Optimisation of Corrosion Protection and Prevention at Thermo King

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Abstract

Corrosion of metals affects their function in many engineering applications, limits the useful life, and thereby causes increased costs for industry estimated at up to €300 billion per annum in the United States[1]. The prevention of corrosion is of major economic significance, and is a subject of intrinsic scientific interest due to the complex chemistry involved. The chemical protection of metals has to be moderated to conform to increasingly demanding environmental standards. There are relatively few effective alternatives to traditional phosphate coatings dating from 1869[2].

In the case of refrigeration technology, the refrigeration cycle is largely conducted on metallic equipment exposed to repeated episodes of the thermal cycle. The metals used in portable or truck mounted refrigeration equipment must resist corrosion for periods of ten years in aggressive environments. In this project a scientific examination of the process steps used by Thermo King, a leading refrigeration manufacturer, was conducted.

In this project, with the full support of the Thermo King Corporation, the process steps in the phosphate protection process were simulated in the laboratory to characterise various chemical changes and monitor changes over time. A study on the literature and technology of alternative corrosion protection relevant to the current processes was conducted. Accelerated corrosion tests were carried out on metallic samples used in the Thermo King production of refrigeration units. These samples were also characterised by scanning electron microscopy. Implementation of the findings in Thermo King had four major effects;

1. Decrease in phosphate levels to meet IPC licence requirements, for the first time in Thermo King
2. Substantial cost reduction through water conservation
3. The improved performance of Thermo King's spray treatment line resulted in obtaining 700 hours, in a salt spray chamber in accordance with ASTM B177. This improved accelerated corrosion test result is 75% higher than was achievable prior to this project.

4. Preliminary investigations on the alternatives to phosphate coating were conducted, on silane and autophoretic technologies. These technologies showed promising results however further research is required.

Suggestions are made for future research to obtain a better understanding of underlying principles, and to achieve improved performance from corrosion inhibition techniques.

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Chapter 1 - Introduction

1.1 Project definition

This project sought to establish a modern alternative to classical corrosion protection systems by elimination of treatments using phosphate and heavy metals. In order to investigate new technologies, it was necessary to have a baseline. It was decided that the optimisation of current processes was required for comparison purposes. This included the development of analytical techniques and quality control procedures.

A systematic approach to conversion protection improvement in Thermo King necessitated a detailed study of the system currently in use. An inadequate quality system was evident leading to inconsistent performance. The first twelve months of this project focused on development of chemical test procedures and processes in the laboratory. Modern corrosion treatment systems currently available were identified through liaison with chemical manufacturers. A pilot plant was designed as a model to simulate the conditions of interest to Thermo King while evaluating modern treatment systems. From the knowledge gained a baseline study was carried out on the Thermo King plant in Galway. Management of the spray line and effluent plants was assigned exclusively to this project. A dramatic improvement in plant performance was achieved on a consistent basis (Chapter 7).

1.2 Thermo King

Background

The Galway plant opened in 1976 as the centre of operations for Thermo King Europe. Operated on a 14-acre site, this plant manufactures both truck and trailer refrigeration units. In 1986 the president of Thermo King set up a corrosion committee, to source and solve failures issues. A corporate powder paint expert, a corrosion expert, materials expert, chemical engineer and a manufacturing engineer formed the committee. Influenced by the automotive industry (in particular Volvo) they visited many metal finishing plants around the world. The system in use at Thermo King was based on immersion zinc phosphate tanks followed by a solvent spray paint. The team made the following recommendations:

- Introduction of Galfan (galvanised mild steel): the principle here is sacrificial protection of the iron in that the more reactive zinc coating dissolves in preference to the iron and surrenders electrons thus preventing corrosion.
- Use wet dip paint: this process has the effect of almost eliminating volatile organic compounds VOC's (xylenes in this case)
- Powder paint: this is another alternative to spray wet paint. This process involves electrostatically charged paint being deposited on surfaces with zero solvents and very little waste due to recycling.
- Standardised corrosion resistance for Thermo King globally.

Current Status

Over the course of the past twenty-seven years the company has undertaken a continuous improvement programme in both quality and environmental enhancements.

This has been necessary because of changes in environmental requirements and increasing cost of raw materials.

The Galway plant has two process lines to manufacture the truck and trailer units as shown below.

- An immersion in zinc phosphate process followed by wet dip paint
- A spray iron phosphate process followed by powder paint installed

Figure 1.1 Trailer unit

Figure 1.2 Truck unit

These units are currently made from a mixture of metals and other alloys including mild steel, Galfan (zinc plated mild steel), and aluminium (silicon alloy).

Factors influencing industrial corrosion protection methods

The chemical and mechanical characteristics of metals have a very important consequence for the type of treatment needed for corrosion protection.

As Thermo King uses a mixture of base metals one has to take into account the differing properties of these metals. Alkaline cleaners are used which have different reactivity's with zinc, aluminium and iron. In addition the corrosion of these metals occurs at very different rates. From a practical point of view it is desirable to have a standardised procedure for all metals used. The following outline the principle technical requirements for Thermo King's corrosion protection systems.

1. Quality performance of 700 hours salt spray resistance (ref appendix 1A) in accordance with ASTM B117
2. Environmental compliance to statutory and internal company regulations (chapter 2)

The materials used on the immersion line in Thermo King (TK) are mild steel and Galfan. The diagram below shows the order in which the tanks are laid out, followed by a photograph displaying the actual system in TK.

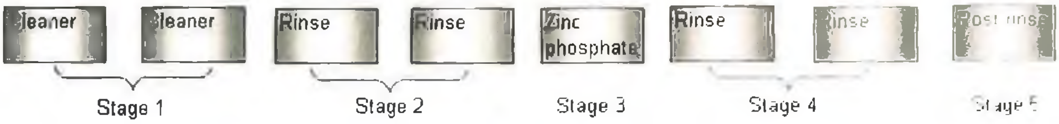


Figure 1.3 Immersion process

Figure 1.4 Photograph of immersion process Thermo King

This is followed by a painting process (wet dip).

Figure 1.5 Dip paint system

The spray tunnel layout is as shown below. Mild steel, aluminium and Galfan are treated with iron phosphate.

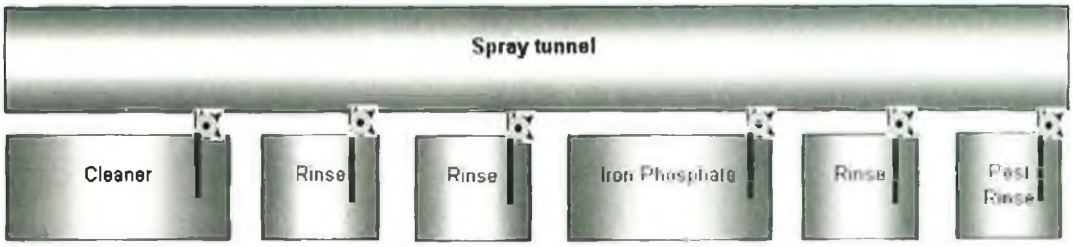
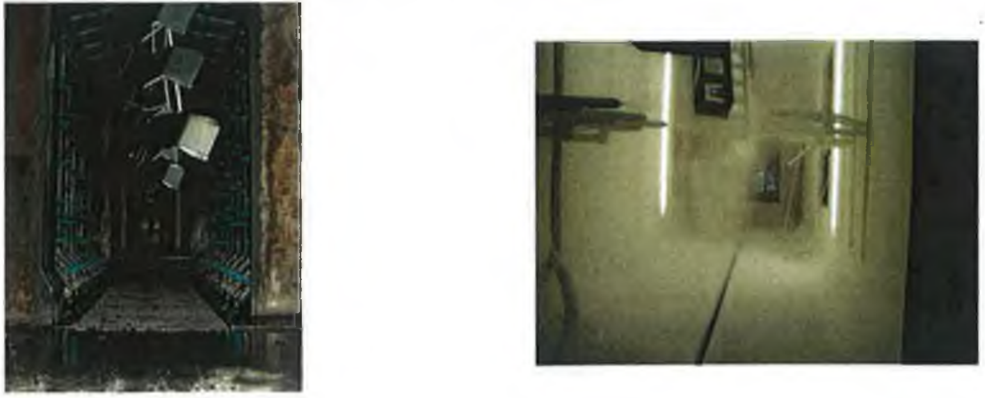


Figure 1.6 Spray process



Treatment spray tunnel

Powder paint system

Figure 1.7

1.3 Material selection

Different materials vary immensely in cost per meter squared. Aluminium is far more costly than mild steel, but gives a much higher corrosion resistance. The quality of the finished product needs to comply with both international and corporate standards.

The base materials used in Thermo King are mild steel (ASTM A 569), aluminium (ASTM B209) and Galfan (ASTM A875). These materials are used in specific areas of the unit.

Steel is used to give mechanical strength to the unit. The more corrosive resistant aluminium is used on the front of the unit, which is subjected to most of the environmental exposure. Galfan is considerably less expensive than aluminium but is difficult to weld. It also has superior corrosion resistance to mild steel. The units are made using all these metals to obtain optimum mechanical and corrosion resistance performance in a cost effective way.

As Galfan is a less expensive material than aluminium, Thermo King have replaced most of the aluminium and some mild steel components with Galfan. The advantage of the of this material is the superior corrosion resistance obtained, due to the sacrificial protection of the zinc coating placed on the underlying mild steel. The steel and aluminium have not been completely replace by Galfan due the their welding properties.

1.4 Metallic corrosion

The metals discussed above corrode at different rates under fixed conditions due to oxidation of the substrate. Iron/mild steel form a red oxide, while zinc and aluminium give a white oxide. In the case of iron, the oxide is porous, thus allowing corrosive media direct access to base metal. However aluminium oxide is impermeable and therefore corrosion is very much slower. Even if the aluminium is scratched the metal reacts immediately with oxygen from air to form the hard non-porous oxide. Other metals such as copper and zinc are less corrosive than iron and more than aluminium. Certain chemicals, which make contact with the surface, (such as acids, bases, anions etc) accelerate corrosion[3].

From an electrochemical point of view general corrosion can be explained as a mini galvanic cell being formed. In order for a current to flow there must be a potential difference present between one part of the surface and another. The reaction at the anode is loss of electrons and at the cathode a gain of electrons as shown below.

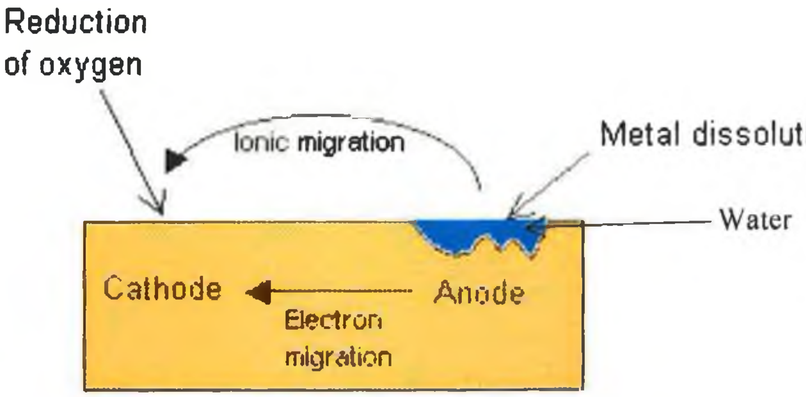


Figure 1.8 Basic Corrosion

The reaction occurring at the anode for iron is as follows

$$Fe \rightarrow Fe^{++} + 2e^{-}$$

The electrons flow from the anode to the area of higher potential, the cathode. Positively charged cations such as H^+ and Na^+ migrate to the cathode while anions such as OH^-, migrate to the anode. The following reactions[4] can occur at the cathode site.

1. Reduction of hydrogen

   $4H^+ + 4e^- \rightarrow 4H \rightarrow 2H_2$

2. Oxygen reduction

   $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Increasing strength of reducing agents

Reduction half reaction	**E^0(V)**
$Au^{+3}(aq) + 3e^-$	1.500
$Cu^{+2}(aq) + 2e^-$	0.337
$2H^+(aq) + 2e^-$	0.000
$Ni^{+2}(aq) + 2e^-$	-0.250
$Fe^{+2}(aq) + 2e^-$	-0.440
$Zn^{+2}(aq) + 2e^-$	-0.763
$Al^{+3}(aq) + 2e^-$	-1.660
$Mg^{+2}(aq) + 2e^-$	-2.370

Increasing strength of oxidising agents

Table 1.b Standard Reduction potentials[5]

1.5 Industrial protection methods

Galvanising / cathodic protection

It can be seen from these E^0 values that zinc is more reactive than iron. This means that when iron and zinc are in contact the zinc is oxidized and electrons are released, which protect the iron from rusting. This is cathodic protection. Galfan (galvanising) is an example of this[6].

Industrial protection methods

Conversion coatings are the most widely used products for corrosion control. These coatings provide long-term protection in a wide variety of corrosive environments. The coatings in themselves provide no increased strength to the substrate but they do protect it from oxidation. Protective coatings occupy only a tiny fraction of the total volume of a system but have heavy requirements imposed. A conversion coating must provide a continuous barrier to a substrate. If for any reason the barrier becomes broken, the conversion coating must impede corrosion travelling from this point to elsewhere on the substrate. Coatings can be split into three main categories as follows: metallic, inorganic, and organic.

Methods of inorganic coating applications

Inorganic coatings are created by chemical reaction with or without an electrical current applied to the base metal. The application of this type of coating changes the outer surface layer of metal into a film of metallic oxide or compound, which has an increased corrosion resistance. There are many types of inorganic coating methods such as, anodising, chromate filming, nitriding and phosphating.

Methods of organic coatings applications

Paint is a permeable (to water and air) organic and inorganic coating which when used in addition to conversion coating provides adequate corrosion resistance.

Modern painting systems consist of a conversion coating such as iron phosphate followed by application of one layer of powder paint. This type of system is present throughout industry and in most Thermo King plants across the world. There are many advantages to powder painting[7]. These include the following:

- No liquid solvent handling
- No air or water pollution
- No liquid mixing or pumping problems
- Very little waste since over spray can be reused
- Less expensive than wet paint
- Enhanced quality performance

Powder paint has a static charge while the component is earthed and thus the paint particles are attracted to the substrate. The diagram[8] below shows the electromagnetic field around the component. The powder particles are electrically charged and are attracted to the metal surface where they lose their charges to earth.

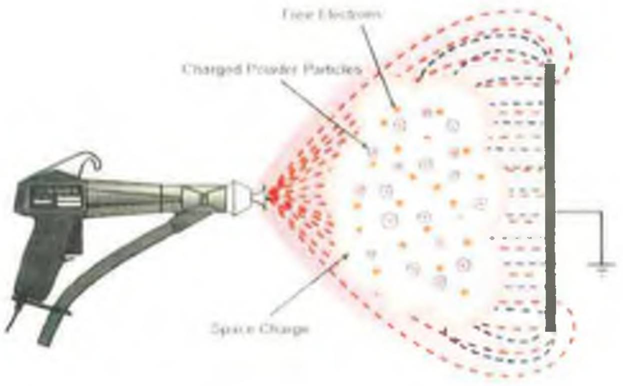


Figure 1.9 Powder painting electromagnetic field

Phosphating

Aqueous phosphate coating solutions are available in many forms. The solutions used in Thermo King are zinc calcium phosphate and iron phosphate. The same basic principles apply to all; the following equation explains how a coating based on a tertiary zinc phosphate[9] protects the underlying metal.

$$3Zn^{++} + 2H_2PO_4^- \leftrightarrow Zn_3(PO_4)_2\downarrow + 4\,H^+$$

For the above reaction to occur corrosion of the base metal to be protected must take place. Known as the acid consumed ratio, the below ratio is not widely used within industry to calculate the quantity of phosphate bonded to the surface. The ratio used in industry to define the above reaction is

$$\text{Acid ratio} = \frac{(P_2O_5)\quad \text{Free}}{(P_2O_5)\quad \text{Total}}$$

Coating control

A control panel is treated, then the coating removed and gravimetrically analysed (appendix 3). The value obtained for weight loss is compared with the internal Thermo King standard (appendix 1a)

Chapter 2 – Environmental constraints on chemical processes

This chapter discusses the legislative and internal company standards Thermo King processes must meet.

2.1 Introduction

The Thermo King Galway plant is subjected to a considerable number of internal and external standards to which it must conform. These include Thermo King corporate standards, Thermo King Galway internal standards, IPC licence requirement, local authority requirements and Health and Safety restrictions.

Statutory requirements	**External voluntary requirements**	**Thermo King Standards**
Local Authority	ISO 14000	Corporate
IPC licence	EMS	-
H +S requirements	ISO 9000	-

Table 2a Environmental constraints

Note: The IPC licence is a compulsory statutory requirement for Thermo King.

2.2 Statutory requirements

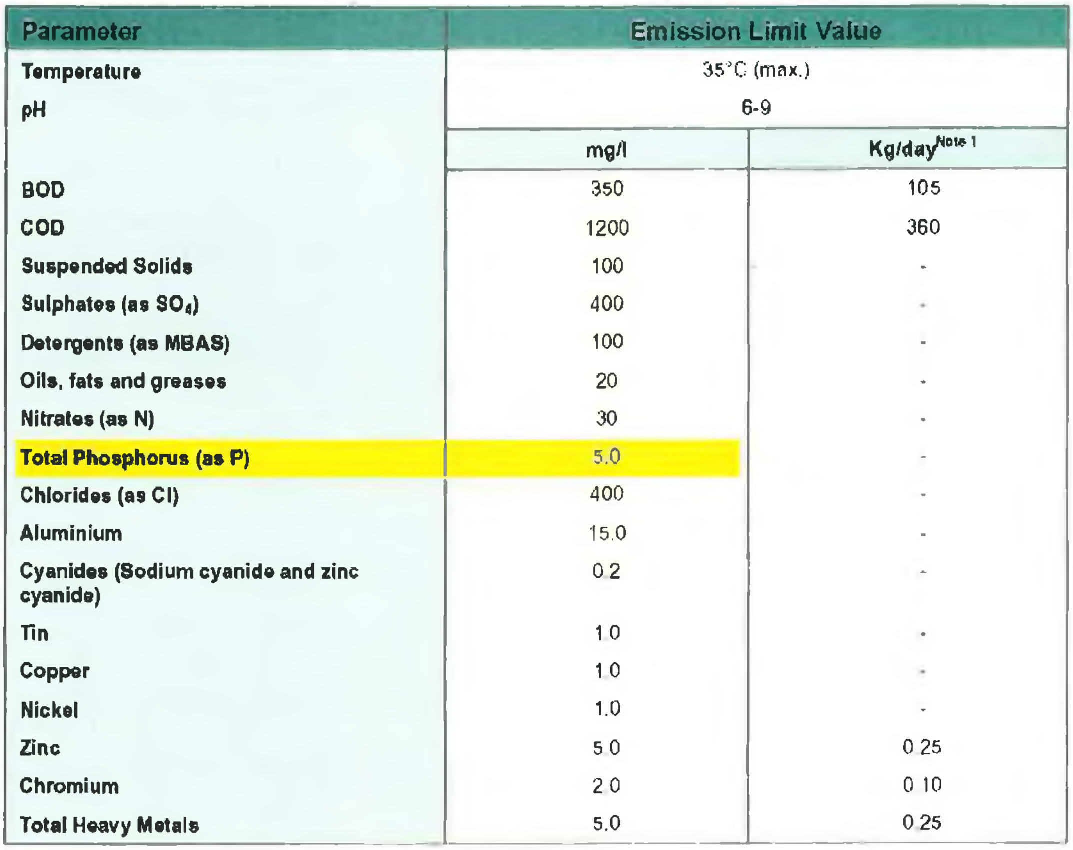
Local authority discharge licence

At present the company's environmental restraints are specified by an IPC licence. However when the company improves its performance it is likely to revert to a local authority discharge licence.

Integrated pollution control licence (IPC)

IPC licences are issued by the Environmental Protection Agency. The IPC licence monitors the effect a plant has on the environment as a whole. These licences apply to institutions that are capable of causing a large quantity of pollution[10]. When imposing an IPC licence on Thermo King the EPA did so due to the quantity of solvents being used on site. Use of solvents has now been dramatically reduced with the change over from wet spray paint, to dip and powder paint. The licence sets out when, and how samples of potential chemical pollutants are to be taken. The EPA must ratify the analytical methods and procedures in laboratories used by Thermo King, for analysis of samples.

The extract below from the Thermo King IPC licence indicates the limits imposed on emissions to the public sewer. The only parameter that has caused any trouble for Thermo King in recent years is phosphate. The highlighted section indicates the limit for this parameter. There has been no difficulty in meeting the other limits.



Parameter	Emission Limit Value	
Temperature	35°C (max.)	
pH	6-9	
	mg/l	Kg/day[Note 1]
BOD	350	105
COD	1200	360
Suspended Solids	100	-
Sulphates (as SO_4)	400	-
Detergents (as MBAS)	100	-
Oils, fats and greases	20	-
Nitrates (as N)	30	-
Total Phosphorus (as P)	5.0	-
Chlorides (as Cl)	400	-
Aluminium	15.0	-
Cyanides (Sodium cyanide and zinc cyanide)	0.2	-
Tin	1.0	-
Copper	1.0	-
Nickel	1.0	-
Zinc	5.0	0.25
Chromium	2.0	0.10
Total Heavy Metals	5.0	0.25

Table 2b IPC licence – Thermo King[11] emission limit values

Health and Safety

The plant adheres to health and safety authority guidelines with regard to storage and use of chemicals, protective clothing, staff training etc. As part of the IPC licence requirements annual checks are carried out on air emissions and noise levels.

2.3 External voluntary requirements

These are standards that Thermo King have applied in their operation in order to improve their quality and environmental impact.

Environmental Standard ISO14001

The International standards organisation issued ISO14001, which set out the framework for the development of both the system and the supporting auditing programme. ISO 14001 was first published in 1996 and specifies the requirements for an environmental management system. It applies to environmental aspects, which a company has control over.

This standard contains a continuous improvement section forcing companies to reduce environmental impact on the surroundings. It states procedures must be written on how chemicals must be stored, controlled, discharged and handled. Both internal auditing and independent external auditing are used to quantify adherence.

