EGE UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

(MSc. THESIS)

APPLICATION OF BORIC ACID FOR SURFACE CLEANING BEFORE METAL COATING

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We, the undersigned, have in accordance with Ege University, Regulations for Graduate Education and Training, and Ege University, Institute of Applied Sciences, Instructions for Education and Training evaluated and found worth of discussion this study, titled “**Application of Boric Acid For Surface Cleaning Before Metal Coating**’’ and submitted by Melda GEDİKLİ as a graduate thesis and the candidate has successfully passed the thesis interview conducted on 28/08/2007 upon the committee action of unanimity/majority.

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ÖZET

METAL KAPLAMA ÖNCESİ YÜZEY HAZIRLAMADA BORİK ASİTİN SINANMASI

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Yüksek Lisans Tezi, Kimya Bölümü
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Yüzey hazırlama metal kaplamada nihai ürün kalitesini belirleyen en önemli adımlardan biri olup amaç; malzeme üzerindeki yağ ve oksit tabakasının giderilmesi olarak tanımlanabilir. Günümüzde yaygın ve seçeneksiz gibi kabul edilen toksik siyanür banyolarının yerine alternatif olarak düşünülen borik asit ile, yüzey hazırlama işleminde hem daha sağlam yapılı nihai ürün eldesi, hem de çevre dostu bir ürünü endüstriye kazandırmak hedeflenmektedir.

Bu düşünceye dayalı olarak İZMİR 44. Bakım Merkezi Komutanlığı ilgili atölyelerinde bu konu ile ilgili çalışmalar yapılmış ve Metal Kaplama Öncesi yüzey hazırlama kimyasalı olarak kullanılan siyanürlü toksik siyanür banyolarına alternatif olarak düşündüğümüz borik asit ile yüzey hazırlama işlemi gerçekleştirilmiş, her iki yüzey hazırlama işlemi sonrasında da malzemeler aynı banyolarda kaplanarak krom kaplama işlemine tabi tutulmuş ve nihai malzeme kalitesi ile ilgili testler yapılmıştır. Borik asidin metal kaplama öncesi yüzey temizliğinde gerçek anlamda başarılı olduğu değerlendirilmiştir.

Anahtar Sözcükler: Bor Minerali, Borat (Borik Asidin tuzu veya esteri), Yüzey Hazırlama

ABSTRACT

APPLICATION OF BORIC ACID FOR SURFACE CLEANING BEFORE METAL COATING

MSc. Thesis, Chemistry Department

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Surface preparation is one of the most important steps in metal coating determining the quality of the final product, and the aim can be defined as removing the oil and the oxide layer on the material. Both a more stable final product acquisition and bringing in an environment friendly product to the industry are aimed with boric acid, considered as an alternative to toxic cyanide baths which are widespread and considered to have no alternatives nowadays.

Studies regarding this subject have been conducted in the related workshops of IZMIR 44th Maintenance Center Commandership based on this idea, and a surface preparation process has been implemented using boric acid which we considered as an alternative to the toxic cynanide baths used as a surface preparation chemical Before Metal Coating. The materials have been coated in the same baths after both surface preparation processes and been subjected to chromium coating, and tests have been conducted regarding the quality of the final product. It has been evaluated that boric acid is successful in surface cleaning in the literal sense.

Key words: Boric Acid, Borates (Salt or ester of Boric Acid), Boron minerals, Surface Pretreatment

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1. INTRODUCTION

Surface preparation before Metal Coating is one of the most important steps affecting the quality of final product after coating. Besides increasing the efficiency of coating, the surface process also increases the corrosion resistance and the coating quality of the material. So the surface cleaning is more important than the coating process. However a good applied coating system is, it cannot be expected that the coating provides a long term protection unless the foreign materials on the surface (oil,oxide layer, etc.) are completely removed. Because oil, corrosion and foreign materials will negatively affect the main features expected from coating, such as adhesion, hardness, inflammation, resistence, etc., the material will cause time and energy loss.

Deoiling Process can usually be applied in various application areas such as immersion, electrical fat removing and local practise, at 50-90°C, for 5-10 minutes. The chemical can be alkaline, acidic or neutral. The applied system varies according to the conditions of the metal and the enterprise.

