BY ZHANG SHENG-LIN*,[1] ZHANG XIAO-LIN[2] ZHANG MING-MING[3]
1 CHEMISTRY & ENVIRONMENTAL SCIENCE COLLEGE, HENAN NORMAL UNIVERSITY, XINXIANG, HENAN, 453007, CHINA; 2 SCHOOL OF CHEMISTRY AND CHEMICAL ENGINEERING, HENAN UNIVERSITY OF TECHNOLOGY, ZHENGZHOU, HENAN, 450052, CHINA; 3 TECHNICAL INSTITUTE OF PHYSICS AND CHEMISTRY, CHINESE ACADEMY OF SCIENCES BEIJING 100080, CHINA

Effects of Alkaline Cleaners and Cleaning Methods on the Phosphate Coating Weight

The effects of some alkaline cleaners and cleaning methods on the phosphate coating weight are discussed in this paper. Specifically, the morphologies of the phosphate coatings were investigated through scanning electron microscopy (SEM). Single alkaline cleaners are not advantageous to formation of the fine phosphate coatings. Additives, such as sodium ethylene diamine tetracetate, sodium glycerophosphate, sodium tripolyphosphate and trisodium phosphate in compound alkaline cleaners can mitigate alkali corrosion of metal, resulting in the surface roughness of metal to be decreased. The coating weight of phosphate coating formed on the sample cleaned by compound alkaline cleaners is lighter than it would be for single alkaline cleaners. Compared with immersion cleaning, spray cleaning contributes to the formation of the tiny phosphate crystal grains.

Phosphate coatings are produced on ferrous and nonferrous metal surfaces, and are composed of tiny crystals of iron, zinc, or manganese phosphates. These inorganic coatings produced on metal surfaces retard corrosion and promote better paint bonding. Phosphate coatings are formed after precleaning in a combination bath known as a phosphating solution. [1-3] Phosphate coatings are generally used by the metal finishing industry for the following reasons: 1.) to provide a base for bonding organic finishes such as paints, lacquers, plastics, adhesives, etc.; 2.) to provide a base of oils, waxes, and rust preventives to reduce metal corrosion; 3.) to provide a base for lubricant on bearing surfaces to reduce friction; and 4.) to aid in drawing and forming of metals. [4]

It is often said, and widely believed, that the most important step in any phosphating process is the cleaning stage. The cleaning is designed to remove oils, dirt, and other soils that may interfere with the development of a good-quality phosphate coating or cause surface defects. If the cleaning does not fulfill its function, then the subsequent steps in the phosphating process will not adequately protect the metal surface.

There are four general ways to remove oils, dirt, and other soils from the metal surface: 1.) mechanical action; 2.) detergency; 3.) solvent activity; and 4.) chemical reaction.[5] Mechanical action is achieved by the impingement on the metal surface by either massive quantities of solution or through the use of extreme pressure. In severe cases, actual contact with brushes may be required. In any case, physical contact with the soil affects its removal. Mechanical action coupled with detergency forms the basis for soil removal in a phosphate cleaning process.[6] Detergency is derived from cleaner additives, which emulsify and actually lift the soil from metal surface and then disperses it in the main body of the cleaner. This typically does not change the surface characteristics of the metal. [7]

Soils can also be removed through the use of a solvent cleaner. Such a cleaner dissolves or softens the soil, thereby removing it from metal surface. Solvent cleaner was traditionally done, but it has largely been supplanted by modern solvent/water or alkaline cleaners because of the environmental and health hazards associated with solvent cleaner. Chemical reactions can be utilized in cleaning by choosing cleaner constituents, which react with the soil, so that it is lifted and removed from metal surface through this reaction. Highly caustic additives in cleaners serve this function.

The cleaners used in the metal finishing industry today can be assigned to one of three general categories: neutral cleaners, acid cleaners, and alkaline cleaners. The real workhorse today, prior to the phosphating operation, is an alkaline cleaner. These are versatile enough to effectively clean the metal surface by lifting the soil up and dispersing it into the main cleaner body.

The phosphating process has certain prerequisites to achieve maximum benefits. In order to provide for the development of small, tight crystal formation, and to get

---

*Corresponding author: Chemistry & Environmental Science College, Henan Normal University, Xinxiang, Henan, 453007, China.
Tel.: +86-373-3325824.
E-mail address: zslhnxx@yahoo.com.cn.

improved paint adhesion and control the coating weight,[8,9] incoming surfaces of the metal should be free of soil and uniformly active.