Quality Standard ISO9000

Issued by International standards organisation. This places a level of quality performance on a company. In the current competitive environment, any company which does not have this standard will fail to gain new business. Both internal auditing and independent external auditing are used to quantify adherence.

2.4 Thermo King chemical standard

Throughout the Thermo King Corporation there are engineering standards, which each plant must comply with, including quality, process, materials and equipment procedures. One of these standards describes what the chemical composition of pre-treatment chemicals must comply to. The table below shows an extract from this procedure.

Cleaner	Rinse water	Zinc phosphate	Iron phosphate	Post rinse
No caustic	<200mg Ca/Mg	Coating	Coating	Alkaline not acidic
No silicates		150-500mg/sq ft	25-75 mg/sq ft	
Minimum phosphate		Non carcinogenic	Non carcinogenic	Non carcinogenic
Non carcinogenic				

Table 2c Thermo King chemical composition requirements

End of life legislation

This legislation obliges EU member states to take the necessary measures to ensure that the rate of reuse and recycling of end-of-life vehicles shall be increased to a minimum of 80% of average weight per vehicle by 1 January 2006. Thus any corrosion coating on the units must be removed into solution so the metal can be reused. The coating must then be treated and removed from solution[12].

2.5 Thermo King Environmental status

Progression of work

Until May 1997, Thermo King had separate discharge licences for air, water and waste from the local authority (Galway County Council). The company became subject to an Integrated Pollution Control (IPC) licence as the plant's use of xylene was in excess of 10 tonnes per year. Thermo King received its IPC licence from the Environmental Protection agency (EPA) in May 1997. The use of xylene in the paint process has been eliminated.

The plant registered to the ISO 14001 Environmental management Standard in April 2000.

Goals to be achieved

Thermo King has committed to improving the environmental performance in its operations; sustainable development through product design to provide a long-life product with lowers maintenance costs and lower fuel consumption. The environmental targets are as follows:

- Reduce hazardous waste
- Reduce solvent use
- Recycle where possible
- Reduce energy and water
- Reduce noise level
- Reduce risk of chemical spill
- Substitute with less hazardous chemicals
- Improve supplier environmental performance

The EPA set a list of objectives and targets with time scales up to 5 years and carries out regular audits on Thermo King's activities. Ingersol Rand, Thermo King's parent company has set out environmental targets with the objective of producing zero hazardous waste by 2004. Local authorities in each country in relation to EU hazardous waste directives define hazardous waste.

Chapter 3 -Chemistry of corrosion

This chapter details corrosion theory dealt with in 1.4 and alternative protection methods.

3.1 Characterisation of corrosion

There are many forms of corrosion, defined according to topography of the site and localisation. Valuable information for the solution to corrosion problems can be obtained by a careful examination of corroded equipment. There are many corrosion types and those relevant to the Thermo King protection process are discussed briefly below.

Uniform corrosion

Uniform attack is when a large area of the surface becomes thinner by chemical or electrochemical reaction, the decreases in cross-sectional area eventually leading to failure. Incorrect material choice or inadequate corrosion protection treatments are the main causes. The photograph below displays a mild steel panel exposed to the environment for two days after cleaning, with no protection.

Figure 3.1 Uniform Corrosion

Galvanic corrosion

Galvanic corrosion occurs when two dissimilar metals are immersed in a conductive medium and their respective reactivities eventually cause a current to flow.

Figure 3.2 Galvanic corrosion photograph

Figure 3.3 Galvanic corrosion diagram

Crevice corrosion

Crevice corrosion is usually associated with stagnant small volumes of electrolyte, thus intensely localized corrosion occurs[13]. It occurs at inaccessible corners produced by bad design and beneath foreign matter, which settles on the surface. A crevice must be wide enough to permit liquid entry, but it needs to be sufficiently narrow to maintain an electrolyte zone. To prevent this type of corrosion, parts are welded instead of bolted to reduce electrolyte zones forming. Parts are also designed to allow complete drainage, this facilitates cleaning, thus preventing soil build up. By placing a protective coating this can reduce the likelihood of this form of corrosion.

Figure 3.4 Crevice Corrosion Photograph[14] and diagram

Filiform corrosion

Filiform corrosion occurs mostly under protective films. This type of corrosion does not weaken or destroy metallic components but only affects surface appearance The attack appears as a network of corrosion trails, these trails having the reddish brown colour of ferric oxide when the base metal is iron. Relative humidity between sixty-five and ninety percent enables this type of corrosion. During growth the head of the trail is supplied with water from the surrounding environment by osmotic action due to the high concentration of dissolved ferrous ions. Osmosis then tends to remove water from the inactive end of the trail due to low concentration of soluble salts as the ferric oxide is reacted with, to become ferric hydroxide. Corrosion is restricted to the front of the trail where hydrolysis of the corrosion products produces an acidic environment. There are no completely satisfactory methods for preventing this type of corrosion, only by storing components in low relative humidity environments, also by placing low permeability coatings relative to the environment. The photograph[15] below is a clear example of filiform corrosion on a mild steel panel, phosphated and painted

Figure 3.5 Filiform corrosion photograph

Pitting

Pitting is extremely localised corrosion attack that leads to holes in the surface of the metal. Pits may be so localised that they seem to create a rough surface rather than many holes. Usually growing in the direction of gravity, pits seldom appear on vertical surfaces. This process is said to be self-stimulation and self-propagating. Rapid dissolution of metal within a pit produces excess positive ions, which in turn migrate to the surrounding area. Within a pit there is a high concentration of cations, which initiate further dissolution of metal. Most failures are caused by chloride ions due to the acid forming tendency of this anion and the high strength of its free acid (HCl). Pitting occurs when stagnant conditions are present for example if stainless steel is used to pump sea water continuously it will work sufficiently for long periods, however if the pump is switched off for an extended period pits will form. The best prevention of pitting is improve selection of materials. The photograph below is a clear example of pitting on a gear-tooth[16].

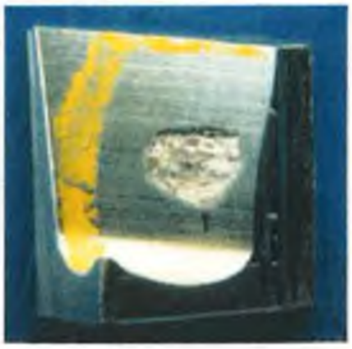


Figure 3.6 Pitting photograph

Inter-granular corrosion

Inter-granular corrosion is the localised attack at and adjacent to grain boundaries with relatively little corrosion of the grains. This form of corrosion causes alloys to disintegrate and loose their strength. Impurities at grain boundaries, depletion of one of the elements, or enrichment of one alloying elements causes this phenomena. Weld decay occurs due to inter-granular corrosion around weld structure, when welding is prolonged. If electric arc welding is used rather than gas welding this reduces the time and thus the effected area.

Figure 3.7 Inter-granular diagram and photograph[17]

Erosion corrosion

Erosion corrosion is an increase in the rate of deterioration on a metal due to the relative movement between a corrosive fluid and the surface of a metal. The metal may be removed as dissolved ions or by the formation of solid corrosion products which are then mechanically swept from the surface of the metal. This creates the appearance of grooves, waves and rounded holes, which form usually in a directional pattern. The diagram and photograph below are examples of erosion corrosion[18].

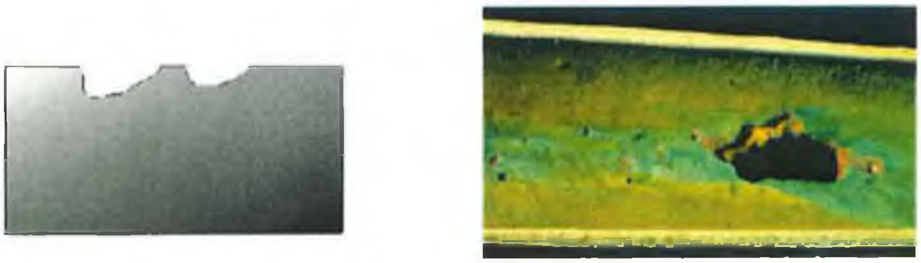


Figure 3.8 Erosion corrosion diagram and photograph

Stress/Fatigue Corrosion

Fatigue corrosion, the tendency of the metal to fracture under repeated cyclic stressing. Stress corrosion is the cracking caused by the presence of both tensile stress and a corrosive medium. An example of two types are, seasoned cracking of brass and caustic embitterment of steel. Season cracking is a particular type of stress corrosion brass usually associated with atmospheric exposure but which can also occur with immersed conditions. The stress corrosion of brass occurs with both inter-granular and trans-granular manner. More trans-granular erosion indicates mechanical factors. The photograph below gives an example of stress corrosion[19].

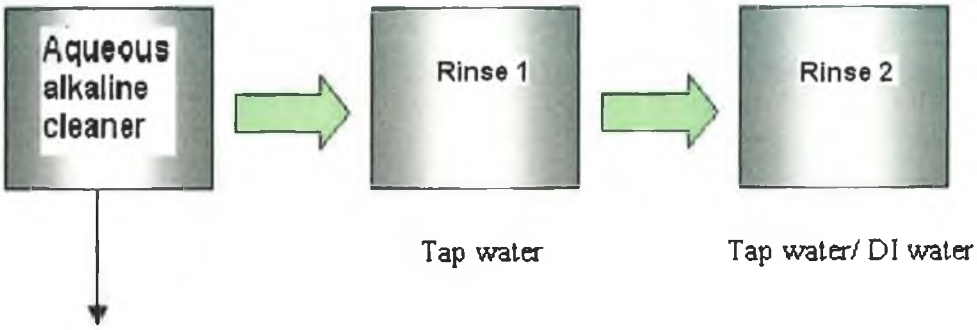
Figure 3.9 Stress Corrosion

3.2 Corrosion Protection

Metal surfaces need to be clean for effective corrosion protection systems to work properly. There are many important considerations in choosing a suitable corrosion protection process. These include the substrate (metal) being treated, the reactivity of the latter with the cleaner and other chemicals, environment, safety and cost. The type of dirt involved is also critical is evaluating suitable chemistry for cleaning products.

Cleaning

Cleaning is a critical process in corrosion protection. It is necessary to remove different types of soils such as clay, greases, mineral oil etc. These materials need to be dislodged, emulsified/dispersed or fragmented by hydrolysis. The mechanism and thus the composition of a cleaner depend on the dirt present. Greases (animal and plant esters) are hydrolysed by caustic solution and are emulsified by surfactants. Silicates and borates retard attack by alkali on zinc and aluminium and also acts as dispersants. Polyphosphates or ethylenediamine tetraacetic acid (EDTA) are present to add sequestering properties. Builders such as hydroxides, carbonates or amines provide the alkaline medium[20].



- Builders (hydroxide/carbonates/amines)
- Surfactants (anionic and non-ionic)
- Inhibitors (borax/silicate)

Figure3.10 Cleaning process and composition

Cleaner composition chemicals

Builders

Builders are inorganic alkali metal salts. They create the etching ability of a cleaner.

Metal Hydroxides

Sodium hydroxide or potassium hydroxides are almost always present in alkaline cleaners. As hydroxides dissociate without hydrolysis they are highly alkaline however they do not have any free alkalinity reserve.

$$NaOH \rightarrow Na^{+} + OH^{-}$$

Carbonates

Carbonates are favoured by manufacturers due to their low cost, but are much weaker bases than hydroxides. They are used for slightly soiled material or with very reactive metals such as zinc and aluminium.

Silicates

Silicates have the following properties. They act as emulsifiers and disperse soils.

$$Na_2SiO_3 \leftrightarrow 2Na^{+} + SiO_3^{-2}$$

$$2Na^{+} + SiO_3^{-2} + 3H_2O \leftrightarrow 2Na^{+} + 2OH^{-} + H_4SiO_{4(ppt)}$$

Silicates have low alkalinity. A complication is that they form a silicic acid precipitate, which exists as a colloidal suspension. This suspension gives dispersion properties to the cleaner solution. The caustic present ensures that all the silicic acid precipitates out. If the silicates are removed from the solution then the caustic will attack the substrate, as the silicates have inhibition properties. However this silicic acid colloidal precipitate can cause further problems during rinse stage[21].

Phosphates

Complex phosphates have many functions, acting as effective detergent boosters by aiding surfactants. Phosphate reduces water hardness by the sequestering of calcium and magnesium ions.

$$\text{e.g.} \quad 2P_3O_{10}^{-5} + 5Ca^{+2} \rightarrow Ca_5(P_3O_{10})_2$$

Borates

Borates have a lower pH than the previously discussed builders. Similarly to silicate they have inhibition properties. These builders also aid in water softening. Borates are extremely cheap but are not as commonly used in industrial applications as silicate is for inhibition. Borates are less soluble than silicates at room temperature, but have the advantage of being easier to rinse than silicate.

Surfactants

Surface-active agents, or surfactants, are characterised by having two ends: a hydrophilic (water loving) end and hydrophobic (water hating) end. The hydrophilic end is soluble in water and other polar liquids and the other end soluble in oil and other non-polar liquids. The hydrophilic end dissolves up organic matter and the hydrophobic helps solublise this. It also decreases surface tension loosing the dirt.

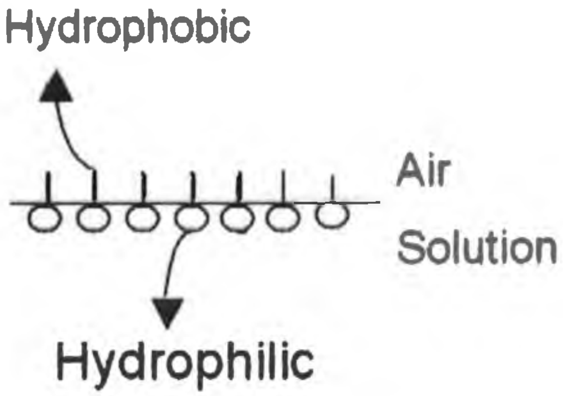


Figure 3.11 Surfactant[22]

There are three different groups within surfactant chemicals. These are classed according to the polarity of the chemical.

Cationic: positive charge

Anionic: negative charge

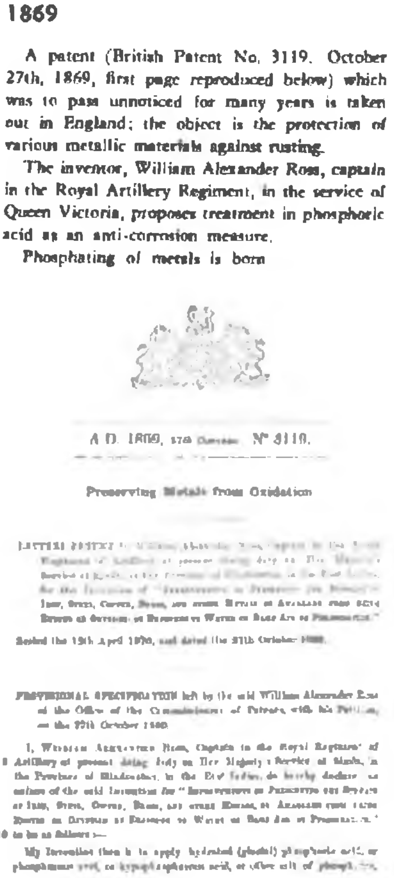
Non ionic: no charge

Anionic surfactants also have their charge on the hydrophilic end of the molecule. The solubility of anionic surfactants increases with raises in temperature. Cationic surfactants have their positive charge on the hydrophilic end of the molecule. These surfactants are rarely found in industrial cleaners. They are most commonly found in fabric softeners and germicides.

Conversion coating

Historical background

Almost 150 years ago the first patent was taken out, on the use of phosphoric acid as a form of corrosion protection.



1869

A patent (British Patent No. 3119. October 27th, 1869, first page reproduced below) which was to pass unnoticed for many years is taken out in England; the object is the protection of various metallic materials against rusting.

The inventor, William Alexander Ross, captain in the Royal Artillery Regiment, in the service of Queen Victoria, proposes treatment in phosphoric acid as an anti-corrosion measure.

Phosphating of metals is born

A.D. 1869, 27th October. N° 3119.

Preserving Metals from Oxidation

Figure 3.12 First phosphating patent

- The British 1864 patent began the revolution of phosphating. This was entitled "the treatment of red hot iron with a mixture of coal dust and calcium dihydrogen phosphate in order to improve corrosion resistance of the metal surface"[24].

- Another British patent in 1906 stated an alternative process, which involved heating the phosphoric acid prior to treating the iron. This improved the adhesion with oil, varnish and chromate, thus further improving resistance performance.
- In 1909 it was discovered that by adding zinc dihydrogen phosphate to phosphoric acid, significantly improved corrosion protection resulted
- A 1911 British patent described phosphoric acid solutions containing manganese dihydrogen phosphate as a means of corrosion protection
- 1917 saw the development of phosphate as an anti-rust treatment on industrial plant in Detroit, USA
- In 1933, half of all automobile mudguards produced in the US were phosphated.
- In 1940, researchers in Leningrad developed and put in production, manganese iron dihydrogen phosphate with additional free phosphoric acid
- Forty five million cars (most metallic components), equivalent to 2.7 billion m^2 were phosphated in 1986
- In 2002, 150 million cars manufactured world wide used conversion coating systems.

Zinc phosphate

When the surface of the substrate capable of reacting is brought in contact with the phosphate solution, pickling takes place, in which hydrogen ions are used up. The solution next to the surface then becomes neutralised and poorly soluble solid phosphate phase builds up. When sufficient crystallisation nuclei are formed at the interphase between solution and surface, the coating process begins. During this deposition, the orientation of the depositing phosphate crystals largely follows that of the underlying substrate. The coating process completes when the surface of the metal is so fully covered by crystalline phosphate that no sufficient further neutralisation of the near surface liquid can take place[25].

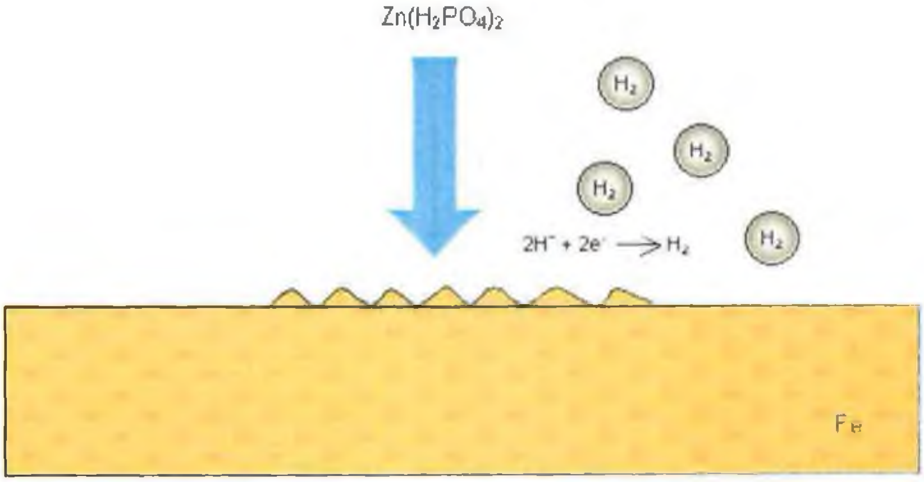


Figure 3.13 Zinc phosphate coating mechanism

Alkaline metal phosphates – Iron phosphate

Alkaline metal phosphates are light weight phosphates and are commonly known as 'iron phosphates'. The main difference between this process and zinc phosphate is that only the anion in the solution plays a role in the coating process. The cation is supplied by the substrate itself. The main ingredients in these solutions are ammonium. dihydrogenphosphate, pH being 3.5 to 6.0. At a pH of 6 virtually no coating occurs. Similarly to zinc phosphate, the coating formation is split into two phases: etching reaction and coating reaction. The etching reaction dissolves some of the metal substrate into solution; this dissolved metal is then used in the coating formation.

Etching reaction

$$Fe + 4NaH_2PO_4 \rightarrow Fe(H_2PO_4)_2 + 2Na_2HPO_4 + H_2\uparrow$$

Coating reaction

$$4Fe + 4NaH_2PO_4 + 2O_2 \rightarrow Fe_3(PO_4)_2 + FeO\downarrow + 2Na_2HPO_4 + 3H_2O$$

As the pH of these solutions are relatively higher than that of the zinc phosphates, the rate of etching is slower. The etch reaction rate can also be altered by temperature, concentration, bath composition, degree of agitation and cleanliness of the substrate surface being treated. It has been shown by research conducted in the mid 1950's that higher coating weights are achieved by spraying alkali metal phosphates than by immersion. As can be seen by the coating reaction equation quite a large quantity of oxygen is required to form the coating (see chemical equation). With extended treatment time total weight of the coating is increased and with spray treatment the rate is much greater.

As well as ammonium dihydrogen phosphates, oxidising agents or accelerators are added to the solution to speed up the rate at which a coating forms. The most commonly used are chlorates, bromates, or nitrates. Research indicates that each of these accelerators have optimum concentration and pH levels[26]. Other ingredients include complexing agents and surface-active agents (surfactants). The addition of polyphosphates reduces sludge that forms on the surface of the coating, which occurs after heavy bath use when orthophosphates are used. Sludge formation is caused by the build up of finely divided insoluble iron phosphate over time. Spray phosphating systems use low foaming non-ionic surfactants. The combination of ingredients gives excellent degreasing properties.

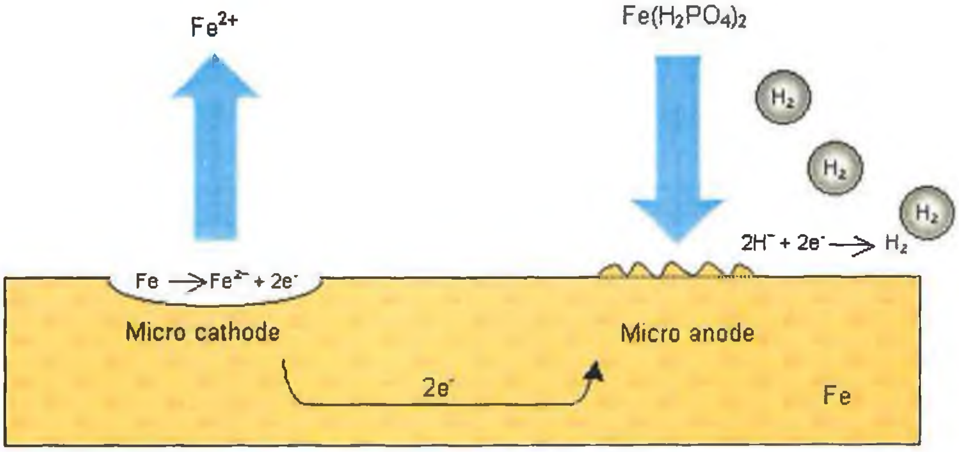


Figure 3.14 Iron phosphate coating mechanism

Post rinse treatment

Subsequent to phosphating the substrate is rinsed first with water and then with a non-chrome rinse. This non-chrome treatment was a substitute, for the previously used chrome VI treatment, which reduced gaps in the coating, minimising electrochemical and other attack. The mechanism for this is the likely formation of complex transition metal phosphates. The non-chrome treatments use zirconium fluoride complexes[27].