In metal coating work, cyanide salts (usually as potassium and sodium cyanide – KCN, NaCN) are widely used in surface cleaning, and the processes containing cyanide need to be replaced with simplier applications which do not contain cyanide because of the toxic effect it creates in terms of people and environment. Cyanide is a group formed by combining Carbon and Nitrogen. This group is known as CN, creates cyanogen (HCN) if it combines with the hydrogen in water in uncontrolled conditions, especially in acidic environment, which is very toxic when inhaled in high dosages.

Boric acids have strategical importance in terms of fields of usage. So, considering that Turkey has such a power and that the petrolium resources will run out in time, we may evaluate boric acid, a surface preperation before metal coating, as the pioneer of a boron based project.

With boric acid, considered as an alternative to toxic cyanide baths which are accepted to have no alternatives nowadays, it is aimed to bring in to the industry a final product which is environment friendly and also has a more stable structure.

2. BASIC INFORMATION

Chemical and mechanical methods used in the Metal Coating Workshop of IZMIR 44th Maintenance Center Commandership are similar with ones generally used in industry.

2.1. CHEMICAL METHODS

Deoiling from the surface of the material to be coated

2.1.1. Surface cleaning with immersion method (Removal of oil and oxide layer in different baths)

2.1.2. Surface cleaning with electrical degreasing bath.

2.2. MECHANICAL METHODS

2.2.1. Polishing (Smoothing the material surface to be coated with a proper sandpaper)

2.2.2. Sanding (Erroding the material surface to be coated with steel balls of 0.3 mm diameter in the sanding machine and removing the corrosion and paint layer on the surface)

2.1 CHEMICAL METHODS :

2.1.1 SURFACE CLEANING WITH IMMERSION METHOD

2.1.1.1 Removal of Oils

Bath Material = Stainless steel (AISI 304)

Operating Temperature = 75-80°C

Duration of Process = 5-15 minutes

Bath Concentration = 3-5 % (By mass)

Contents of the Chemical Product Used (By mass) :

NaOH 30-50 %

Na_2CO_3 less than 20 %

Na_2SiO_3 10-25 %

Alcohol less than 5 %

Alkyl Benzene Sulphonate less than 5 %

Fattyalcoholethoxylate less than 5 %

2.1.1.2 Removal of the Oxide Layer

Bath Material = Polypropylene

Operation Temperature = 20°C

Duration of Process = 5-10 minutes

Bath Concentration(by volume)= 20 %

Contents of the Chemical Product Used =

H_3PO_4 less than 40 %

H_2SO_4 more than 50 %

Fattyalcoholethoxylate less than 5 %

The materials to be coated are filled into baskets, and immersed to oil and oxide layer removal baths in turn. Hot and cold rinsing is done after each process.

2.1.2 SURFACE CLEANING WITH ELECTRICAL DEGREASING BATH

Bath Material = Polypropylene (PP)

Operating Temperature = 40°C

Electrical Potential = 6-10 Volts

Current (D.C.) = 5-10 Amp / dm^2

Chemicals Used = for 100 L water

1.5 kg NaOH

4 kg Na_2CO_3

1.5 kg $Na_3PO_4.12H_2O$ (Trisodium phosphate)

0.8 kg Na_2SiO_3 (Sodium silicate)

1.5 kg Sodium cyanide

With the electrolysis method; the electrical current entering from the anode plate connected to the positive pole of the current source exits from the cathode plate connected to the negative pole of the current source after passing through the solution. The material to be degreased is suspended as cathode. Nickel coated plates are used as anode. Duration of oil removal is approximately 5 minutes.

When the oil removal process is completed, the material is taken out from the bath, strained and rinsed, than it is immersed in to sulphuric acid barrel and is rinsed again.

3. EXPERIMENTAL SECTION

CAN BORIC ACID BE A NEW ALTERNATIVE IN SURFACE PREPARATION?

ANHYDRIDE BORIC ACID* (B_2O_3) (<u>AN EFFECTIVE SURFACE ACTIVE MATERIAL</u>)

B_2O_3 = Anhydre Boric Acid ($T_{melting}$= 450 ^{0}C)

$MeO + B_2O_3 \leftrightarrows Me(BO_2)_2$ (I)

$Oils + B_2O_3 \rightarrow CO_2 + 2B$ (II)

In the method we applied; the carbons in the oil structure have come out as carbondioxide and the carbons in the oil structure have been detached and become carbonized because of the surface active feature of boric acid.

PROCESS STAGES:

- Oily and rusty pipe specimens have been prepared.
- The oily and rusty pipe specimen without a surface cleaning is as seen in Figure 3.1.

