAWS	Squad Automatic Weapons System
Navy standard missile motion chamber	
Mark 32 torpedo air flask	
Metallic belt links	
Grenades	42 MM
Hand Grenades	
Projectiles	

Black Oxide Process:

Cylinder, rifle, M-14
Spring, safety, M-14
Nut, cylinder, M-60
Extension, gas, M-60
Spring, catch, M-60
Shield, seed mechanism, M-60

INSTRUCTIONS: In a continuing effort to make our standardization documents better, the DoD provides this form for use in submitting comments and suggestions for improvements. All users of military standardization documents are invited to provide suggestions. This form may be detached, folded along the lines indicated, taped along the loose edge *(DO NOT STAPLE)*, and mailed. In block 5, be as specific as possible about particular problem areas such as wording which required interpretation, was too rigid, restrictive, loose, ambiguous, or was incompatible, and give proposed wording changes which would alleviate the problems. Enter in block 6 any remarks not related to a specific paragraph of the document. If block 7 is filled out, an acknowledgement will be mailed to you within 30 days to let you know that your comments were received and are being considered.

NOTE: This form may not be used to request copies of documents, nor to request waivers, deviations, or clarification of specification requirements on current contracts. Comments submitted on this form do not constitute or imply authorization to waive any portion of the referenced document(s) or to amend contractual requirements.

(Fold along this line)

(Fold along this line)

DEPARTMENT OF THE ARMY

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE $300

BUSINESS REPLY MAIL
FIRST CLASS PERMIT NO 12062 WASHINGTON D C

POSTAGE WILL BE PAID BY THE DEPARTMENT OF THE ARMY

Army Materials & Mechanics Research Center
Attn: AMXMR-SMS
Watertown, MA 02172-0001

STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

(See Instructions – Reverse Side)

1. DOCUMENT NUMBER	2. DOCUMENT TITLE

3a. NAME OF SUBMITTING ORGANIZATION

b. ADDRESS (Street, City, State, ZIP Code)

4. TYPE OF ORGANIZATION *(Mark one)*

☐ VENDOR

☐ USER

☐ MANUFACTURER

☐ OTHER *(Specify)*: ______

5. PROBLEM AREAS

a. Paragraph Number and Wording:

b. Recommended Wording:

c. Reason/Rationale for Recommendation:

6. REMARKS

7a. NAME OF SUBMITTER *(Last, First, MI)* – Optional

b. WORK TELEPHONE NUMBER *(Include Area Code)* – Optional

c. MAILING ADDRESS *(Street, City, State, ZIP Code)* – Optional

8. DATE OF SUBMISSION (YYMMDD)

DD FORM 82 MAR 1426

PREVIOUS EDITION IS OBSOLETE.