Chrome	Non-Chrome
Effluent problems	No present restrictions
Carcinogenic	Non carcinogenic
Requires high temperature	Low temperature – cost effective

Table 3.a Chrome verses non-chrome post rinses

The alternative post rinse treatments are:

- Allow to dry at ambient temperature
- Dry in oven

Flash drying is the preferred option to minimise chemical deposition formation following immersion processes. The post rinse solution is heated to 70°C and rinse water evaporates. In the spray system the substrate is passed through an oven at 120°C.

3.3 Alternative new technologies

Silane

A new technology based on silane chemistry has been developed to meet changing environmental requirements. This treatment based on the use of functional and organofunctional silanes has been developed for use on steel, aluminium and galvanised coated steel. This replaces phosphate/chromate pre-treatment. Organofunctional silanes are hybrid organic – inorganic compounds that are used as coupling agent across the organic – inorganic interface. The functional silanes have a structure $X_3Si\ (CH_2)_nY$, where X is the hydrolysable group such as methoxy or ethoxy and Y an organofunctional group. Nonfunctional silanes are recommended as cross linkers for organofunctional silane film. The group attaches its self to the paint polymer that is applied on top of the silane coating[28].

The diagram below shows the structure of the final surface after treatment, which is illustrated with the cross – linked bis-2, 2-(triethoxysilyl)ethane (BTSE). BTSE forms hydrolytically stable bonds with the metal oxide immediately.

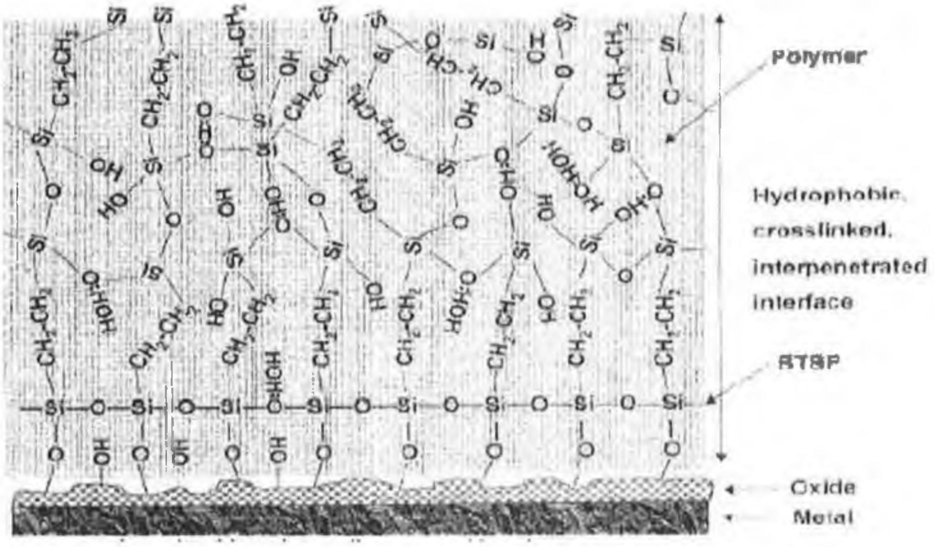


Figure 3.15 Silane coating[29]

Modern commercial silane treatments also consist of functional silane and non-functional silane[30].

- Functional silane e.g. Vinyl Silane

  $CH_2{=}CH\ Si(OCH_3)_3$

- Non-functional silane e.g. B.T.S.E.

  $(C_2H_5O)_3\ Si\ (CH_2)_2\ Si\ (OC_2H_5)_3$

These silanes can be applied by both spray and immersion. The operating conditions include process time from 1 second to 1 minute. The solution concentration of 10-30% and a pH range of 4 to 6 applies to this process. The substrate is dried at temperature between ambient and 120°C. A biocide may be necessary to control bacteria.

Film thickness is apparently determined by solution concentration solely and not by dipping time[31]. Recommended solution controls include pH monitoring, and colorimetric test for concentration.

Autophoretic/Autodeposition

Autodeposition is a process of applying an anti-corrosive layer to metal by means of a chemical reaction. There are many similarities between electro-less plating and conventional painting. Autodeposition has many benefits over painting. It is a waterborne process that depends on chemical reactions to achieve deposition. This process has been in commercial use since 1975. Since then, the practice of autodeposition has grown and matured.

An autodeposition bath consists of mildly acidic latex emulsion polymer, DI water, and other proprietary ingredients. The bath solids are normally between 4% and 6% by weight. The bath viscosity is close to that of water with little or no organic solvents in the coating bath. The continuous formation of coating provides a film with a high degree of surface protection and corrosion resistance. A unique feature of the autodeposition process is the formation of a very uniform film over the entire surface of the work piece, even in difficult-to-reach areas.

Unlike coating processes that require a charge to deposit the coating (i.e., where electrical energy is required to "throw" the coating into recessed areas) autodeposition will coat tubular, assembled, or intricate-design areas uniformly. Autodeposition coating film thickness is controlled by diffusion of reactants in the bath and through the coating already formed on the surface of the substrate. This diffusion control leads to a uniform coating thickness on complex shapes and in recessed areas.

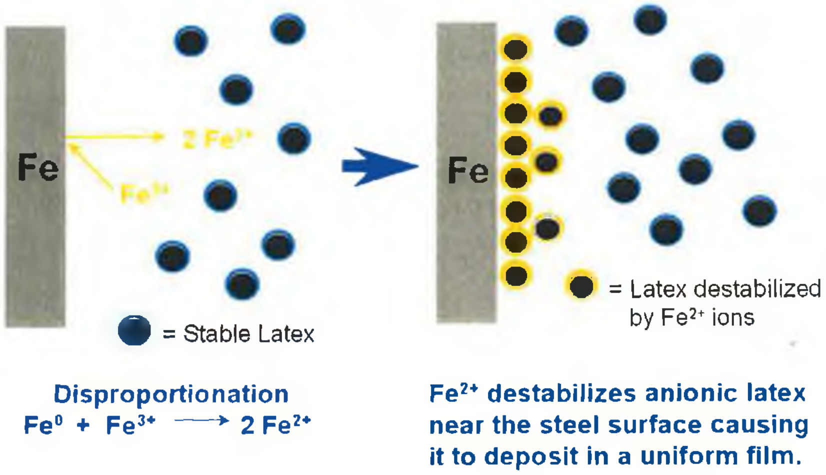


Figure 3.16 Autodeposition mechanism[32]

It should also be mentioned that the autodeposition process does not require a chemical conversion coating. The elimination of these stages leads to considerable savings in required floor space, energy, and operating costs, as well as the total elimination of toxic metals from the process. Considerably lower temperatures are required to cure the autodeposited parts.

Chapter 4 – Experiments and results

This chapter details laboratory and plant experimental work. There were three distinct sections in the experimental work carried out including laboratory test development, laboratory research and development, and pilot plant/Thermo King plant investigation. These were carried out in GMIT, Thermo King, Henkel (Milton Keynes), Chemetall (Milton Keynes), as part of the project.

4.1 Laboratory test development

The following tests were developed to enable analysis of effluent streams. Orthophosphate and polyphosphate are present in Thermo King waste water, as discussed earlier a discharge limit of 5mg/l total phosphate is permitted by EPA under IPC license. In order to achieve this limit flocculants were examined, aluminium sulphate and Fe^{3+} sulphate.

Test for orthophosphate

Analysis of orthophosphate was carried out by the ascorbic acid method. The results were found to be linear in the range of 0-5ppm as P. The method developed is a standard test in which quantified phosphate levels are measured using a spectrophotometer after the formation of a blue phosphomolybdic acid complex. The optimum ratio for reactants ammonium molybdate and ascorbic acid was found to be 3:2. As glassware is often cleaned with phosphate containing detergents, it was found necessary to wash glassware with 0.1% sulphuric acid/deionised water between test runs.

Subsequently a micro test (appendix 2) for orthophosphate was derived that reduced quantities of chemicals by a factor of 10. The micro tests were faster, cheaper and more environmentally friendly.

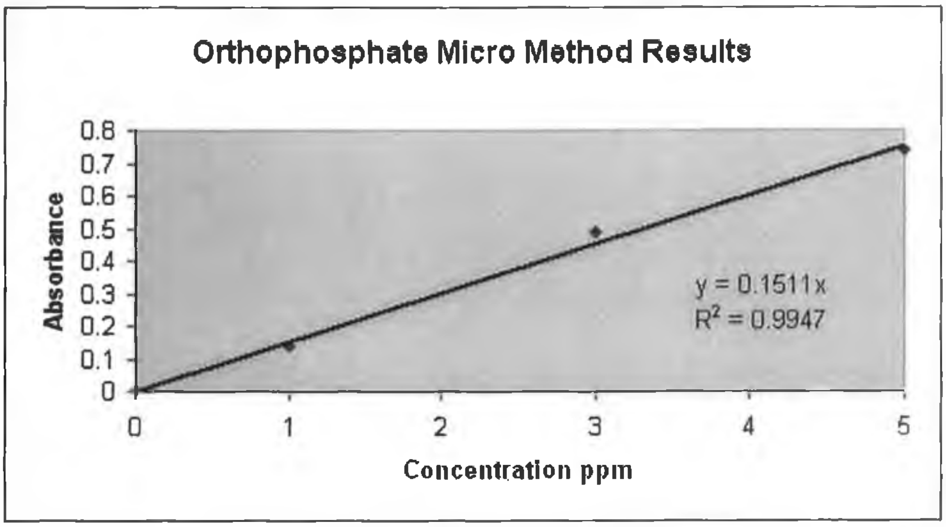


Figure 4.1 Orthophosphate micro method results

Reproducibility of phosphate tests

The absorbance value of the standard varied from run to run because of sensitivity to minute changes in pH and temperature. It was therefore necessary to duplicate standards in all cases. The results in figures 4.1 and 4.2 show excellent linearity with a correlation coefficient of approximately 0.99.

Test for total phosphate

The total phosphate test[33] (appendix2), was developed using a similar process. This test necessitated an acid hydrolysis step to hydrolyse the P- P bond in polyphosphate such as ($Na_2P_4O_7$) tetrasodium pyrophosphate. It was discovered that after the hydrolysis stage obtaining the correct pH level to phenolphthalein end point (8.3pH) was vital to create the characteristic blue colour. Instead of adding a set quantity for each flask it was found that more reproducible results were obtained when each flask was altered independently until correct pH was reached. Similarly to the macro test the micro test needed careful additions using a drop at a time to obtain the correct pH.

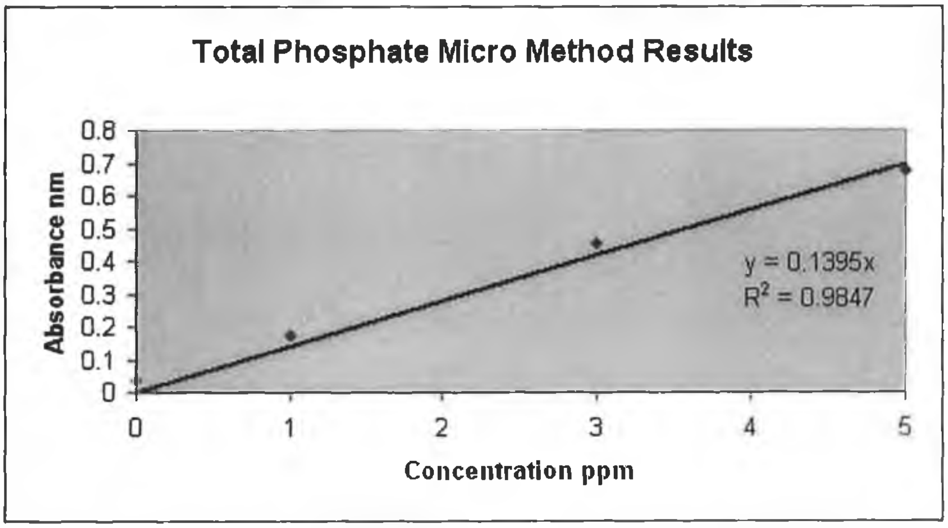


Figure 4.2 Total phosphate micro method results

Test for Fe^{3+}

The test for Fe^{3+} (appendix 2) used to obtain a standard curve was the ammonium thiocynate method. This worked successfully without any difficulty. A scan was completed to obtain the correct wavelength for maximum absorbance. This was then followed by the preparation of standard solutions. The absorbance was found to be 464 nm. A pink colour developed in the presence of iron. Reducing the quantities by a factor of 10 derived the micro Fe^{3+} method.

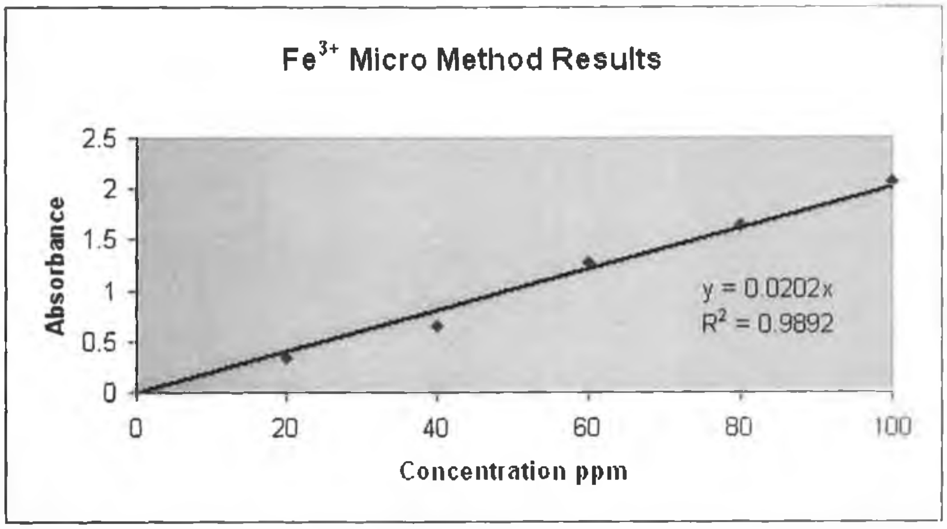


Figure 4.3 Fe^{3+} micro method results

Test for aluminium

The colorimetric determination of aluminium was completed using eriochrome cyanine R. This method (appendix 2) produces a yellow colour for blanks and red for the presence of aluminium. The wavelength of maximum absorbance for the aluminium complex was 535nm. This method worked without any difficulty and a micro method was also developed.

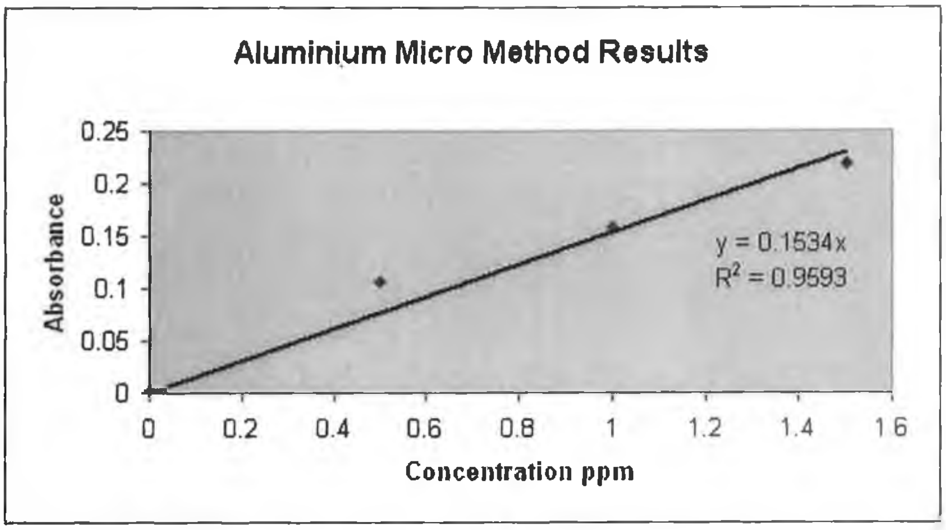


Figure 4.4 Aluminium micro method results

4.2 Laboratory research and development

Electro coagulation / electro floatation

Chemical coagulation has been used since the beginning of the 20th century in industry. It is a method of destabilising colloidal suspensions, to help precipitation of soluble metal species from aqueous solutions leading to their removal through filtration or settlement. This process tends to liberate large volumes of sludge with a very high water bound content. To overcome this problem and other problems such as high dissolved solids making effluent unacceptable for reuse, alternating current electro coagulation technology was developed in the early 1980's.

The principle of electro coagulation was based on colloidal chemistry using alternating (AC) electrical power and electrophoretic metal hydroxide coagulation. This means that as current alternates between the two electrodes it liberates metal hydroxide into solution, this then works on the same principle as chemical flocculation by precipitating out dissolved metals. The flocculation enabled particles to join together forming a floc or sludge, caused by the van der Waals attractive forces[34].

Electro coagulation experiments were carried out in the laboratory using both direct and alternating current and different electrode materials were also used. The different electrodes used included brass, stainless steel, aluminium and mild steel. Each of these electrodes gave a different coloured sludge.

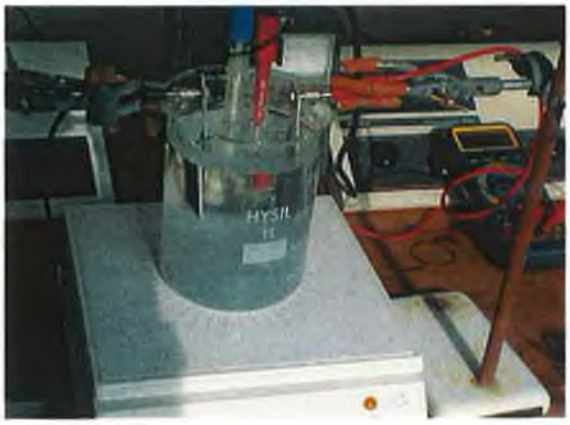


Figure 4.5 Electro-coagulation with alum electrodes after AC process

Direct Current electro-coagulation

In order to initiate the process for direct current (DC) electro-coagulation, a $10cm^3$ aliquot of 2M-sodium hydroxide was added to 1 litre of phosphate solution. A precipitate formed on the metal anode. The phosphate solution was 100ppm pyrophosphate made up with deionised water. The voltage was set at 30V and the current was shown to be 0.8A. A magnetic stirrer was placed in the beaker to aid the process. There was a large amount of gas liberated from the cathode, while no gas was liberated from the anode.

Anode – electrode at which oxidation occurs

Cathode – electrode at which reduction occurs

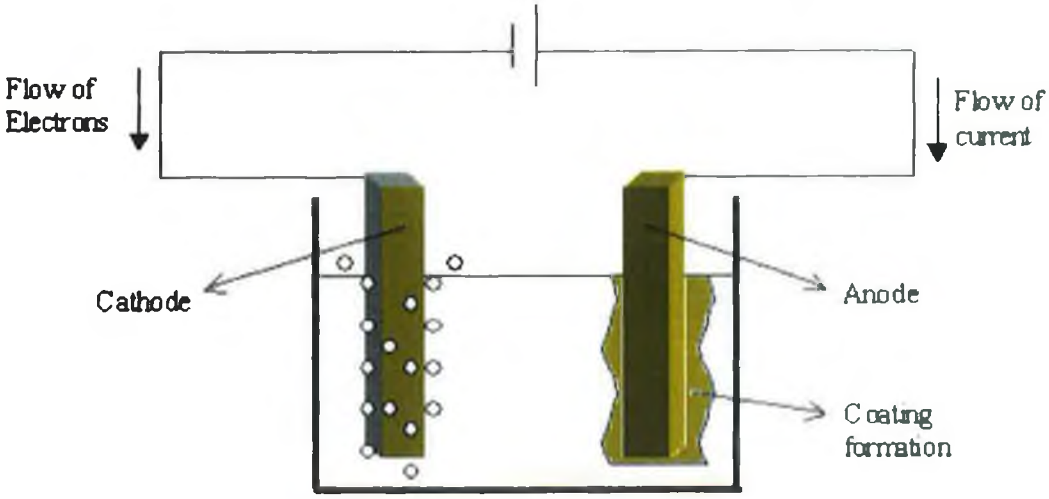


Figure 4.6 Electro-coagulation using DC power

Alternating Current electro-coagulation

The alternating current (AC) experiments were powered by using an ac transformer, which was connected to the mains and the voltage was set at 18V. Once again 10ml 2M-sodium hydroxide was added to the 1 litre phosphate solution to help begin the process. While the power was turned on there was a large amount of gas liberated from both electrodes. There was also a magnetic stirrer in the beaker to help speed up the process.

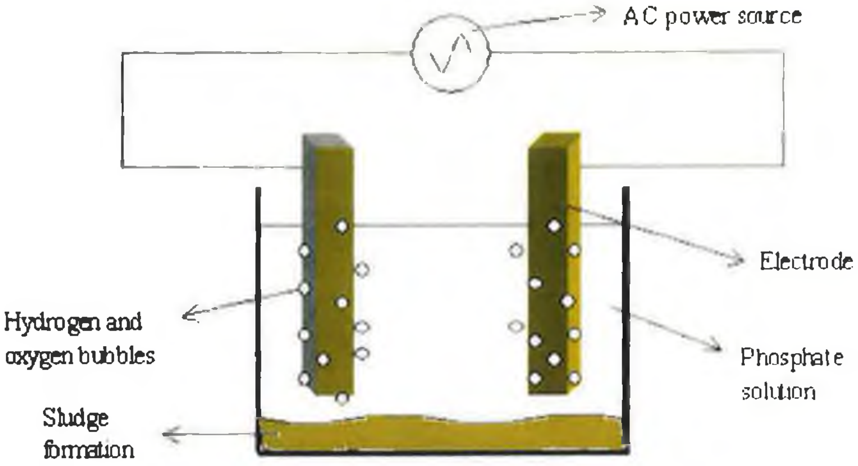


Figure 4.7 Electro-coagulation using AC power

The photograph below shows sludge after the use of a brass electrode. The blue colour was due to precipitated copper from the brass.