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* Boric acid samples taken from the 25 cm height of the pot. These samples were diluted with various amount of carmin red solution. There was no bor detected after these tests.

Figure 3.1. Piece of oily and rusty pipe specimen.

- Oil layer of one piece of pipe was removed with electrolysis in the electrical oil removal bath (Figure -3.2). Oxide layer was removed in the oxide removal bath with the immersion method. Lastly, the surface was coated with copper, nickel and chromium in turn. (Figure-3.3)

Figure 3.2. Electrical deoiling bath

Figure 3.3. Chromium coated pipe specimen

*** TREATMENT WITH BORIC ACID :** Two pieces of oily and corroded pipe specimens were prepared in the foundry section, in the silicone carbid based melting pot with 375 mm height, 302 mm opening diameter, 203 mm ground diameter, to be treated in a process.

* 2 kg boric acid (ETIBANK) was weighted and put into the blacklead melting pot. The melting temperature was monitored with laser temperature measuring device. Two pieces of iron pipe specimens were dropped into the boric acid melted at T=453°C. The specimen surfaces were checked with intervals of 10 minutes and the process was terminated after 40 minutes. The specimens were taken out from the pot and left to cool down in open air.

The pictures below are those of the performed study.

Figure 3.4. Detection of the melting point of boric acid inside the melting pot with the laser measuring device

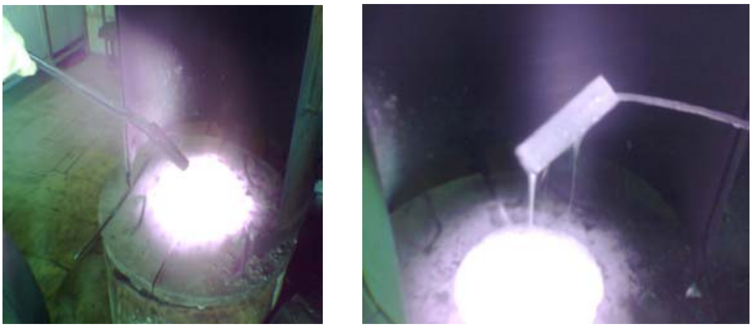

Figure 3.5. Control of pipes by taking them out of the pot regularly

Figure 3.6. Pipe specimens taken out from the pot and left to cool down

Figure 3.7. Cooled down pipe specimens

- The oil and corrosion on the cooled down iron pipe were completely removed. However the cooled boric acid crystals were adhered to the pipes in patches. (As seen in Figure 3.7)

- The outer surface of the pipe treated with boric acid became ready for coating after being sanded in the polishing machine. Lastly, the surface was coated with copper, nickel and chromium. (as seen in Figure 3.8)

Figure 3.8. The pipe treated with boric acid was coated with chromium after polishing.

Physical and Chemical Properties of the Crystal Boric Acid Used in the Experiment :

Chemical Formula: H_3BO_3

Form: Hard

Colour: White

Smell: Odorless

Anhydride Boric Acid

Melting Point: 450°C

Inflammation Point: Not flammable

Vapor Pressure: 2.7 hPa (at 20°C)

Density: 1.44 g/cm^3 (at 20°C)

pH Value (33 g/L H2O): 3.8-4.8 (at 20°C)

Carbon film coating, which almost eliminates friction, on the surface treated with boric acid both increases the material life, and decreases maintenance costs.

Copper Coating Bath:

Bath Material = Polypropylene

Bath Dimensions(cm) = 90*150*100

Electrical Potential = 3-6 V

Temperature = 45°C ± 5

pH = 11 – 12

Specific Gravity = 1.09±0.01 g/cm^3

Bath Mixture = 8 kg Sodium Cyanide / 100 L water

6 kg Copper Cyanide / 100 L water

0.2 L copper humidifier / 100 L water

0.2 L copper polishing / 100 L water

Nickel Coating Bath:

Bath Material = Polypropylene

Bath Dimensions(cm) = 90*150*100

Electrical Potential = 3-6 V

Temperature = 55°C ± 5

pH = 4.5 – 5.5

Specific Gravity = 1.16±0.01g/cm^3

Bath Mixture = 30 kg Nickel Sulphate / 100 L water

6 kg Nickel Chloride / 100 L water

1 L Nickel polishing / 100 L water

0.5 L Nickel Supporter / 100 L water

0.2 L Nickel Humidifier / 100 L water

Chromium Coating Bath:

Bath Material = Polyvinyl Chloride (PVC)