Many authors have studied pretreatment processes on steel and its alloys.[10-15] Tang et al.[16] have used the EIS method to investigate the performance of the pretreatments of cold rolled steel and hot-dipped galvanized steel. The corrosion resistance and adhesion of the conversion coatings on hot rolled steel was correlated by using different test methods. However, there has been nothing specific undertaken on the phosphate coating weight.

The purpose of this paper is to evaluate the effect of different alkaline cleaners and cleaning methods on the coating weight of phosphate coating formed on steel.

Experimental. The substrate material used in this study was a carbon steel (1015) with the specimen size of 20×30×2mm. The chemical compositions of the material are given in Table 1.

Because of the existence of the various soils, rusts and iron oxide scales on the samples surfaces, the samples surfaces were mechanically polished with SiC sandpaper (up to 1200 grit) in order to exactly evaluate the effect of the different alkaline cleaners and cleaning methods on the coating weight of phosphate coating. After polished, all samples were ultrasonically cleaned in acetone and methanol and dried in a warm air stream; then the polished samples were smudged by the manmade greasy dirt. Subsequently, these smudged samples were degreased in different alkaline cleaning solutions and rinsed. Afterwards, a water break test to determine cleanliness of surface was conducted. Finally, they were dipped in the phosphating solution for 10 min, at 35±2.

C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Fe
0.118	0.023	0.310	0.020	0.016	0.024	0.028	0.002	≤.25	Balance

Table 1 The Composition of carbon steel (1015) (in *wt%*)

The coating weight was measured according to equation 1:

$$W\,(g/m^2)\ \frac{W_2 - W_1}{S} \qquad (1)$$

Where W is the phosphate coating weight (g/m2), W2 is the sample weight (g) after phosphating, W1 is the sample weight (g) before phosphating, and S (m2) is the surface area of the sample. The composition of phosphating solution is shown in Table 2. The composition of manmade greasy dirt is shown in Table 3.

The coating surface was observed using scanning electron microscopy (SEM) with a field emission gun operated at 30 kV.

Component	content (g/l)
ZnO (98%)	25
H_2SO_4 (85%)	23
HNO_3 (65%)	45
H_2O	70

Table 2 The composition of phosphating solutions

Component	content (in *wt%*)
Lanolinum magnesium soap	15
Barium alkysulfonate	15
Vaseline	30
20# lubrication oil	25
Al_2O_3	15

Table 3 The composition of greasy dirt

RESULTS AND DISCUSSION

3.1 Single alkaline cleaner. Alkaline cleaners based on sodium hydroxide are very economical and the most common method of soil removal for metal preparation prior to the application of phosphate coating. Alkaline cleaners apply specifically to the soils that contain carboxylic acid and ester functionality that can react with alkaline cleaning media, because they can turn these soils into soap[17] (shown in equation 2) and make these soils dissolve or suspend in cleaning solution.

$$(RCOO)_3C_3H_5 + 3NaOH \xrightarrow{\text{At certain temperature}} 3RCOONa + C_3H_5(OH)_3 \qquad (2)$$

The components of alkaline cleaner mainly include hydroxides (sodium hydroxide, potassium hydroxide), silicates (sodium metasilicate, sodium orthosilicate), phosphates (trisodium phosphate, sodium tripolyphosphate, tetrasodium pyrophosphate), carbonates (sodium carbonate, sodium bicarbonate), and so on.

Table 4 shows the coating weight of phosphate coating formed on the samples cleaned with the different single alkaline cleaners. The cleaning method uses the immersion method. It is necessary to note that coating weight shown is the average coating weight of many measurements.

Single alkaline cleaner	Cleaning condition	Coating weight (g/M²)
Sodium hydroxide	2%, 45°C, 10 min	8.1
Potassium hydroxide	2%, 45°C, 10 min	7.9
Sodium mestasilcate	2%, 45°C, 10 min	6.6
Sodium orthosilicate	2%, 45°C, 10 min	6.8

Table 4 Coating Weights

SEM photographs of phosphate coatings formed on the samples cleaned by sodium hydroxide and sodium metasilicate solutions, respectively, are shown in Fig.1.

From the SEM photographs shown in Fig.1 it can be seen that the phosphate grains formed on the sample cleaned by sodium hydroxide solution (a) are bulkier than those formed on the sample cleaned by sodium metasilicate solution (b). In addition to cleaning, sodium hydrox-