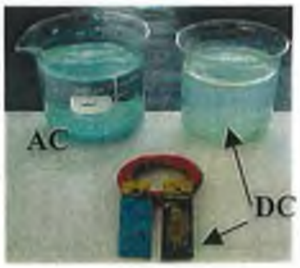


Figure 4.8 Photograph of brass electrodes and solutions after AC and DC power

Chemical Precipitation

A series of experiments were completed in the laboratory to determine the correct pH required for precipitation of each flocculant and also the optimum concentration required for removal of phosphate. The method for determining pH range for precipitation of each chemical was the same. It involved adding excess flocculant to a set concentration of phosphate solution. The pH of the solution was altered using either sulphuric acid or sodium hydroxide. The solution was filtered using filter paper. The filtrate was analysed for phosphate. To determine the correct quantity of flocculant required for removal, a known quantity was added to a phosphate solution and the pH altered to within the correct range for that particular chemical. Once again the solution was filtered and then tested for phosphate. The following results were obtained:

Flocculent	**Colour**	**pH range**	**Quantity of flocculant required for 200ml of phosphate at 100ppm**	**Settling time**
Alum	Grey	7-8.5	3ml at 5%	Medium
Lime	Light grey	9-11	5ml at 2%	Slow
Fe^{3+}	Reddish/brown	6-9.5	5ml at 5%	Fast

Table 4.a Comparison of flocculants

The pH limits given by Thermo King's IPC licence are 6-9 for effluent discharge, as a result lime was not used for plant trials. Both aluminium sulphate and Fe^{3+} sulphate were suitable for large-scale trials, and Thermo King was advised to purchase 1000 litres of aluminium sulphate and Fe^{3+} sulphate. Plant trials lasted one month for each chemical, during which time close monitoring of system was completed daily. The effectiveness of the phosphate removal is clear from the photograph below. The supernatant liquid was found to have 0.05ppm phosphate on analysis.

Figure 4.9 Fe^{3+} sulphate floc in phosphate solution

Thermo King phosphate removal

The following chart highlights the improvement in effluent phosphate levels. The samples were obtained from a flow related composite sampler taking 100ml from every cubic metre of effluent discharged to drain. The graph shows the dramatic improvement achieved. When this improvement was achieved the project focus was changed. Unfortunately the plant phosphate removal performance reverted to pre-project variability (see figure 7.1).

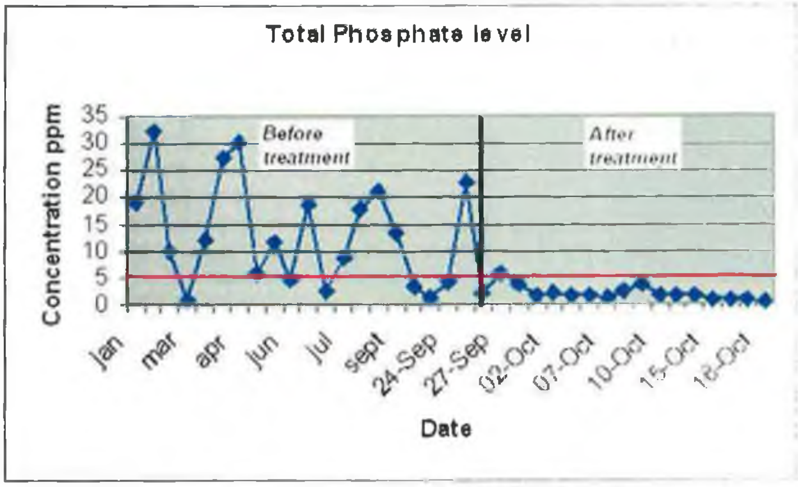


Figure 4.10 Total phosphate level

When Fe^{3+} sulphate treatment was installed in the plant, virtually all of the phosphate was precipitated as floc. This was then removed by plate and frame filter giving the results shown above in figure 4.10.

4.3 Pilot plant/Thermo King plant

Alkaline Cleaning

Cleaning prior to applying a conversion coating is essential, as oil and dirt will block any chemical bond forming between the base metal and the conversion coating. It was decided to examine the mechanism of action of the following two cleaners produced by Henkel and Chemetall, the leaders in finishing chemical manufacture

Cleaner	**Novaclean 177D**	**Gardoclean TP10528**
pH	>11.5	<10
Composition	Caustic	Non-caustic amines
Inhibition	Silicate	Borax

Table 4.b Cleaner composition

It was noted that the pH of Novaclean was 11.5, consistent with its caustic content. The Gardoclean had a much lower pH of <10. This cleaner consists of amines and carbonates.

There are several cleaning effectiveness tests, most of which are extremely time consuming and destructive (leading to the component being rejected). The most commonly used procedures are white glove test (appendix3) and water break test (appendix 3), both of which were extensively used during this project.

Laboratory cleaner experiments

Both cleaners were made up to manufacturers guidelines in the mini tank system. The cleaning effectiveness tests performed were water break, white glove and paint evaluation. Each cleaner performed adequately for water break and white glove tests. To carry out the paint evaluation the test panels were coated with zinc phosphate followed by a non-chrome post rinse. Panels were then oven dried at 120°C for 15 minutes, and painted in Thermo King. Impact, adhesion, 24 hour and salt spray tests were performed. Both cleaners performed within all specifications of the test requirements see appendix.

Water

The water used in the mini system was from Galway's municipal supply. Where necessary DI water was obtained from GMIT DI supply (USF ELGA). The conductivity of each was measured to determine water quality and the following results were obtained.

Municipal supply	250	µS
Deionised water	4	µS

Deionised water was used only in the silane experiments. The limit imposed by manufacture for silane use was 50µS/cm^3.

Pilot plant water control

The rinse tanks in the GMIT pilot plant were changed at three-day intervals, and conductivity monitored during tests, as contamination of rinse waters leads to poor cleaning properties.

Thermo King plant water control

Conductivity meters were introduced into the rinse tanks and daily checks were carried out by pH titration. Rinse tanks were dumped once per week and scale removed by power washing. Screens were checked daily and cleaned as necessary, usually every two days.

The graph below displays the volume of water consumption versus time since the beginning of this project. The rise in consumption around the 4th quarter of 2002 was due to a change in chemicals being used for conversion coating.

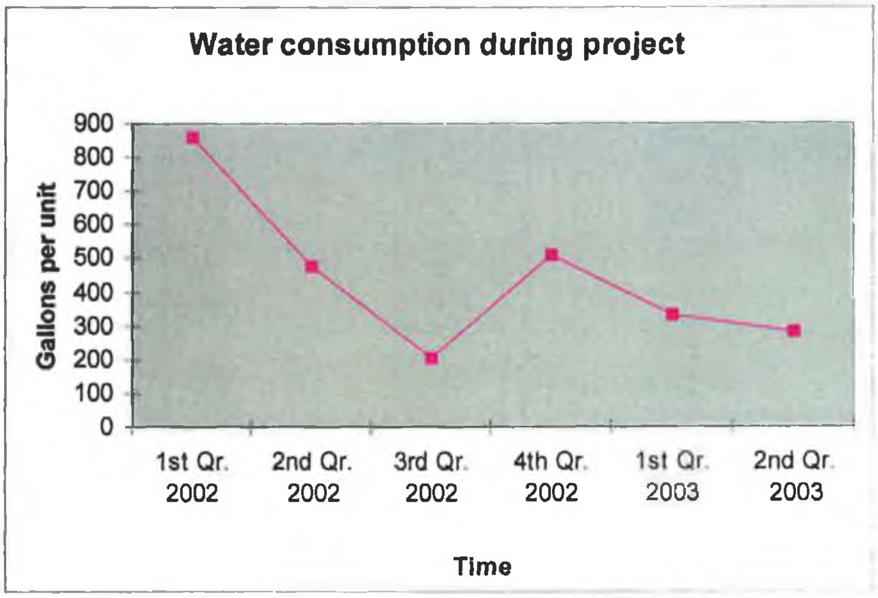


Figure 4.11 Water consumption during project

Zinc Phosphate Coating

Conversion coating using zinc phosphate is a long established successful technology. A critical aspect of the process was considered to be nitrite acceleration. A series of experiments was carried out to establish the mechanism/effectiveness of this catalyst. Sets of panels were treated with different concentrations of accelerant (nitrite) to establish optimal levels. It was discovered that the absence of the nitrite led to complete failure in all cases.

Zinc phosphate solution forms a suspension when diluted with water. Literature studies suggest that it is this suspension of zinc calcium phosphate that forms the conversion coating in the presence of the nitrite anion.

Iron Phosphate

Due to the oxygen consumption (page 31) of iron phosphate, spray application was found to be superior to immersion treatment.

New cleaner with iron phosphate

The use of a mini spray system became available in Chemetall, which was used to test the iron phosphate with Gardoclean TP10528 before installation of this new cleaner on the spray line in TK. This proved to be a successful combination.

Alternative two stage process for iron phosphate

Panels were tested to examine the possibility of using a two-stage iron phosphating spray system instead of the current cleaner-coat process as outlined below:

Cleaner-coat system	**Two-stage iron phosphate system**
Clean	Iron Phosphate
Rinse	Rinse
Rinse	Iron Phosphate
Iron Phosphate	Rinse
Rinse	Post Rinse
Post Rinse	

Eight mild steel production panels were processed on each process. Two panels were subjected to mechanical testing, two for salt spray and two for 24-hour testing. Both processes passed all of the above assessments. Finally two were measured for coating weight. The average coating weights obtained were found to be;

Cleaner-coat system	0.1608 g/m^2
Two stage iron phosphate system	0.193 g/m^2

It was noted the two-stage iron phosphate system yielded higher coating weights, thus improved adhesion. This new process has the advantages of fewer chemicals and less steps. However cost benefit analysis would need to be under taken.

Post Rinse

The zirconium post rinse solution is very expensive and plant trials were carried out which enabled optimisation of this step. Tighter control parameters and new dumping procedures led to chemical consumption being halved while maintaining quality.

Silane technology

The first experimental work on silanes was conducted in Chemetall Milton Keynes plant. These trials looked at two different silanes and processed them by immersion. The substrates treated were standard steel, production mild steel, production galfan, and production aluminium. These panels were powder painted in Thermo King. To ensure adequate paint adhesion the paint is tested using a standard phosphate panel which when painted correctly will achieve 700 hours salt spray resistance. Accelerated corrosion tests, 24 hour and salt spray were conducted along with mechanical tests of mandrel bend and impact to ensure adhesion of paint to the conversion coating. Oxsilan al500 silane failed the 24-hour test along with salt spray. This chemical was then withdrawn from further trials. The successful chemical Oxsilan mm705, with concentration in the range 10 – 15 % was found to provide 700 hours salt spray protection when followed by powder paint. However when this was then followed by wet dip paint there were adhesion problems. The mild steel and galfan panels failed impact tests. The manufacturer was contacted and an alternative chemical investigated for immersion treatment followed by wet dip paint. This chemical proved to be more successful and passed the adhesion test along with salt spray and 24 hours tests. The chemical was tested at varying concentrations and it was found the optimum levels were between 15 20 %.

The following is the process used to obtain silane conversion coating in all experiments in which the new environmental cleaner was used.

1. Clean - 3 minutes – 10% concentrate
2. Rinse – 15 seconds - <400μS
3. Rinse – 15 seconds - <400μS
4. Rinse – 15 seconds - <50μS
5. Silane – 2 minutes – different concentrations depending on silane
6. Drip - 2 minutes
7. Dry
8. Paint – Powder/wet paint

The following tests were carried out to confirm process effectiveness.

1. Paint thickness
2. Mandrel bend
3. Direct and indirect impact
4. Adhesion
5. Hardness

Mechanical tests

6. Salt spray
7. 24 hour test

All of the above tests were performed in duplicate.

	Material	Reason for inclusion in test to show
1	Standard bare steel UMA	Steel production panels are correct composition
2	Standard iron phosphated steel	To ensure quality of paint
3	Steel used in production	Effectiveness of silane on production material
4	Aluminium used in production	Effectiveness of silane on production material
5	Galfan used in production	Effectiveness of silane on production material

Table 4.c Panels and reasons for inclusion

Panels were put through two processes, to mimic the production facilities at Thermo King (spray and immersion). The spray process was conducted at Chemetall and then sent to Thermo King to be powder painted. The immersion process was conducted at GMIT and then dip painted at Thermo King.

	Panels required	# of materials	# of process	Total panels
Mechanical tests	2	5	2	20
Salt spray	2	5	2	20
24 hour test	2	5	2	20
Chemetall	2	5	2	20
Thermo King	6	5	2	60
Total panels	14	5	2	140

Table 4.d Tests on substrates

The total of each material was fourteen due to the test requirements as shown in table 4.d. The table 4.e below details the each material type and the processes, which were undertaken.

Material	Immersion Silane followed by wet paint	Spray silane followed by powder paint
Standard bare steel UMA	14	14
Standard iron phosphated steel	14	14
Steel used in production	14 painted only	14 painted only
Aluminium used in production	14	14
Galfan used in production	14	14

Table 4.e Processes on substrates

The following is a photograph taken in the Chemetall laboratory. It shows the pilot spray system used in trials.

Figure 4.12 Photograph of pilot spray plant in Chemetall

Autophoretic technology

All work on autophoretic processes was conducted at the Henkel laboratory in Milton Keynes. A series of both production panels and standard panel were processed. The process involved the following steps:

1. Spray cleaned – 2 minutes
2. Immersion cleaned – 2 minutes
3. Tap water rinse – 15 seconds
4. Deionised rinse – 20 seconds
5. Autophoretic – 3 minutes
6. Deionised rinse – 20 seconds

7. Reaction rinse – 30 seconds
8. Curing 20 minutes

The photographs below show the tank of autophoretic in operation. As can be clearly seen there is a large amount of agitation.

Figure 4.13 Autophoretic solution and process line

During a visit to Henkel Surface Technologies, Milton Keynes, mild steel panels were coated using the 800 series of autophoretic chemicals, which cannot be painted due to its in compatibility with high temperatures. Panels coated with the 900 series of autophoretic chemical capable of high temperature were also obtained. One of each series was painted and one left blank, these were corrosion tested using the 24-hour test.

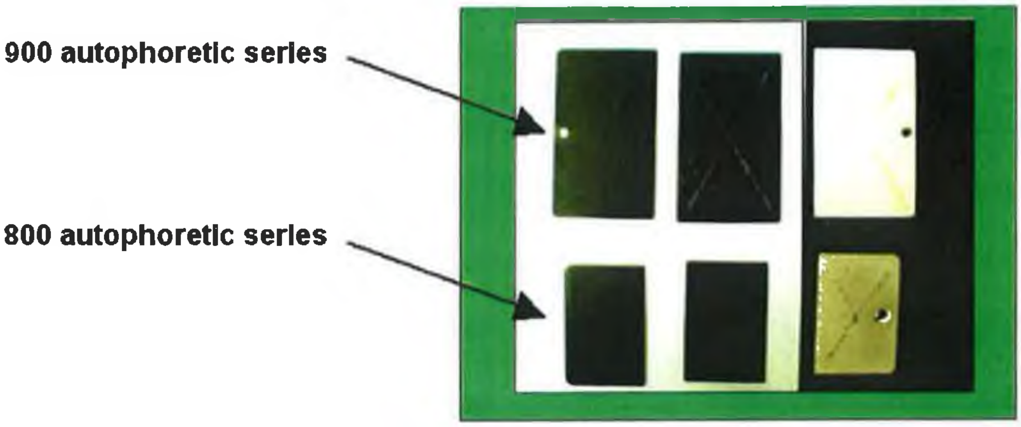


Figure 4.14 Autophoretic panels

The coating thickness of the autodeposited film is time and temperature related. The film thickness continues to grow as long as ionic species are being produced at the coating/metal interface. Initially, the deposition process is quite rapid, but slows down as the film increases in thickness. Typically, film thickness produced is controlled from 15-25μm.

4.4 Scanning electron microscope

The scanning electron microscope SEM was used to view the microscopic structure of the various conversion coatings used during this project. On the basis of personal observation over the course of this project both iron phosphate and zinc phosphate conversion coatings give adequate protection when properly applied. However, zinc phosphate treatment was found to be far less sensitive to minor fluctuations in chemical composition. Observation of the physical structure of zinc phosphate shows to be far more crystalline than the iron phosphate. It is reasonable to expect paint particles to adhere more to a rough crystalline surface in preference to an amorphous flat area.

The crystalline structure of zinc phosphate explains why this coating has the best adhesion to paint and is more resistant to variation.

500 times magnification **2000 times magnification**

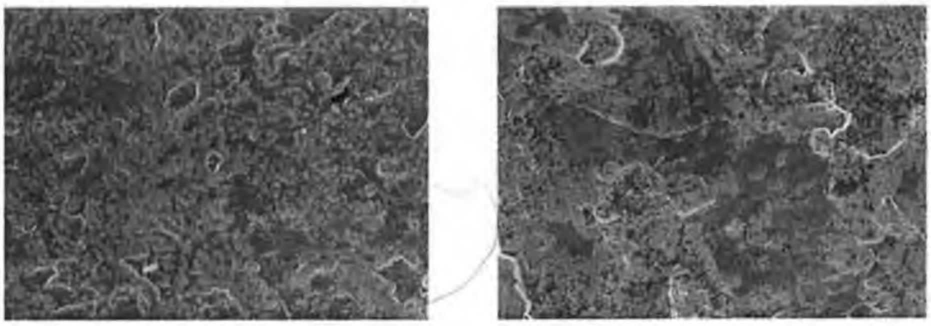


Figure 4.15 Steel with no conversion coating

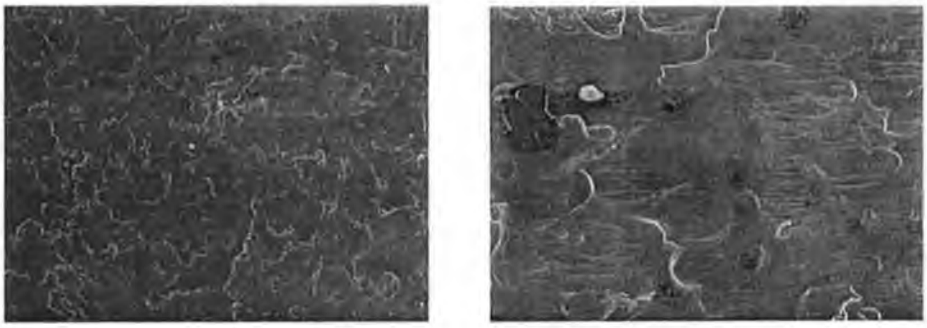


Figure 4.16 Steel with iron phosphate coating applied in Thermo King plant

Figure 4.17 Steel with iron phosphate coating applied under laboratory conditions

500 times magnification **2000 times magnification**

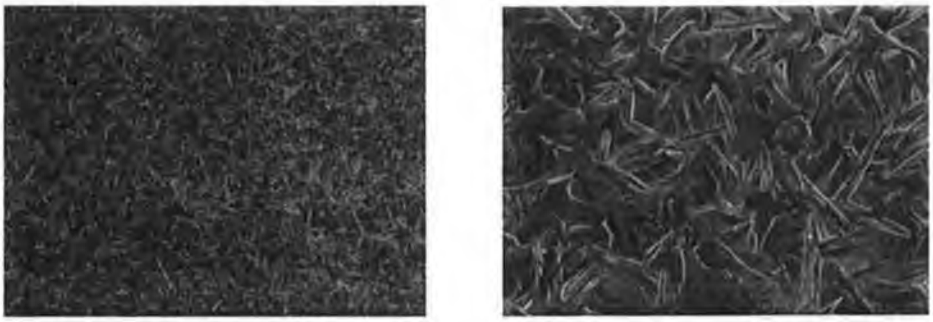


Figure 4.18 Steel with zinc phosphate coating applied under laboratory conditions

Figure 4.19 Steel with Silane mm705 applied under laboratory conditions

Chapter 5 - Pilot Plant

An objective of this project was to design, manufacture and install a pilot plant capable of carrying out tests on substrates using current and new process technologies. A preliminary design was valued, and budget of €1000 was sanctioned.

The pilot plant was designed following a visit to Chemetall and Henkel research laboratories. Factors that were considered of critical importance were ease of use, modular design and ease of manufacture.

It was noted that work involving the pilot plant had to take several factors into account, which were not important in a small-scale laboratory simulation. Mass heat transfer and agitation of solutions on a large scale requires suitable instrumentation.

5.1 Requirements

Pilot plant comparison with Thermo King immersion system

The plant was designed to simulate conditions present in Thermo King. The immersion process was thought to be a more clear-cut design than a spray application. Two critical factors in the design specification were temperature control and agitation performance. Trials were performed using 2.5 litre beakers to determine if conditions could be replicated. Several problems arose including control of temperature, costly agitation, and processing of multiple panels. The pilot plant designed had the following features: heating element, agitation control and adjustable temperature control. This was modelled on the Thermo King plant. As discussed earlier the TK immersion plant contains eight stainless steel tanks each with a volume of 8000 litres. The temperature is adjustable up to 80°C. The speed and ease of use were also critical in the design of the pilot plant. The ability to change chemicals and perform tests within one day was required.

Specifics for pilot plant:

1. 5 tanks constructed of chemical resistant material
2. Temperature control up to 70°C in at least 2 tanks
3. Capacity minimum of 30 litres for all tanks
4. Agitation system for at least 1 tank

5.2 Design alternatives

Many alternative design concepts had to be abandoned because of cost considerations. Water baths used in many laboratories have the above features and would be ideal to use, but as each one costs in excess of €1000, their use was excluded at the outset.