Bath Dimensions(cm) = 90*150*100

Electrical Potential = 5-8 V

Temperature = 43°C ± 3

pH = 0

Specific Gravity = 1,17±0.01 g/cm^3

Bath Mixture = 15 kg Chromic Acid / 100 L water

0.5 L Sulphuric Acid / 100 L water

0.25 L Chromium degasser / 100 L water

3.1 Examining the Effect of Surface Preparation Process on Coating Quality

In order to examine the effect of surface pretreatment on the quality of the final product, two chromium coated pipe specimens, the surface of which were cleaned before coating with chromium, one with boric acid, the other with electrolysis method, were waited in the Salt Spray Test Chamber SC/KWT 450 device, in the 9 Eylül University Engineering Faculty, Material and Metallurgy Engineering Department Laboratory, for 24 hours in order to test their corrosion resistance, and the corrosion resistance was measured. The measurement was done according to the

ASTM B-117-97 standard. From the two specimens waited in the salt spray cabinet for 24 hours, while one of the specimens, the surface preparation process of which was done with boric acid, did not show any change, the other one treated with cyanide showed pitting crevice corrosion start. Corrosion was observed on the pipe specimen, surface cleaning of which was done with cyanide and subjected to salt spray test for 24 hours as shown on Figure 3.9. On the other hand, corrosion was not observed on the pipe specimen, surface cleaning of which was done with boric acid. This can also be seen on Figure 3.10. (on the left side)

Figure 3.9. The pipe specimen cleaned with cyanide.

Figure 3.10. Corrosion resistance of pipe specimens after salt spray test.

Fig.3.11. Salt Spray Test Chamber SC/KWT 450 device(Closed form)

Fig.3.12. Salt Spray Test Chamber SC/KWT 450 device(Open form)

ASTM B 117-97 : Standard Practise for Operating Salt Spray (Fog Apparatus)

This practise provides a controlled corrosive environment which has been utilised to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber.

The apparatus which are required for salt spray (fog) exposure consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. All water used for this practice shall conform to TYPE IV water in specification D 1193. This does not apply to running tap water.

- Specimens suitably cleaned.

- The position of the specimens in the salt spray chamber during the test such that the following conditions are met .

- The specimens supported or suspended between 15^0 and 30^0 from the vertical and preferably paralel to the principal direction of flow of fog through the chamber, based upon the dominant surface being tested.

- The specimens did not contact each other or any metallic material or anymaterial capable of acting as a wick.

- Salt solution from one specimen did not drip on any other specimen.

- The salt solution was prepared by dissolving 5±1 parts by mass of sodium chloride in 95 parts of water conforming to Type IV water in specification D 1193. The salt used is sodium chloride substantially free of nickel and copper and containing on the dry basis not more than 0.1 % of sodium iodide and not more than 0.3 % of total impurities.

- The pH of the salt solutıon was such that when atomized at 35 ^{0}C the collected solution will be in the pH range from 6.5-7.2.

- The compressed air supply to the nozzle or nozzles for atomizing the salt solution was free of oil and dirt and maintained between 70 and 175 kPa (10 and 25 psi)

- Conditions in the Salt Spray Chamber: The exposure zone of the salt spray chamber maintained at 33.7-36.1 ^{0}C

- At least two clean fog collectors placed within the exposure zone that no drops of solution from the test specimens or any other source shall be collected. The sodium chloride concentration of the collected solution shall be 5±1 mass %. The pH of the collected solution shall be about 6.5 to 7.2.

- Exposure periods of multiples of 24 h suggested.

- Specimens were gently washed or dipped in clean running water not warmer than 38^{0}C to remove salt deposits from their surface, and then immediately dried.

4. RESULTS AND DISCUSSION

With boric acid, considered as an alternative to toxic cyanide baths, it is aimed to bring in to the industry a final product which is both environment friendly and has a more stabile structure. In this study, when boric acid is compared to the other surface pretreatment chemicals, it is being evaluated that it will be acceptable to use it as a surface pretreatment chemical in the industry because of the following reasons: It

a) Enables the oil and corrosion removal processes to be implemented in one step, and therefore minimizes the cost,

b) Removes the threatening effect on human health when compared to toxic cyanide,

c) Is easily applicable,

d) Decreases the duration of the surface preparation process, and so provides time saving,

e) Enables to obtain coating surfaces with more stabile structures

f) Has a disadvantage which is high energy consumption because of high melting temperature of boric acid.

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