Proposal	Capacity	Material	Unit cost	Total Cost
1	28 litres	Stainless steel	501.12	2505.60
2	55 litres	Glass	58.82	294.1
3	20 litres	Polypropylene	254.6	1217.3
4	45 litres	Stainless steel	Free	Free

Table 5.a Materials selection for pilot plant

In terms of compatibility with process streams, glass was unsuitable because of its reactivity with halogens (e.g. fluoride), and concentrated alkali, which are present in the pre-treatment chemicals. Glass being brittle was unsuitable. Stainless steel was considered the best of the options because of its non-reactivity with process chemicals and its durability.

Fortunately a supply of high grade stainless was obtained free of charge form Thermo King. Proposal 4 was adopted from the above table. A flat sheet of stainless steel was cut and then stainless steel welding was carried out in Thermo King. The design can be seen below from a 3d model generated through ProEngineer.

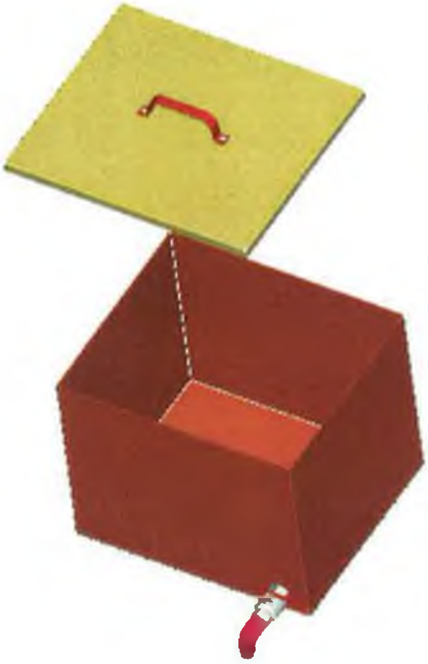


Figure 5.1 Tank design 3-d model

Heating was affected by inserting a 2kW element. The alternatives considered are set out in table below. Three tanks were equipped with elements. These were chemical resistant stainless steel elements with thermostatic control.

Proposal	Material	Component	Cost €	Total Cost €
1	Coated mild steel	Portable Heating rod	135.44	135.44
2	Stainless steel	Portable immersion heated	169.12	169.12
3	Stainless steel	Element	105	315

Table 5.b Heating proposals for pilot plant

Proposals one and two were dismissed due to the extended time required to heat solutions and difficulty in maintaining temperatures.

Figure 5.2 Element design

A mechanical stirrer supplied agitation. This was created by connecting a redundant electric motor to a stainless steel shaft which had a welded propeller attached. The alternative air agitation was considered inferior because of degradation of the cleaner by carbon dioxide absorption and bacterial formation. The alternatives considered were documented in table 5c below.

Proposal	Component	Cost €
1	Peristaltic pump drive	764.71
2	Overhead stirrer	1367.65
3	Alternative using scrap	Free

Table 5.c Agitation proposals for pilot plant

To drive the motor rechargeable batteries were, supplied by Thermo King. The 3D diagram below shows the motor with attached rod and propeller.

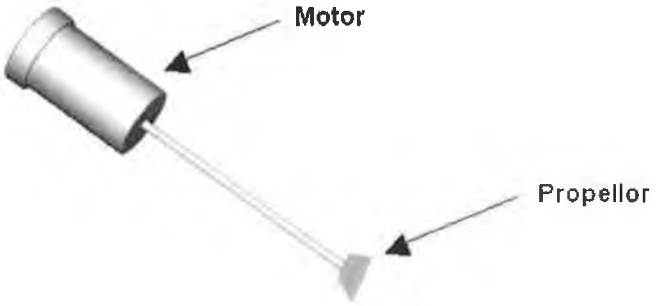


Figure 5.3 Agitator design

In order to maintain reproducibility a jig was required to hold the panels fixed within tanks. Since some processes require several minutes, a design was constructed to allow the jig to "sit" on the tank. Below is the design drawing and photograph of the final jig.

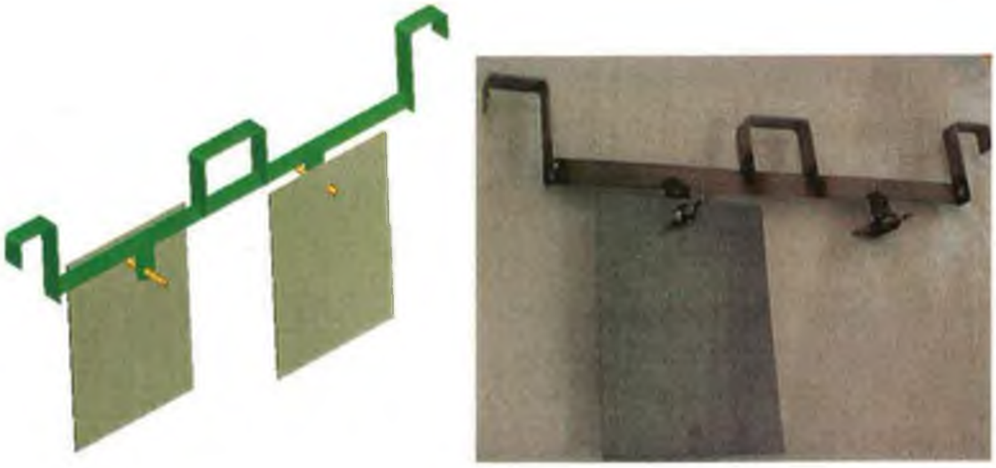


Figure 5.4 Jig design and photograph

5.3 Comparison between Thermo King and Pilot Plant

The table below (table 5d) shows the comparison between the Thermo King immersion plant and the pilot plant. As can be seen there are similar features so as the pilot plant may work as miniature simulation. Although the TK has eight tanks it was only necessary to use five tanks in the pilot plant to simulate process, as TK had three duplicate stages to facilitate production. The pilot plant had identical chemicals concentrations and residence time. The agitation was of necessity different, as air agitation promotes bacterial growth. Test panels were run through the pilot plant and though the Thermo King immersion plant to confirm the process were of identical performance.

	Thermo King immersion plant	Immersion pilot plant	Comment
Temperature	Adjustable on 3 stages up to 75°C	Adjustable on 3 stages up to 80°C	-
Material	Stainless steel	Stainless steel	-
Agitation	Air	Mechanical	Air promotes growth of bacteria
Stages	5 stages - 8 tanks	5 stages - 5 tanks	Extra tanks to aid in tight production schedules
Capacity	8000 litres	45 litres	Ratio 178:1
Jigging	Can hold 2 frames	Can hold up 6 test panel	Stainless steel jigging on both plants

Table 5d Comparison of Thermo King and pilot immersion plants

The following diagram shows the assembly drawing for the tanks, followed by a photograph of the tanks after the manufacture.

Figure 5.5 Assembly 3D model of pilot plant

Figure 5.6 Photograph of pilot immersion plant

Operation

Test panels were mounted on jigs and immersed successfully in tanks. The pilot plant was set up by heating the necessary tanks to 80°C (90 minutes). Cleaning performance was judged by two tests white glove and water break tests (appendix 1c).

Validation of Silane using Pilot Plant

A set of panels was processed through the system, and a corresponding set kept for external corporate validation by Thermo King International. In order to gain corporate approval six of each substrate were sent to Thermo King headquarters in Minneapolis. A further two of each substrate was sent to the manufacturer of the chemicals. The processing of the panels was carried out in the GMIT laboratories.

Chapter 6 – Chemical engineering in Thermo King

This section highlights improvements made to each process step in Thermo King. These processes include cleaning, conversion coating, corresponding rinses and painting.

6.1 Alkaline cleaning

Thermo king uses a variety of metals and these have different reactivities with different cleaners (as discussed in chapter 1). During the course of the project a selection of different cleaners was used on the spray line plant in Thermo King.

Used	Manufacture	Name	Properties	Cleaning ability
2000 to October 2002	Chemetall	Gardoclean 5204	Low caustic, high phosphate, silicate	Did not meet requirements
November and December 2002	Henkel	Novaclean 177d	High caustic, high phosphate, silicate	Good
January 2003 to present	Chemetall	Gardoclean TP10528	No caustic, low phosphate, no silicate	Good

Table 6a. Thermo King's spray cleaner usage

The basic test for cleaning effectiveness is the water break test, according to Thermo King specification (appendix 1a). The Thermo King specification for water effluent also dictates no silicate, no caustic and minimal phosphate. As the environmental requirements change there is a corresponding need to change the composition of pre-treatment chemicals. Successions of alternative cleaners from different manufactures were tried in the factory from October 2002 to March 2003. The Gardoclean 5204 and Novaclean 177d had to be replaced because of caustic content. The Gardoclean TP 10528 met the specification requirements.

The changeover from the Novaclean 177d to the Gardoclean TP 10528 was complicated by precipitation of residual silica sludge and excessive reactivity. In order to rectify this the tank was dumped and "acid cleaned" to remove all particulates from the walls and floor.

Metal attack was overcome by increasing the concentration of borax, which inhibits metal attack. Monitoring of borax concentration in Gardoclean TP 10528 on a daily basis was deemed necessary to ensure proper inhibition of the metal. The fact that units can be left for prolonged periods on the TK plant necessitates controlling the reactivity of the cleaners with inhibitors. This is not normally a problem on a laboratory or even pilot scale work.

At laboratory scale all equipment was washed thoroughly and components were never left in cleaner stage for extended periods. These issues could not have been anticipated at laboratory scale. They were all due to localised conditions, none of which occurred on the immersion mini system at GMIT or spray mini system at Chemetall.

6.2 Phosphating

Iron Phosphate coating

Initially laboratory procedures to quantify iron phosphate coating weight and corrosion resistance were developed (appendix 3c). Optimisation of plant performance was carried out by varying process chemical parameters and equipment settings. Average corrosion resistance times were improved from 300/400 hours to 700 hours salt spray resistance. Coating weights, which had been erratic were now all to specification at 25 – 75 mg coating/m^2

The acidity of the tank was increased, which in turn increased the coating weight, and the adhesion to paint. An alternative faster, 24 – hour corrosion resistance test was developed from a Rover engineering standard, to accelerate corrosion testing. This test was calibrated with salt spray and in conjunction with coating weights was used to monitor progress of performance. Once the correct operating parameters were established, the spray line quality improved and as a result chemical consumption variation was eliminated.

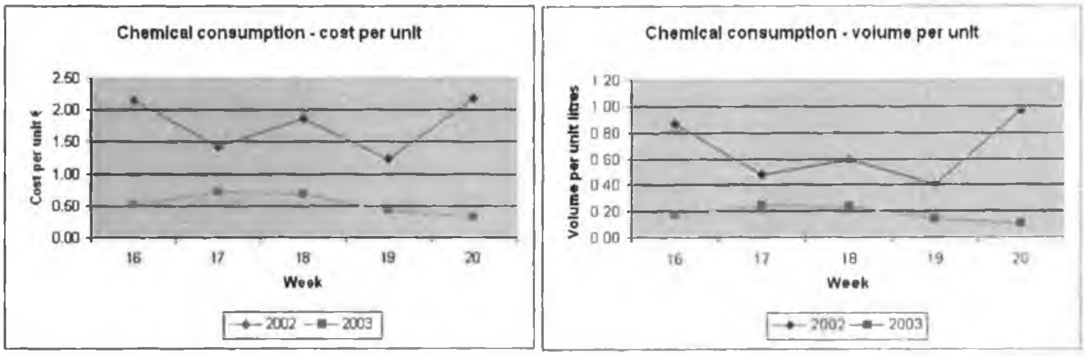


Figure 6.1 Chemical consumption per unit

Note: Corresponding weeks were compared to seasonal variation. A breakdown of figures can be found in Appendix 5.

Zinc phosphate Coating

A dust, which sometimes developed on the zinc phosphate coating, was caused by an inadequate accelerator (nitrite) concentration. New process control procedures for nitrite were initiated and the problem was eliminated.

6.3 Water reduction

One of the major successes of this project was the great reduction in water usage per unit manufactured. In order to reduce water consumption conductivity meters were installed on the spray and immersion lines. These were calibrated regularly and since then, water usage dropped significantly. From experience in the US, a conductivity of 500μSm^{-1} was adapted for rinse water. When rinse water reached this value, fresh water was added automatically. The diagram below shows the set up on the immersion line. Prior to conductivity meter use, there was a constant flow of water to the rinse stages on both processes.

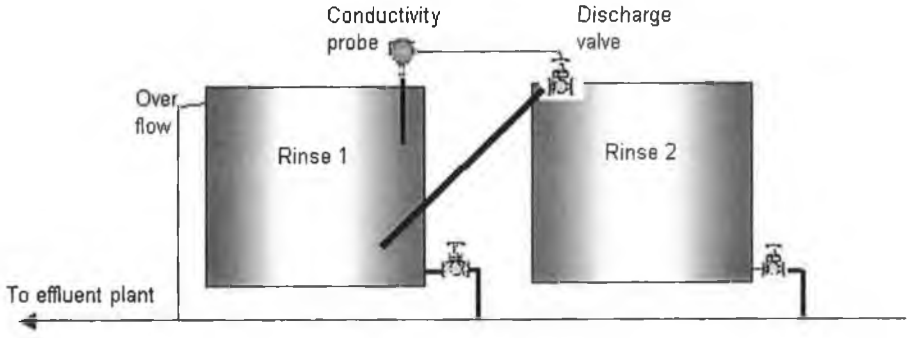


Figure 6.2 Conductivity controlled water supply

The water quality of the rinse was also monitored by acidity titration using phenolphthalein indicator. The components were held in position over the chemical tanks for one minute, post treatment to facilitate draining and minimise chemical drag-out.

Due to a design fault iron phosphate from the spray tunnel was being directed into the cleaner rinse tank. This was corrected by installation of an elevated floor as shown below.

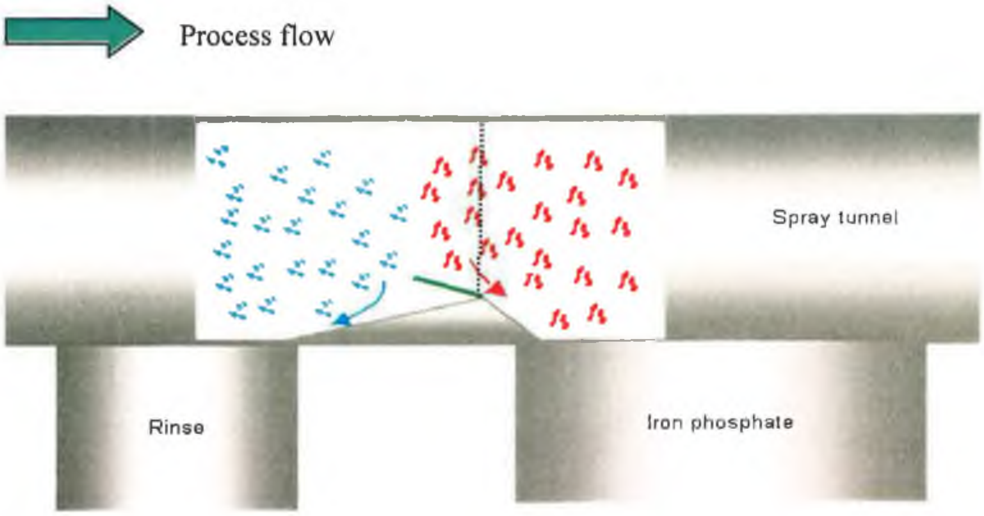


Figure 6.3 False floor in spray tunnel

The new flooring (green line) reduced the amount of phosphate mist flowing into the rinse tank, thus reducing the amount going to the effluent plant. The broken line shows the amount of mist being captured which was previously lost to the rinse tank. The improvement was measured by monitoring the acidity of the rinse tank by pH titration.

6.4 Industrial phosphate removal

A systems approach was taken in order to efficiently remove phosphate from effluent stream. A block diagram is shown below.

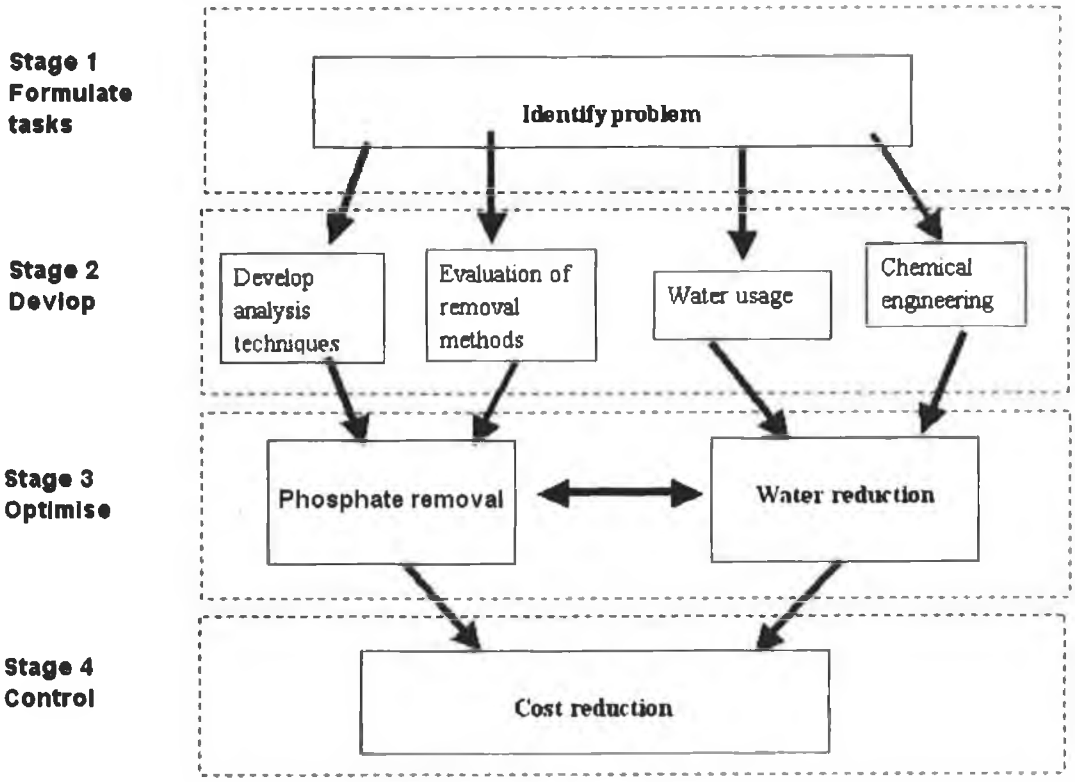


Figure 6.4 Troubleshooting guide for phosphate removal

The alkaline cleaners, iron and zinc phosphate were the main sources of phosphate. All streams contributing to the effluent were analysed to establish the quantitative amount of phosphate. The following steps were taken:

- Examination of process layout and creation of clear flow charts.
- Analysis/development of control procedures (including phosphate)
- Flow rates of various streams
- Plant optimisation of effluent treatment plant

Precipitation at plant scale

Phosphate was removed by chemical precipitation using alum sulphate and Fe^{3+} sulphate at plant scale.[35] A series of experiments was completed to determine the correct pH required for precipitation and also the optimum quantity required for removal.

In each case some difficulty was encountered in obtaining a floc. Many factors were believed to be the cause. These included, not having enough time to settle, being broken up by too much aeration in the mixing tank and finally inconsistent dosing. A honeycomb type mesh has been added to the settlement tank to aid settling.

Brown colour is ferric floc resting on mesh

Figure 6.5 Mesh added to settlement tank to aid settlement

A trial was completed to determine the possibility of reducing the amount of air going through the mixing tank. However this created another problem, the balancing of pH. In order to comply with the IPC licensing the pH had to be maintained between six and nine. A compromise had to be reached on air agitation. Too rapid agitation resulted in floc fragmentation, but when the flow rate was too low, inadequate mixing resulted. This was overcome by increasing the effluent level in the tank. The mechanical action of the air was reduced but the mixing was adequate for pH balancing[36].

The control system for the effluent was found to be very unreliable. A new system was installed which had a duplicate secondary detection system. The diagram below shows both the old and new level control system.

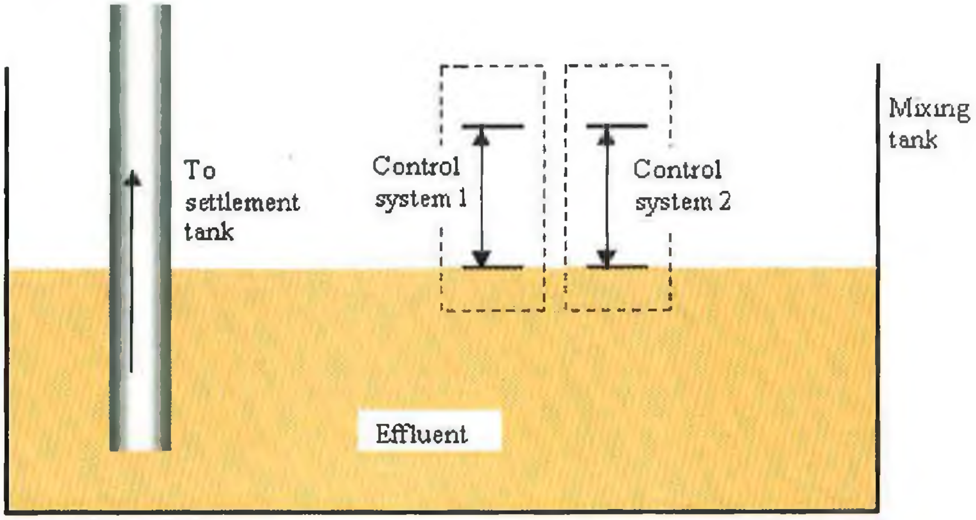


Figure 6.6 Level control system – mixing tank

The flocculant was metered into the mixing tank and a set volume added per hour during production. Many variables were monitored including water consumption, flocculant input, filter press maintenance and level of mixing tank during the phosphate removal trial. The water consumption was kept below 50m^3 per day, as this was the limit of the effluent plants capacity. The flow rate of 40% concentrate Fe^{3+} sulphate was set at 1.5 litres per hour to ensure the correct concentration of flocculant. Filter press maintenance was essential to ensuring floc removal from effluent system. It was established that the filter press needed to be emptied once every 48 hours.

Chapter 7 – Discussion and recommendations for future work

7.1 Major achievements

Applying research findings to the Thermo King plant led to four major areas of improvement:

1. **Water conservation** – water usage per manufactured unit was reduced by 67%
2. **Phosphate removal** – Thermo King achieved consistent conformance to IPC phosphate levels for the first time.
3. **Quality**- salt spray performance of >700 hours was achieved for the first time consistently in the spray corrosion protection process plant
4. **Cost of chemical** – reduced by €35,000 in 2003

7.2 Phosphate removal

Discussion

Thermo King was having difficulty with phosphate residues in effluent (IPC requirements). Figure 7.1 summarises the dramatic improvements resulting from project work. Detailed work on phosphates was carried out from the beginning of October to the end of November 2002.

Recommendations

It can be noted that the system needs constant technical supervision, as it went out of control once again when the project direction changed. The need for superior technical supervision i.e. a qualified technologist assigned to project can be seen from graph below.

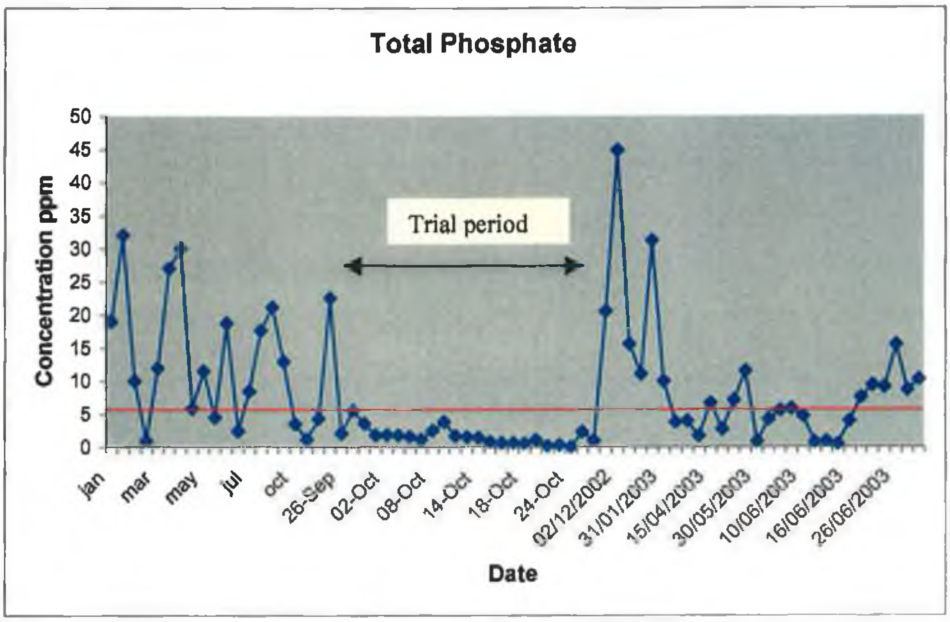


Figure 7.1 Total phosphate results

To further improve performance of phosphate removal the following is suggested:

- Increase settlement tank size
- Trained personnel to monitor effluent plant
- Sand filter should be installed to replace plate and frame as main filter. The latter should be used as polishing filter

7.3 Water Conservation

Discussion

The commissioning of conductivity meters had a dramatic effect on the water consumption within Thermo King. A 27.6% reduction in volume from 2001 to 2002 occurred as a direct result. Further initiatives, resulted in additional reduction.

The table below shows how effective the conservation management section of the project worked. In spite of 69% price increase from €2.60 to €3.75 per 1000 gallons, the overall cost was reduced.

Recommendations

However there was an unacceptable variation in the cost per unit of water usage, clearly showing the necessity for proper technical support and need for constant technical monitoring. The following is recommended to further reduce water consumption:

- Recycling of water should be optimised
- In addition rinse water should be used where appropriate to make up cleaner and phosphate tanks.

	Total Units produced	Total volume (1000 gallons)	Cost per 1000 gallons (€)	Total cost (€)	Cost per unit (€)	Volume per unit (1000 gallons)
1st Qr. 2002	5467	4683.7	€2.60	€12,177.62	€2.23	0.86
2nd Qr. 2002	6161	2916.9	€2.60	€7,583.94	€1.23	0.47
3rd Qr. 2002	9380	1902.2	€2.60	€4,945.72	€0.53	0.20
4th Qr. 2002	4682	2383.9	€2.60	€6,198.14	€1.32	0.51
1st Qr. 2003	5178	1716	€3.75	€6,435.00	€1.24	0.33
2nd Qr. 2003	4748	1339	€3.75	€5,021.25	€1.06	0.28

Table 7.a Water consumption and cost

7.4 Environmental pre-treatment

Discussion

This project looked at two new environmental corrosion protection systems based on silane and autophoretic chemistry. Both these processes had advantages over the present conversion systems.

Two new cleaners were examined and compared with the system in operation – Gardoclean 5204, which was considered inadequate for this particular application. Novaclean 177d was a high caustic, phosphate detergent and this proved very effective for cleaning purposes, but did not conform to Thermo King corporate standards. Gardoclean TP 10528 was custom designed by Chemetall for Thermo King. This detergent complied with all Thermo King specification and was very effective by spray application. It was also effective on pilot scale immersion process. Initial problems of attack of zinc and aluminium were overcome by rigid quality control procedures.

This project was successful in modifying the iron phosphate conversion process to achieved Thermo King specification objectives for corrosion protection on a consistent basis for the first time.

Recommendations

Continuous technical monitoring should be introduced. On the basis of the research it is recommended the following steps be taken:

Alkaline cleaners

- Extension of Gardoclean TP 10528 cleaner to immersion plant in Thermo King
- Regular auditing of control results on plant and checked in laboratory
- Automatic titration measuring concentration linked to dosing pump

Iron phosphate/zinc phosphate

- Change iron phosphate to two phosphate stage process (page 67)
- Link automatic titration measurement of concentration to dosing pump
- Develop more reliable method of monitoring of phosphate tanks (ie. the $FePO_4$ concentration)

7.5 Pilot plant

Discussion

The pilot plant was designed to enable simulation of plant performance on a miniature scale. A possible future development of this plant is to incorporate a spray system as in the Henkel and Chemetall plant. A possible extension to this system is as shown below converting it to spray. Thus the pilot plant could mimic all operations with the pre-treatment area in Thermo King.

Recommendations

It is recommended that this extension be carried out to facilitate future changes in Thermo King spray systems.

It might be noted that a basic heat pump is necessary for this unit process to enable mass transfer without temperature decline.

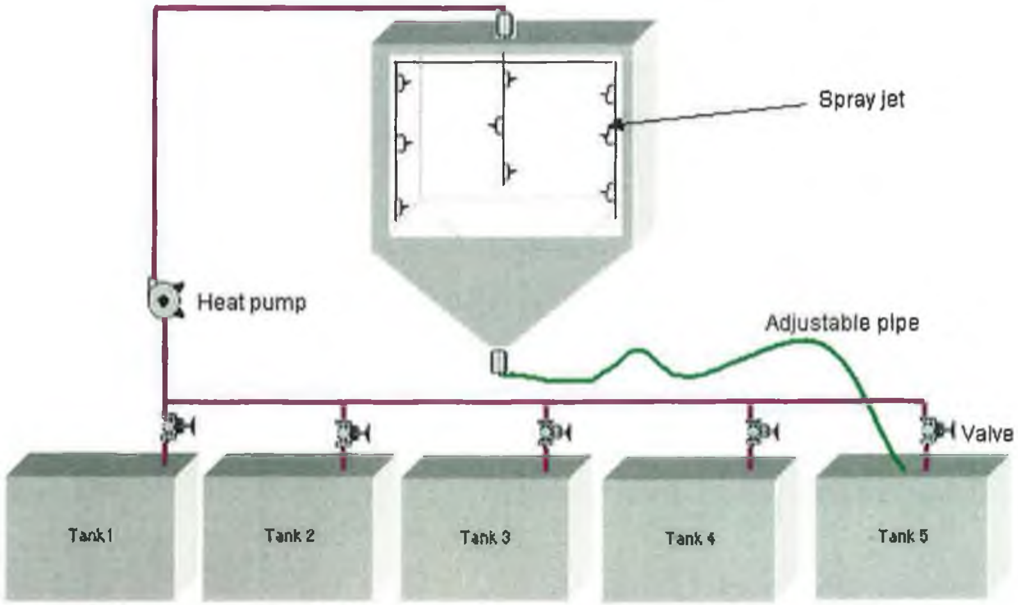


Figure 7.2 Proposed mini spray plant

7.6 Conclusion

The test procedures made available by manufactures do not in the cases tested here enable proper control. For example the phenolphthalein titration for Gardoclean TP10528 does not distinguish between carbonates and amines. Even where iron phosphate concentration is the target analyte, a pH titration is specified. This is an indirect and unsatisfactory procedure, which will encourage wastage of expensive chemicals.

It is necessary to further investigate silane and autophoretic processes. These are far more environmentally friendly but require more intensive management practices. During the course of this project, dramatic improvements were recorded at many critical points. However, as soon the project focus changed much of the improved performance was reversed. Total phosphate in effluent is a particular example of this (page 73).

7.7 Recommendation

The significant success temporarily brought about on the Thermo King process as shown in this project highlights the cost effectiveness and need to have a continuous expert monitoring of corrosion protection process in Thermo King. Steps should be taken to incorporate the findings of this project into the process specification.

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Appendices

Appendix 1 – Standards and process diagrams

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Appendix 4 – Pilot plant and design drawings

Appendix 5 – Cost saving figures

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Appendix 1 – Standards and process diagrams

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B. Process Diagrams
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    b. Spray
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C. ASTM
    a. Hardness
    b. Adhesion
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A. Thermo King specification

a. Pre-treatment chemicals

Thermo King standard TKS10016

THERMO KING ENGINEERING STANDARD

1.0 **SCOPE**

1.1 Scope:

This specification establishes standard limits for metal cleaning, surface pretreatment processes and approved chemicals for metal finishing used by Thermo King Corporation

2.0 **APPLICABLE DOCUMENTS**

2.1 Chemical conversion and pretreatment coatings shall be of the following types

TT-C-490 (Ref. Only) For improving the corrosion resistance of ferrous and non-ferrous metals, and to provide a surface for good paint adhesion

Zinc phosphate - 150 to 500 mg/ft^2
Iron phosphate - 25 to 75 mg/ft^2

MIL-C-5541 (Ref. Only) For improving the corrosion resistance of aluminum and aluminum alloys, and to provide a surface for good paint adhesion.

Chromate coating - 10 to 70 mg/ft^2
Non-chrome coating - Spot test to determine if the conversion coating adhered to the substrate and whether there are areas that did not get coated

2.2 ASTM-F-22 - Water break-free surface shall be obtained after rinsing

3.0 **REQUIREMENTS**

3.1 Material:

All material used shall be as specified herein

3.2 Operating Instructions:

Solution operating parameters, process controls and solution maintenance shall be established by the chemical supplier and material engineer. The operation of metal cleaning and systems preparation shall be governed by individual facility instructions.

Approval		THERMO KING CORPORATION	Sheet 1 of 6
Date		MINNEAPOLIS, MN	
Engr		TITLE METAL CLEANING AND PREPARATION	TES 10 016
Liaison		PROCESS REQUIREMENTS	REV. T

TI_E02

THERMO KING ENGINEERING STANDARD

3.3 Water Quality:

The water used in all metal finishing operations shall not exceed a total hardness of 200 PPM.

3.4 Agitation:

Eductors shall be used for mixing instead of air.

3.5 Cleaning:

The metals shall be thoroughly free of oil, grease, wax, dirt, scale, rust, and other foreign matter upon existing the process. The parts shall be chemically cleaned such that a water break-free surface is obtained after rinsing.

3.6 Rinse:

Adequate rinsing shall be performed to remove any chemical remaining after the operation. Special care shall be exercised in rinsing complex shapes. A minimum of two rinses shall be used after chemical processes:

1st rinse MAX TDS-850 ppm
2nd rinse MAX TDS-400 ppm

The rinse shall be overflowed or counter flowed to maintain quality, also, a conductivity meter shall be used to regulate the flow of rinse water and to determine rinse water quality.

3.7 Deoxidizer:

Parts which exhibit evidence of rust or smut shall be treated with a deoxidizer.

3.8 Final Seal:

A seal shall be used on all ferrous parts. It could be a chromate or non-chromate solution.

3.9 Appearance:

The conversion coating shall be uniform in appearance. It shall be continuous and free from area of powdery.

3.9.1 Drying:

Thorough drying shall be the final step. Care shall be exercised to ensure complete drying in crevices, seams or other difficult to dry areas.

4.0 QUALITY ASSURANCE

4.1 Responsibility for Inspection:

Unless otherwise specified, the facility quality assurance group is responsible for testing, performing or auditing all inspections to assure compliance to the requirement specified. Log sheets shall be audited on a regular basis.

b. Process Control

Thermo King standard TK10023

SCOPE

This standard is applicable to all Thermo King plant locations and Thermo King vendors.

PURPOSE

This specification establishes the requirements for all paint procurement for use on Thermo King equipment; also, for Thermo King and vendor's painted parts. This specification defines the methodology and quality criteria used when inspecting the appearance of a painted part.

REQUIREMENTS

Shall meet the performance requirements below:

PROPERTY	REQUIREMENT	TEST METHOD
Adhesion	≤ 5 Mils: 2 mm squares; no squares removed – classification 5B	ASTM D-3359 Method B
	> 5 Mils: X-cut tape test; no peeling or removal – 5A classification	ASTM D-3359 Method A ASTM D-3330
Adhesion - Second Coat	No Squares Removed	ASTM D-3359 Method B
Impact Resistance, Direct	50 inch-pounds, no fail	ASTM D-2794
Impact Resistance, Indirect	20 inch-pounds, no fail	ASTM-D-2794

Mandrel Bend	1/8 inch, no fail	ASTM D-1737
▲ Salt Spray Resistance	700 hours, 1/16 inch creep, max total from scribe, no blisters, no rust	ASTM B-117 Blisters – ASTM D-714 Classification No. 10 (no blisters) Rust – ASTM D-610 Classification No. 10 (no rust)
Salt Spray Evaluation		ASTM D-1654 (Procedure A, Method 2) Water Borne Products ASTM D-1735, 7.9 & 7.9.1

PROPERTY	REQUIREMENT	TEST METHOD
VOC	$\leq$ 2.80 lb/gal unless approved by Engineer.	ASTM D-3960
Humidity Resistance	500 hours, no blisters	ASTM D-2247
QUV	500 hours, maintain 75% of gloss	ASTM-G53
Chemical Resistance		
Ethylene Glycol	No Effect	24 hours @ 25°C under watch glass
Diesel Fuel	No Effect	
Motor Oil	No Effect	
Petroleum Grease	No Effect	
Detergents (5% Tide)	No Effect	
Refrigerants	No Effect	Canister @ 140 psi for 24 hours
Gasoline	Slight discoloration, but no softening	
Hardness	H minimum	ASTM D-3363
Abrasion resistance	90 mg loss, max.	FED-STD-141 Method 6192, CS-1000 g load 1000 cycles

PROPERTY	REQUIREMENT	TEST METHOD
Color	White – TK RAL-9016 Color equation (numerical data) – FMC-2 Observer - 10° Illuminant – D65 Sphere geometry Specular component included Total Δ E 0.5 max.. Tolerance: +b yellow/blue –b = 0.2 blue –b -L black/light +L = 0.2 light +L +a red/green –a = 0.1 green –a Other Colors RAL numbers or color chips	ASTM D-1729 Color spectrophotometer measurement
Hiding	Per supplier recommendation	Bar chart
Gloss	High gloss products 85° min. @ 60° angle 65° min. @ 20° angle Semi gloss products 25° to 60° @ 60° angle	Gloss meter ASTM D-523
Orange Peel	Comparison with ACT Orange peel standards. Must be between plaque 5 to 10.	Wave scan meter

Steel substrates shall be zinc or iron phosphate coated pre TT-C-490 or E-coated; and aluminum substrates shall have a chemical conversion coating or E-coated.

Zones:
The standard uses the definition of zone to classify the importance of the defect.

ZONE	DESCRIPTION
A	Area visible at any time, and not hidden by a decal or other part. Surface finish is extremely important.
B	Area visible at any time, not hidden by a decal or other part, but located in such a way that it can be shadowed.
C	Area is never visible or permanently covered by another part.

Methodology:

Lighting: Inspection lighting source must be white fluorescent light. Intensity must be 80 – 120 foot-candles minimum.

Appendix 1

Viewing conditions: Inspection must be performed at a 24 – 36 in from the part. Light can be reflected on the part to ease inspection. Inspector gaze must sweep the surface in a continuous movement, without stopping more than three (3) seconds at a particular location.

Part surface: Part surface must be clean, without dust or other contaminant impairing defect inspection.

Surface Finish/Texture:
Unless a texture is specified on the drawing, surface should be smooth.

* Conformance of a textured surface finish is to be made by comparing a part to a Mold Tech[2] texture plaque. Comparison is by the eye.

ATTRIBUTE	DESCRIPTION/ PROCEDURE	CRITERIA ZONE A	ZONE B	ZONE C
Gloss	ASTM D-523	• 85° minimum at 60° angle • 65° minimum at 20° angle	85° minimum at 60° angle	N/A
Orange peel	Comparison with ACT Orange Peel Standards from ACT Laboratories[3]	Must be between plaque 7 to 10	Must be between plaque 5 to 10	N/A
Dirt	Irregularity (in color or surface) caused by a contaminant. Same requirement for specks, dust, contaminant, hair, lint, etc.	• Maximum 0.040" diameter • Minimum 4" separation • Maximum of 3 per square foot	• Maximum 0.040" diameter • Minimum 2" separation • Maximum of 3 per square foot	N/A
Blister	Concave or convex irregularity on the surface. Substrate or primer is not exposed. Same requirement for fisheye, pinhole, crater, pitting, bubble, etc.	• Maximum 0.020" diameter • Maximum of 2 per square foot	• Maximum 0.040" diameter • Maximum of 6 per square foot	N/A
Scratch	Surface abrasion. Substrate or primer is not exposed. Same requirement for scuff.	• Maximum 0.200" long • Undetectable when rubbing with nail • Maximum 3 per square foot	• Maximum 0.500" long • Undetectable when rubbing with nail • Maximum 6 per square foot	N/A
Gough	Heavy surface abrasion. Substrate or primer is exposed. Same requirement for score.	None allowed.	None allowed.	Must not interfere with fit and function

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[2] Mold-Tech, 17009 Masonic Blvd., Fraser, MI 48026-3927, "Visual Texture Standards" binder.

[3] ACT Laboratories, 273 Industrial Drive, PO Box 735, Hillsdale, MI 49242, "ACT Orange Peel Standards"

* Painted plastic parts only
▲ Not for painted plastic parts

ATTRIBUTE	DESCRIPTION/ PROCEDURE	CRITERIA ZONE A	ZONE B	ZONE C
Paint run	Excess of paint which distorts surface appearance. Same requirement for sag, curtaining, streak, heavy coverage, drop, drip	Not visible under inspection method	Not visible under inspection method	N/A
Peeling	Lack of adhesion. Same requirement for poor adhesion, delamination	None allowed	None allowed	None allowed
Chip	Completely or partially missing paint, substrate or primer is exposed	None allowed	None allowed	Must not interfere with fit and function
Read through	Substrate or primer is visible through paint finish. Same requirement for show through, under spray, poor coverage	None allowed	None allowed	N/A
Crack	Brake in surface which may or may not expose substrate or primer. Same requirement for crazing, alligatoring, tear, separation, pulling apart	None allowed	None allowed	None allowed

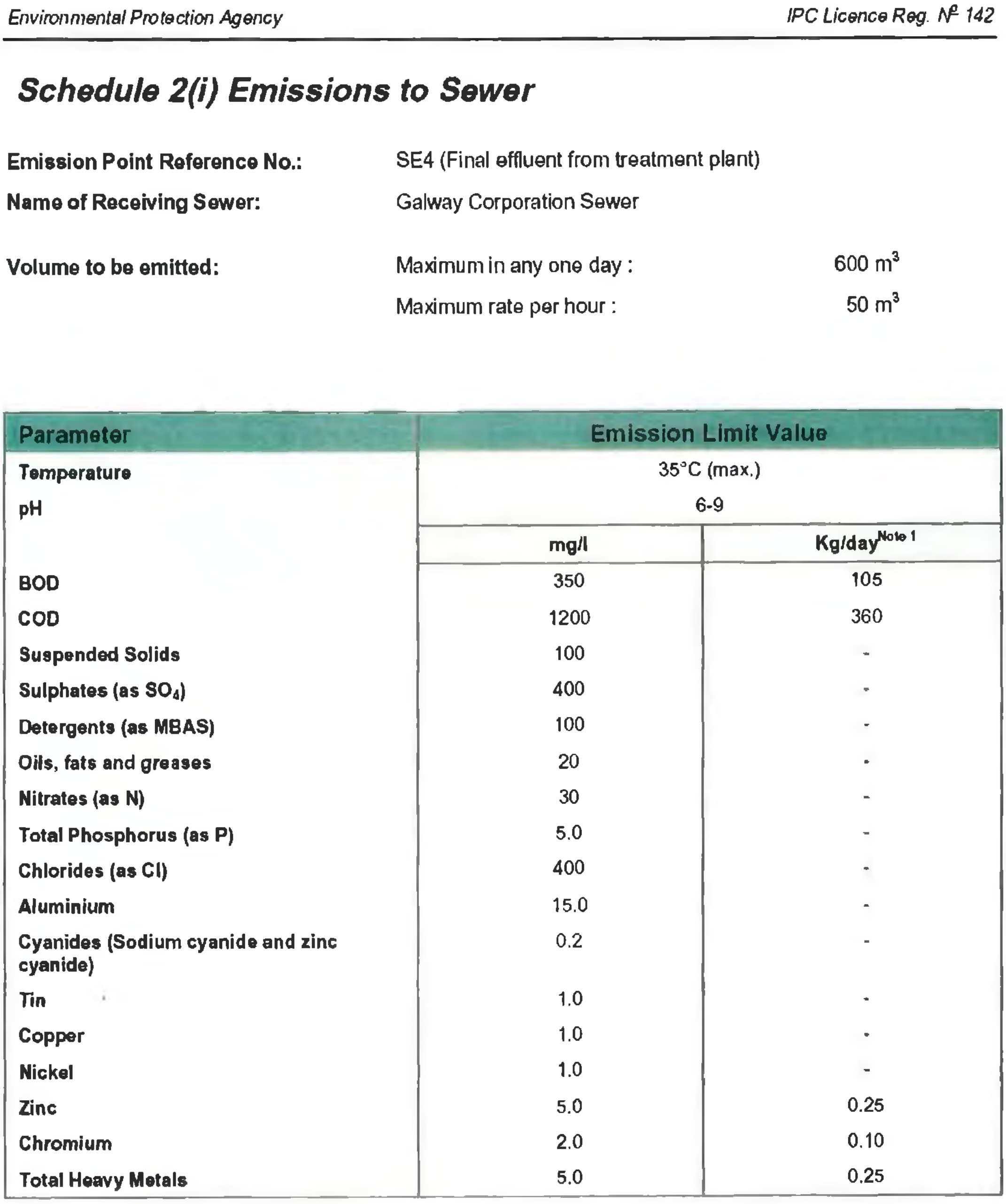
Responsibilities:

The supplier is responsible to verify that the parts meet or exceed the requirements specified in this standard. This is valid for approval parts and for production parts.

PRE-SHIPMENT COLOR-MATCH CHIP

Prior to the acceptance of a lot or batch of material, the manufacturer shall submit a color-match chip to the designated procuring activity with actual representative material from the batch or lot. In the event that the submitted chip does not match the color standard, the lot or batch shall be rejected and returnable at the option of the procuring activity.

c. IPC license extract



Environmental Protection Agency *IPC Licence Reg. No 142*

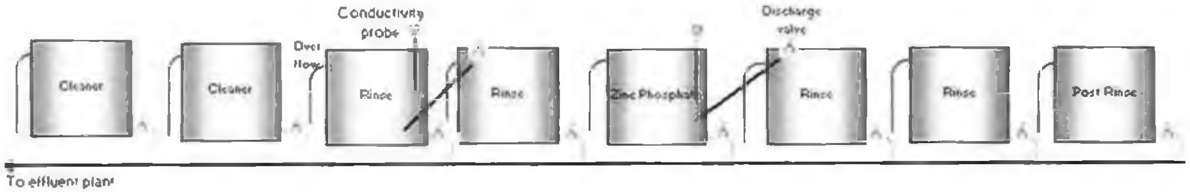
Schedule 2(i) Emissions to Sewer

Emission Point Reference No.:	SE4 (Final effluent from treatment plant)	
Name of Receiving Sewer:	Galway Corporation Sewer	
Volume to be emitted:	Maximum in any one day :	600 m^3
	Maximum rate per hour :	50 m^3

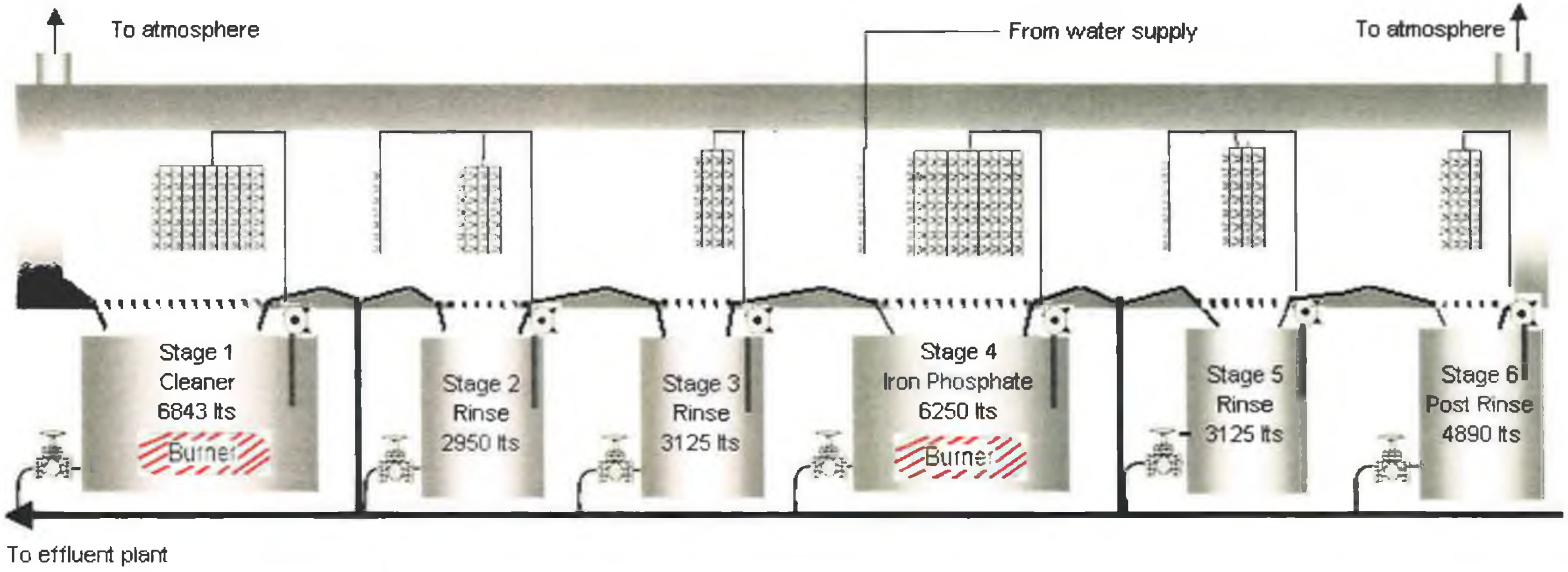
Parameter	Emission Limit Value	
Temperature	35°C (max.)	
pH	6-9	
	mg/l	**Kg/day**[Note 1]
BOD	350	105
COD	1200	360
Suspended Solids	100	-
Sulphates (as SO_4)	400	-
Detergents (as MBAS)	100	-
Oils, fats and greases	20	-
Nitrates (as N)	30	-
Total Phosphorus (as P)	5.0	-
Chlorides (as Cl)	400	-
Aluminium	15.0	-
Cyanides (Sodium cyanide and zinc cyanide)	0.2	-
Tin	1.0	-
Copper	1.0	-
Nickel	1.0	-
Zinc	5.0	0.25
Chromium	2.0	0.10
Total Heavy Metals	5.0	0.25

B. Process diagrams

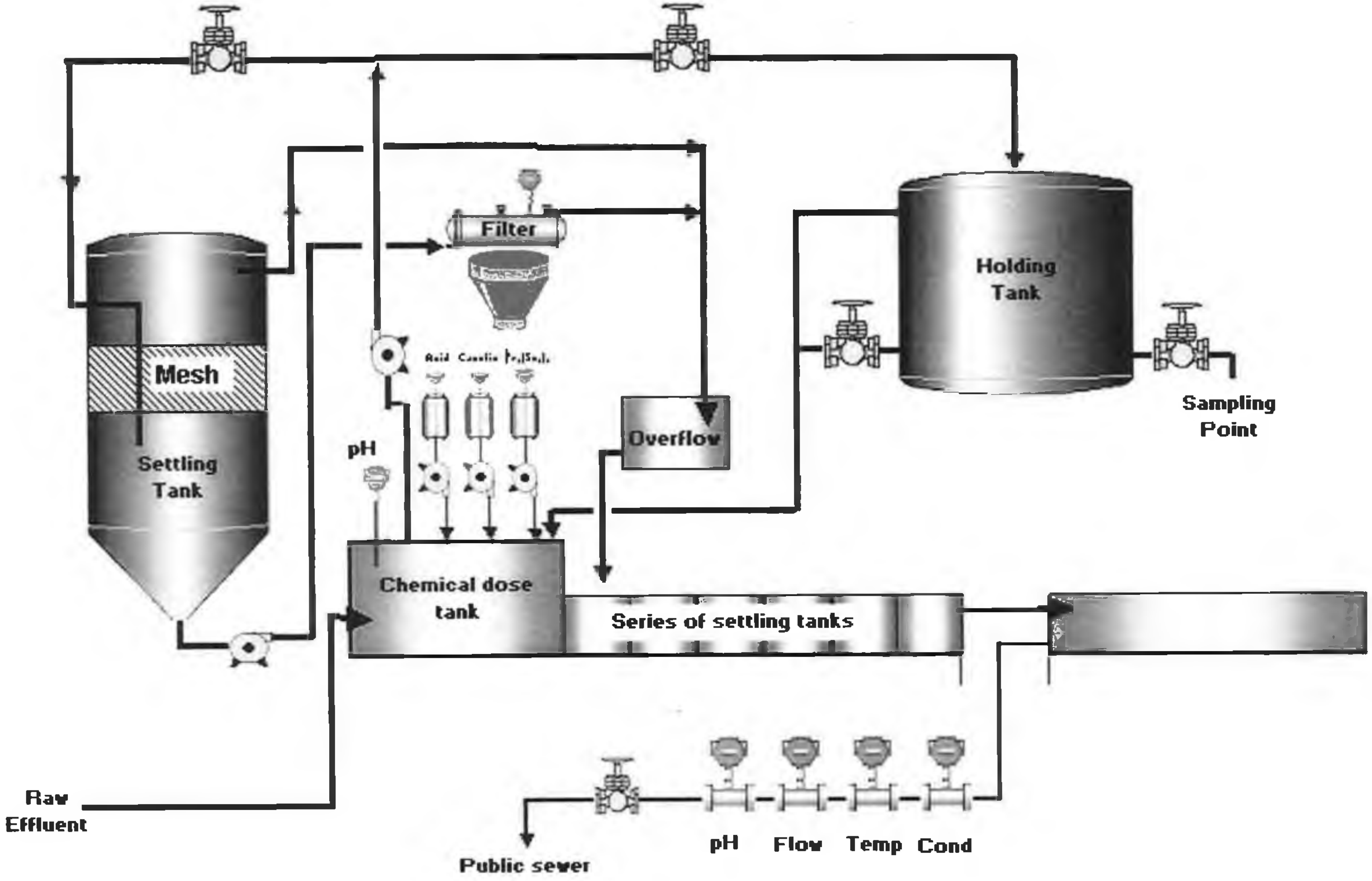
Immersion treatment process



Spray pre-treatment process



Effluent treatment process



C. ASTM

Designation: D 3363 – 00

Standard Test Method for Film Hardness by Pencil Test[1]

This standard is issued under the fixed designation D 3363; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for rapid, inexpensive determination of the film hardness of an organic coating on a substrate in terms of drawing leads or pencil leads of known hardness.

1.2 This test method is similar in content (but not technically equivalent) to ISO 15184.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *Other Standards:*

ISO 15184, Determination of film hardness by pencil test[2]

3. Summary of Test Method

3.1 A coated panel is placed on a firm horizontal surface. The pencil is held firmly against the film at a 45° angle (point away from the operator) and pushed away from the operator in a 6.5-mm ($\frac{1}{4}$-in.) stroke. The process is started with the hardest pencil and continued down the scale of hardness to either of two end points: one, the pencil that will not cut into or gouge the film (pencil hardness), or two, the pencil that will not scratch the film (scratch hardness).

4. Significance and Use

4.1 Pencil hardness measurements have been used by the coatings industry for many years to determine the hardness of clear and pigmented organic coating films. This test method has also been used to determine the cure of these coatings, especially when forced dried using heat.

4.2 This test method is especially useful in developmental work and in production control testing in a single laboratory. It should be recognized that the results obtained may vary between different laboratories when different pencils as well as panels are used. Every effort should be made to standardize the hardness of the lead used and the technique followed.

4.3 If this test method is used as a basis for purchase agreement, maximum precision will be achieved if a given set of referee pencils be agreed upon between the purchaser and the seller.

5. Apparatus

5.1 A set of calibrated drawing leads (preferred) or equivalent calibrated wood pencils meeting the following scale of hardness:

$$\underset{\text{Softer} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{Harder}}{\underline{6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H}} \qquad (1)$$

The difference between two adjacent leads shall be considered one unit of hardness.

5.2 *Mechanical Lead Holder*, for drawing leads if used.

5.3 *Mechanical Sharpener*, draftsman-type, is helpful for trimming wood pencils if used.

5.4 *Abrasive Paper*, grit No. 400.

6. Test Specimens and Conditions

6.1 Apply the surface coating by appropriate means to a smooth rigid substrate and cure properly, or use representative panels cut from coated stock. The panels used, the curing conditions, and the age of the coating prior to the test shall be within the limits agreed upon between the purchaser and the seller.

6.2 The film thickness of the coating shall be as specified or as agreed upon between the purchaser and the seller.

6.3 Conduct the test at 23 ± 2°C (73.5 ± 3.5°F) and 50 ± 5 % relative humidity.

7. Procedure

7.1 For wood pencils, remove approximately 5 to 6 mm ($\frac{3}{16}$ to $\frac{1}{4}$ in.) of wood from the point of each pencil using a draftsman-type mechanical sharpener, being careful to leave an undisturbed, unmarked, smooth cylinder of lead. Holding the pencil holder (when using drawing leads) at an angle of 90° to the abrasive paper, rub the lead against the paper maintaining an exact angle of 90° to the abrasive paper until a flat, smooth and circular cross section is obtained, free of chips or nicks in the edge of the cross section. The desired edge may be obtained

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[1] This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

Current edition approved March 10, 2000. Published May 2000. Originally published as D 3363 – 74. Last previous edition D 3363 – 92a.

[2] Available from American National Standards Institute, 11 W 42nd St., 13th Floor, New York, NY 10036.

by cementing the abrasive paper to a flat motor-driven disk. By supporting the pencil at 90° to the rotating disk a uniform flat lead end may be obtained more reproducibly.

7.2 Place the coated panel on a level, firm, horizontal surface. Starting with the hardest lead, hold the pencil or lead holder firmly with the lead against the film at a 45° angle (point away from the operator) and push away from the operator. Exert sufficient uniform pressure downward and forward either to cut or scratch the film or to crumble the edge of the lead. It is suggested that the length of the stroke be 6.5 mm (¼ in.).

7.3 Repeat the process down the hardness scale until a pencil is found that will not cut through the film to the substrate (either metal or a previous coat) for a distance of at least 3 mm (⅛ in.) (see 8.1.1).

NOTE 1—The operator must watch closely for cutting into or scratching the film. Some finishes contain compounds that may tend to lubricate the film. Checks should be made by close visual inspection and by fingernail feel.

NOTE 2—In conducting the test, if the sharp edge of the lead is slightly chipped or crumbled, the lead must be resharpened.

7.4 Continue the process until a pencil is found that will neither cut through nor scratch the surface of the film. Any defacement of the film other than a cut (gouge) is considered a scratch. Record each end point (if applicable) for gouge and scratch hardness (see 8.1).

NOTE 3—With some films, the two end points will be identical.

7.5 Make a minimum of two determinations for gouge hardness (7.3) and scratch hardness (7.4) for each pencil or lead.

8. Report

8.1 Report the following information:

8.1.1 The two end points as follows:

8.1.1.1 *Gouge Hardness*—The hardest pencil that will leave the film uncut for a stroke length of at least 3 mm (⅛ in.).

8.1.1.2 *Scratch Hardness*—The hardest pencil that will not rupture or scratch the film.

8.1.2 The make and grade of lead or pencil used, and

8.1.3 Any deviation from standard conditions including roughness in the finish.

9. Precision and Bias

9.1 *Precision*—In an interlaboratory test of this test method with three different films on panels, ten laboratories and operators, and repeated by switching leads and panels between laboratories, the within-laboratory standard deviation was found to be 0.52 and the between-laboratory standard deviation was found to be 0.61. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at a 95 % confidence level.

9.1.1 *Repeatability*—Two results obtained by two operators within a laboratory using the same pencils and panels should be considered suspect if they differ by more than one pencil unit on the scale described in 5.1.

9.1.2 *Reproducibility*—Two results, each the mean of at least two determinations, obtained by operators in different laboratories using the same pencils and panels or different pencils with the same panels should be considered suspect if they differ by more than one pencil unit on the scale described in 5.1.

9.1.3 *Bias*—Since there is no acceptable material suitable for determining the bias for the procedure in this test method for measuring pencil hardness, bias cannot be determined.

10. Keywords

10.1 hardness (scratch); pencil hardness

Designation: D 3359 – 97

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Methods for
Measuring Adhesion by Tape Test[1]

This standard is issued under the fixed designation D 3359; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film.

1.2 Test Method A is primarily intended for use at job sites while Test Method B is more suitable for use in the laboratory. Also, Test Method B is not considered suitable for films thicker than 5 mils (125μm).

NOTE 1—Subject to agreement between the purchaser and the seller, Test Method B can be used for thicker films if wider spaced cuts are employed.

1.3 These test methods are used to establish whether the adhesion of a coating to a substrate is at a generally adequate level. They do not distinguish between higher levels of adhesion for which more sophisticated methods of measurement are required.

NOTE 2—It should be recognized that differences in adherability of the coating surface can affect the results obtained with coatings having the same inherent adhesion.

1.4 In multicoat systems adhesion failure may occur between coats so that the adhesion of the coating system to the substrate is not determined.

1.5 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 609 Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products[2]

D 823 Practice for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels[2]

D 1000 Test Methods For Pressure-Sensitive Adhesive-Coated Tapes Used for Electrical and Electronic Applications[3]

D 1730 Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting[4]

D 2092 Guide for Preparation of Zinc-Coated (Galvanized) Steel Surfaces for Painting[5]

D 2197 Test Methods for Adhesion of Organic Coatings by Scrape Adhesion[2]

D 2370 Test Method for Tensile Properties of Organic Coatings[2]

D 3330 Test Method for Peel Adhesion of Pressure-Sensitive Tape at 180° Angle[6]

D 3924 Specification for Standard Environment for Conditioning and Testing Paint, Varnish, Lacquers, and Related Materials[2]

D 4060 Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser[2]

3. Summary of Test Methods

3.1 *Test Method A*—An X-cut is made in the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and adhesion is assessed qualitatively on the 0 to 5 scale.

3.2 *Test Method B*—A lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure-sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

4. Significance and Use

4.1 If a coating is to fulfill its function of protecting or decorating a substrate, it must adhere to it for the expected service life. Because the substrate and its surface preparation (or lack of it) has a drastic effect on the adhesion of coatings, a method of evaluation adhesion of a coating to different substrates or surface treatments, or of different coatings to the same substrate and treatment, is of considerable usefulness in the industry.

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

Current edition approved Nov. 10, 1997. Published September 1998. Originally published as D 3359 – 74. Last previous edition D 3359 – 95a.

[2] *Annual Book of ASTM Standards*, Vol 06.01.

[3] *Annual Book of ASTM Standards*, Vol 10.01.

[4] *Annual Book of ASTM Standards*, Vol 02.05.

[5] *Annual Book of ASTM Standards*, Vol 06.02.

[6] *Annual Book of ASTM Standards*, Vol 15.09.

4.2 The limitations of all adhesion methods and the specific limitation of this test method to lower levels of adhesion (see 1.3) should be recognized before using it. The intra- and inter-laboratory precision of this test method is similar to other widely-accepted tests for coated substrates (for example, Test Method D 2370 and Test Method D 4060), but this is partly the result of it being insensitive to all but large differences in adhesion. The limited scale of 0 to 5 was selected deliberately to avoid a false impression of being sensitive.

TEST METHOD A—X-CUT TAPE TEST

5. Apparatus and Materials

5.1 *Cutting Tool*—Sharp razor blade, scalpel, knife or other cutting devices. It is of particular importance that the cutting edges be in good condition.

5.2 *Cutting Guide*—Steel or other hard metal straightedge to ensure straight cuts.

5.3 *Tape*—One-inch (25-mm) wide semitransparent pressure-sensitive tape with an adhesion strength agreed upon by the supplier and the user is needed.[7] Because of the variability in adhesion strength from batch-to-batch and with time, it is essential that tape from the same batch be used when tests are to be run in different laboratories. If this is not possible the test method should be used only for ranking a series of test coatings.

5.4 *Rubber Eraser*, on the end of a pencil.

5.5 *Illumination*—A light source is helpful in determining whether the cuts have been made through the film to the substrate.

6. Test Specimens

6.1 When this test method is used in the field, the specimen is the coated structure or article on which the adhesion is to be evaluated.

6.2 For laboratory use apply the materials to be tested to panels of the composition and surface conditions on which it is desired to determine the adhesion.

NOTE 3—Applicable test panel description and surface preparation methods are given in Practice D 609 and Practices D 1730 and D 2092.

NOTE 4—Coatings should be applied in accordance with Practice D 823, or as agreed upon between the purchaser and the seller.

NOTE 5—If desired or specified, the coated test panels may be subjected to a preliminary exposure such as water immersion, salt spray, or high humidity before conducting the tape test. The conditions and time of exposure will be governed by ultimate coating use or shall be agreed upon between the purchaser and seller.

7. Procedure

7.1 Select an area free of blemishes and minor surface imperfections. For tests in the field, ensure that the surface is clean and dry. Extremes in temperature or relative humidity may affect the adhesion of the tape or the coating.

7.2 Make two cuts in the film each about 1.5 in. (40 mm) long that intersect near their middle with a smaller angle of between 30 and 45°. When making the incisions, use the straightedge and cut through the coating to the substrate in one steady motion.

7.3 Inspect the incisions for reflection of light from the metal substrate to establish that the coating film has been penetrated. If the substrate has not been reached make another X in a different location. Do not attempt to deepen a previous cut as this may affect adhesion along the incision.

7.4 Remove two complete laps of the pressure-sensitive tape from the roll and discard. Remove an additional length at a steady (that is, not jerked) rate and cut a piece about 3 in. (75 mm) long.

7.5 Place the center of the tape at the intersection of the cuts with the tape running in the same direction as the smaller angles. Smooth the tape into place by finger in the area of the incisions and then rub firmly with the eraser on the end of a pencil. The color under the transparent tape is a useful indication of when good contact has been made.

7.6 Within 90 ± 30 s of application, remove the tape by seizing the free end and pulling it off rapidly (not jerked) back upon itself at as close to an angle of 180° as possible.

7.7 Inspect the X-cut area for removal of coating from the substrate or previous coating and rate the adhesion in accordance with the following scale:

5A	No peeling or removal
4A	Trace peeling or removal along incisions or at their intersection
3A	Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side
2A	Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side,
1A	Removal from most of the area of the X under the tape, and
0A	Removal beyond the area of the X

7.8 Repeat the test in two other locations on each test panel. For large structures make sufficient tests to ensure that the adhesion evaluation is representative of the whole surface.

7.9 After making several cuts examine the cutting edge and, if necessary, remove any flat spots or wire-edge by abrading lightly on a fine oil stone before using again. Discard cutting tools that develop nicks or other defects that tear the film.

8. Report

8.1 Report the number of tests, their mean and range, and for coating systems, where the failure occurred that is, between first coat and substrate, between first and second coat, etc.

8.2 For field tests report the structure or article tested, the location and the environmental conditions at the time of testing.

8.3 For test panels report the substrate employed, the type of coating, the method of cure, and the environmental conditions at the time of testing.

8.4 If the adhesion strength of the tape has been determined in accordance with Test Methods D 1000 or D 3330, report the results with the adhesion rating(s). If the adhesion strength of the tape has not been determined, report the specific tape used and its manufacturer.

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[7] Permacel 99, manufactured by Permacel, New Brunswick, NJ 08903, and available from various Permacel tape distributors, is reported to be suitable for this purpose. The manufacturer of this tape and the manufacturer of the tape used in the interlaboratory study (see RR: D01-1008) have advised this subcommittee that the properties of these tapes were changed. Users of it should, therefore, check whether current material gives comparable results to previous supplied material.

9. Precision and Bias[8]

9.1 In an interlaboratory study of this test method in which operators in six laboratories made one adhesion measurement on three panels each of three coatings covering a wide range of adhesion, the within-laboratories standard deviation was found to be 0.33 and the between-laboratories 0.44. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

9.1.1 *Repeatability*—Provided adhesion is uniform over a large surface, results obtained by the same operator should be considered suspect if they differ by more than 1 rating unit for two measurements.

9.1.2 *Reproducibility*—Two results, each the mean of triplicates, obtained by different operators should be considered suspect if they differ by more than 1.5 rating units.

9.2 Bias cannot be established for these test methods.

TEST METHOD B—CROSS-CUT TAPE TEST

10. Apparatus and Materials

10.1 *Cutting Tool*—Sharp razor blade, scalpel, knife or other cutting device having a cutting edge angle between 15 and 30° that will make either a single cut or several cuts at once[9]. It is of particular importance that the cutting edge or edges be in good condition.

10.2 *Cutting Guide*—If cuts are made manually (as opposed to a mechanical apparatus) a steel or other hard metal straightedge or template to ensure straight cuts.

10.3 *Rule*—Tempered steel rule graduated in 0.5 mm for measuring individual cuts.

10.4 *Tape*, as described in 5.3.

10.5 *Rubber Eraser*, on the end of a pencil.

10.6 *Illumination*, as described in 5.5.

10.7 *Magnifying Glass*—An illuminated magnifier to be used while making individual cuts and examining the test area.

11. Test Specimens

11.1 Test specimens shall be as described in Section 6. It should be noted, however, that multitip cutters provide good results only on test areas sufficiently plane[10] that all cutting edges contact the substrate to the same degree. Check for flatness with a straight edge such as that of the tempered steel rule (10.3).

12. Procedure

12.1 Where required or when agreed upon, subject the specimens to a preliminary test before conducting the tape test (see Note 3). After drying or testing the coating, conduct the tape test at room temperature as defined in Specification D 3924, unless D 3924 standard temperature is required or agreed.

12.2 Select an area free of blemishes and minor surface imperfections, place on a firm base, and under the illuminated magnifier, make parallel cuts as follows:

12.2.1 For coatings having a dry film thickness up to and including 2.0 mils (50 μm) space the cuts 1 mm apart and make eleven cuts unless otherwise agreed upon.

12.2.2 For coatings having a dry film thickness between 2.0 mils (50 μm) and 5 mils (125 μm), space the cuts 2 mm apart and make six cuts. For films thicker than 5 mils use Test Method A.[11]

12.2.3 Make all cuts about ¾ in. (20 mm) long. Cut through the film to the substrate in one steady motion using just sufficient pressure on the cutting tool to have the cutting edge reach the substrate. When making successive single cuts with the aid of a guide, place the guide on the uncut area.

12.3 After making the required cuts brush the film lightly with a soft brush or tissue to remove any detached flakes or ribbons of coatings.

12.4 Examine the cutting edge and, if necessary, remove any flat spots or wire-edge by abrading lightly on a fine oil stone. Make the additional number of cuts at 90° to and centered on the original cuts.

12.5 Brush the area as before and inspect the incisions for reflection of light from the substrate. If the metal has not been reached make another grid in a different location.

12.6 Remove two complete laps of tape and discard. Remove an additional length at a steady (that is, not jerked) rate and cut a piece about 3 in. (75 mm) long.

12.7 Place the center of the tape over the grid and in the area of the grid smooth into place by a finger. To ensure good contact with the film rub the tape firmly with the eraser on the end of a pencil. The color under the tape is a useful indication of when good contact has been made.

12.8 Within 90 ± 30 s of application, remove the tape by seizing the free end and rapidly (not jerked) back upon itself at as close to an angle of 180° as possible.

12.9 Inspect the grid area for removal of coating from the substrate or from a previous coating using the illuminated magnifier. Rate the adhesion in accordance with the following scale illustrated in Fig. 1:

5B	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
4B	Small flakes of the coating are detached at intersections; less than 5 % of the area is affected.
3B	Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.
1B	The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65 % of the lattice.
0B	Flaking and detachment worse than Grade 1.

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[8] Supporting data are available from ASTM Headquarters. Request RR: D01-1008.

[9] Multiblade cutters are available from a few sources that specialize in testing equipment for the paint industry. One supplier that has assisted in the refinement of these methods and of Test Methods D 2197 is given in footnote 10.

[10] The sole source of supply of the multitip cutter for coated pipe surfaces known to the committee at this time is Paul N. Gardner Co., 316 NE First St., Pompano Beach, FL 33060. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[11] Test Method B has been used successfully by some people on coatings greater than 5 mils (0.13 mm) by spacing the cuts 5 mm apart. However, the precision values given in 14.1 do not apply as they are based on coatings less than 5 mm (0.13 mm) in thickness.

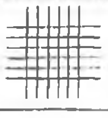
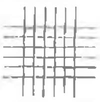
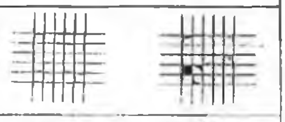
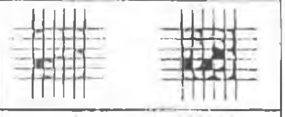
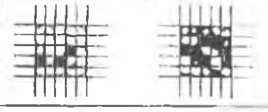
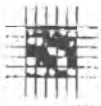
CLASSIFICATION OF ADHESION TEST RESULTS		
CLASSIFICATION	PERCENT AREA REMOVED	SURFACE OF CROSS-CUT AREA FROM WHICH FLAKING HAS OCCURRED FOR SIX PARALLEL CUTS AND ADHESION RANGE BY PERCENT
5B	0% None	
4B	Less than 5%	
3B	5 - 15%	
2B	15 - 35%	
1B	35 - 65%	
0B	Greater than 65%	

FIG. 1 Classification of Adhesion Test Results

12.10 Repeat the test in two other locations on each test panel.

13. Report

13.1 Report the number of tests, their mean and range, and for coating systems, where the failure occurred, that is, between first coat and substrate, between first and second coat, etc.

13.2 Report the substrate employed, the type of coating and the method of cure.

13.3 If the adhesion strength has been determined in accordance with Test Methods D 1000 or D 3330, report the results with the adhesion rating(s). If the adhesion strength of the tape has not been determined, report the specific tape used and its manufacturer.

14. Precision and Bias [8]

14.1 On the basis of two interlaboratory tests of this test method in one of which operators in six laboratories made one adhesion measurement on three panels each of three coatings covering a wide range of adhesion and in the other operators in six laboratories made three measurements on two panels each of four different coatings applied over two other coatings, the pooled standard deviations for within- and between-laboratories were found to be 0.37 and 0.7. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

14.1.1 *Repeatability*—Provided adhesion is uniform over a large surface, results obtained by the same operator should be considered suspect if they differ by more than one rating unit for two measurements.

14.1.2 *Reproducibility*—Two results, each the mean of duplicates or triplicates, obtained by different operators should be considered suspect if they differ by more than two rating units.

14.2 Bias cannot be established for these test methods.

15. Keywords

15.1 adhesion, tape; crosscut adhesion test method; tape adhesion test method; X-cut adhesion test method.

APPENDIX

(Nonmandatory Information)

X1. COMMENTARY

X1.1 Introduction

X1.1.1 Given the complexities of the adhesion process, can adhesion be measured? As Mittal **(1)**[12] has pointed out, the answer is both yes and no. It is reasonable to state that at the present time no test exists that can precisely assess the actual physical strength of an adhesive bond. But it can also be said that it is possible to obtain an indication of relative adhesion performance.

X1.1.2 Practical adhesion test methods are generally of two types: *"implied"* and *"direct."* "Implied" tests include indentation or scribe techniques, rub testing, and wear testing. Criticism of these tests arises when they are used to quantify the strength of adhesive bonding. But this, in fact, is not their purpose. An "implied" test should be used to assess coating performance under actual service conditions. "Direct" measurements, on the other hand, are intended expressly to measure adhesion. Meaningful tests of this type are highly sought after, primarily because the results are expressed by a single discrete quantity, the force required to rupture the coating/substrate bond under prescribed conditions. Direct tests include the Hesiometer and the Adherometer **(2)**. Common methods which approach the direct tests are peel, lap-shear, and tensile tests.

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[12] The boldface numbers in parentheses refer to the list of references at the end of this test method.

X1.2 Test Methods

X1.2.1 In practice, numerous types of tests have been used to attempt to evaluate adhesion by inducing bond rupture by different modes. Criteria deemed essential for a test to warrant large-scale acceptance are: use of a straightforward and unambiguous procedure; relevance to its intended application; repeatability and reproducibility; and quantifiability, including a meaningful rating scale for assessing performance.

X1.2.2 Test methods used for coatings on metals are: peel adhesion or "tape testing"; Gardner impact flexibility testing; and adhesive joint testing including shear (lap joint) and direct tensile (butt joint) testing. These tests do not strictly meet all the criteria listed, but an appealing aspect of these tests is that in most cases the equipment/instrumentation is readily available or can be obtained at reasonable cost.

X1.2.3 A wide diversity of tests methods have been developed over the years that measure aspects of adhesion **(1-5)**. There generally is difficulty, however, in relating these tests to basic adhesion phenomena.

X1.3 The Tape Test

X1.3.1 By far the most prevalent test for evaluating coating "adhesion" is the tape-and-peel test, which has been used since the 1930's. In its simplest version a piece of adhesive tape is pressed against the paint film and the resistance to and degree of film removal observed when the tape is pulled off. Since an intact film with appreciable adhesion is frequently not removed at all, the severity of the test is usually enhanced by cutting into the film a *figure X* or a cross hatched pattern, before applying and removing the tape. Adhesion is then rated by comparing film removed against an established rating scale. If an intact film is peeled cleanly by the tape, or if it debonds just by cutting into it without applying tape, then the adhesion is rated simply as poor or very poor, a more precise evaluation of such films not being within the capability of this test.

X1.3.2 The current widely-used version was first published in 1974; two test methods are covered in this standard. Both test methods are used to establish whether the adhesion of a coating to a substrate is at an adequate level; however they do not distinguish between higher levels of adhesion for which more sophisticated methods of measurement are required. Major limitations of the tape test are its low sensitivity, applicability only to coatings of relatively low bond strengths, and non-determination of adhesion to the substrate where failure occurs within a single coat, as when testing primers alone, or within or between coats in multicoat systems. For multicoat systems where adhesion failure may occur between or within coats, the adhesion of the coating system to the substrate is not determined.

X1.3.3 Repeatability within one rating unit is generally observed for coatings on metals for both methods, with reproducibility of one to two units. The tape test enjoys widespread popularity and is viewed as "simple" as well as low in cost. Applied to metals, it is economical to perform, lends itself to job site application, and most importantly, after decades of use, people feel comfortable with it.

X1.3.4 When a flexible adhesive tape is applied to a coated rigid substrate surface and then removed, the removal process has been described in terms of the "peel phenomenon," as illustrated in Fig. X1.1.

X1.3.5 Peeling begins at the "toothed" leading edge (at the right) and proceeds along the coating adhesive interface or the coating substrate interface, depending on the relative bond strengths. It is assumed that coating removal occurs when the tensile force generated along the latter interface, which is a function of the rheological properties of the backing and adhesive layer materials, is greater than the bond strength at the coating-substrate interface (or cohesive strength of the coating). In actuality, however, this force is distributed over a discrete distance (O-A) in Fig. X1.1, which relates directly to the properties described, not concentrated at a point (O) in Fig. X1.1 as in the theoretical case, though the tensile force is greatest at the origin for both. A significant compressive force arises from the response of the tape backing material to being stretched. Thus both tensile and compressive forces are involved in adhesion tape testing.

X1.3.6 Close scrutiny of the tape test with respect to the nature of the tape employed and certain aspects of the procedure itself reveal several factors, each or any combination of which can dramatically affect the results of the test as discussed **(6)**.

X1.4 Peel Adhesion Testing on Plastic Substrates

X1.4.1 Tape tests have been criticized when used for substrates other than metal, such as plastics. The central issues are that the test on plastics lacks reproducibility and does not relate to the intended application. Both concerns are well founded: poor precision is a direct result of several factors intrinsic to the materials employed and the procedure itself. More importantly, in this instance the test is being applied beyond its intended scope. These test methods were designed for relatively ductile coatings applied to metal substrates, not for coatings (often brittle) applied to plastic parts **(7)**. The unique functional requirements of coatings on plastic substrates cause the usual tape tests to be unsatisfactory for measuring adhesion performance in practice.

X1.5 The Tape Controversy

X1.5.1 With the withdrawal from commerce of the tape

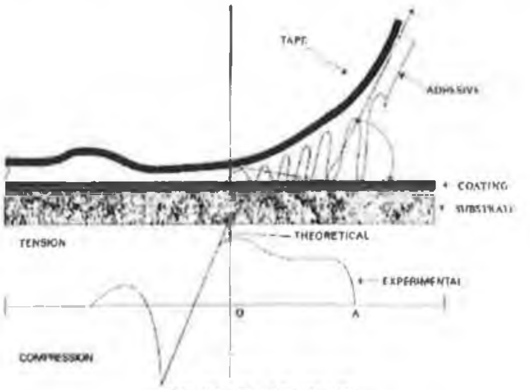

FIG. X1.1 Peel Profile (6)

specified originally, 3M No. 710, current test methods no longer identify a specific tape. Differences in tapes used can lead to different results as small changes in backing stiffness and adhesive rheology cause large changes in the tension area. Some commercial tapes are manufactured to meet minimum standards. A given lot may surpass these standards and thus be suitable for general market distribution; however, such a lot may be a source of serious and unexpected error in assessing adhesion. One commercially available tape test kit had included a tape with adhesion strength variations of up to 50 % claimed by the manufacturer. Also, because tapes change on storage, bond strengths of the tape may change over time **(7, 8)**.

X1.5.2 While there are tapes available that appear to deliver consistent performance, a given tape does not adhere equally well to all coatings. For example, when the peel removal force of the tape (from the coating) used earlier by Task Group D01.23.10 to establish precision of the method, by 3M No. 710 was examined with seven different electromagnetic interference/radio frequency interference (EMI/RFI) coatings, it was found that, while peel was indeed consistent for a given coating, the value varied by 25 % between the highest and lowest ratings among coatings. Several factors that contribute to these differences include coating composition and topology: as a result, no single tape is likely to be suitable for testing all coatings. Further, the tape test does not give an absolute value for the force required for bond rupture, but serves only as an indicator that some minimum value for bond strength was met or exceeded **(7, 8)**.

coatings. Further, the tape test does not give an absolute value for the force required for bond rupture, but serves only as an indicator that some minimum value for bond strength was met or exceeded **(7, 8)**.

X1.6 Procedural Problems

X1.6.1 The tape test is operator intensive. By design it was made as simple as possible to perform, and requires a minimum of specialized equipment and materials that must meet certain specifications. The accuracy and precision depend largely upon the skill of the operator and the operator's ability to perform the test in a consistent manner. Key steps that directly reflect the importance of operator skill include the angle and rate of tape removal and the visual assessment of the tested sample. It is not unexpected that different operators might obtain different results **(7, 8)**.

X1.6.2 *Peel Angle and Rate:*

The standard requires that the free end of the tape be removed rapidly at as close to a 180° angle as possible. If the peel angle and rate vary, the force required to remove the tape can change dramatically. Nearly linear increases were observed in peel force approaching 100 % as peel angle was changed from 135 to 180, and similar large differences can be expected in peel force as peel rate varies. These effects are related as they reflect certain rheological properties of the backing and adhesive that are molecular in origin. Variation in pull rate and peel angle can effect large differences in test values and must be minimized to assure reproducibility **(9)**.

X1.6.3 *Visual Assessment:*

The final step in the test is visual assessment of the coating removed from the specimen, which is subjective in nature, so that the coatings can vary among individuals evaluating the same specimen **(9)**.

X1.6.3.1 Performance in the tape test is based on the amount of coating removed compared to a descriptive scale. The exposure of the substrate can be due to factors other than coating adhesion, including that arising from the requirement that the coating be cut (hence the synonym" cross-hatch adhesion test"). Justification for the cutting step is reasonable as cutting provides a free edge from which peeling can begin without having to overcome the cohesive strength of the coating layer.

X1.6.3.2 Cutting might be suitable for coatings applied to metal substrates, but for coatings applied to plastics or wood, the process can lead to a misleading indication of poor adhesion due to the unique interfacial zone. For coatings on soft substrates, issues include how deep should this cut penetrate, and is it possible to cut only to the interface?

X1.6.3.3 In general, if adhesion test panels are examined microscopically, it is often clearly evident that the coating removal results from substrate failure at or below the interface,

penetrate, and is it possible to cut only to the interface?

X1.6.3.3 In general, if adhesion test panels are examined microscopically, it is often clearly evident that the coating removal results from substrate failure at or below the interface,

and not from the adhesive failure between the coating and the substrate. Cohesive failure within the coating film is also frequently observed. However, with the tape test, failures within the substrate or coating layers are rare because the tape adhesive is not usually strong enough to exceed the cohesive strengths of normal substrates and organic coatings. Although some rather brittle coatings may exhibit cohesive failure, the tape test adhesion method does not make provision for giving failure locality **(7, 8)**.

X1.6.4 Use of the test method in the field can lead to variation in test results due to temperature and humidity changes and their effect upon tape, coating and substrate.

X1.7 Conclusion

X1.7.1 All the issues aside, if these test methods are used within the Scope Section and are performed carefully, some insight into the approximate, relative level of adhesion can be gained.

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Designation: D 2794 – 93 (Reapproved 1999)$^{\epsilon 1}$

Standard Test Method for
Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact)[1]

This standard is issued under the fixed designation D 2794; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ϵ^1 Note—Deleted reference to multiple sources in former Footnotes 3 and 4 in December 1999.

1. Scope

1.1 This test method covers a procedure for rapidly deforming by impact a coating film and its substrate and for evaluating the effect of such deformation.

1.2 This test method should be restricted to testing in only one laboratory when numerical values are used because of the poor reproducibility of the method. Interlaboratory agreement is improved when ranking is used in place of numerical values.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards*

weight is dropped a distance so as to strike an indenter that deforms the coating and the substrate. The indentation can be either an intrusion or an extrusion. By gradually increasing the distance the weight drops, the point at which failure usually occurs can be determined. Films generally fail by cracking, which is made more visible by the use of a magnifier, by the application of a copper sulfate ($CuSO_4$) solution on steel, or by the use of a pin hole detector.

5. Significance and Use

5.1 Coatings attached to substrates are subjected to damaging impacts during the manufacture of articles and their use in service. In its use over many years, this test method for impact resistance has been found to be useful in predicting the performance of organic coatings for their ability to resist cracking caused by impacts.

2.1 *ASTM Standards*

D 609 Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, Lacquer, and Related Coating Products[2]

D 823 Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels[2]

D 1186 Test Methods for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base[2]

3. Terminology

3.1 *Description of Term Specific to This Standard*

3.1.1 *impact resistance, of a coating*—the number of inch-pounds (kilogram-metres) required to produce cracking in the deformed coating.

4. Summary of Test Method

4.1 The organic coatings under test are applied to suitable thin metal panels. After the coatings have cured, a standard

cracking caused by impact.

6. Apparatus

6.1 *Tester*, consisting of a vertical tube to guide a cylindrical weight that is dropped on a punch resting on the test panel.

6.1.1 *Guide Tube*, 24 to 48 in. (0.6 to 1.2 m) long mounted vertically in a base plate. A slot is cut lengthwise on one side of the tube to act as a guide for a cylindrical weight that fits inside the tube. Graduations are marked in inch-pounds along the slot. The base is constructed so that a thin flat panel can be inserted at 2 in. (50 mm) below the tube.

6.1.2 *Weight*, metal cylinder, made to fit inside the guide tube. A pin is fitted into one side of the weight to act as a guide by riding in the slot of the tube, and to serve as a handle by which the weight can be raised and released, and serve as the indicator of inch-pounds (kilogram-metres).

6.2 *Indenter*—A steel punch with a hemispherical head having a diameter of either 0.500 in. (12.7 mm) or 0.625 in. (15.9 mm). The head rests on the test panel and the punch is held vertically by a guide ring.

6.3 *Panel Support*—A steel fixture with a 0.64-in. (16.3-mm) diameter cylindrical hole centered under the indenter for supporting the test panel.

6.4 *Magnifier.*

6.5 *Pin Hole Detector.*

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

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[2] *Annual Book of ASTM Standards*, Vol 06.01.

7. Reagents

7.1 An acidified copper sulfate ($CuSO_4$) solution prepared by dissolving 10 g of $CuSO_4 \cdot 5H_2O$ in 90 g of 1.0 N hydrochloric acid (HCl).

8. Test Specimens

8.1 Apply uniform coatings of the material to be tested to 24-gage (0.025 in. or 0.63 mm) steel panels treated with a conversion coating in accordance with Procedure A of Practice D 609, unless otherwise specified. Prepare a minimum of four coated panels for the material.

NOTE 1—The coatings should be applied in accordance with Practices D 823, or as agreed upon between the producer and the user. Other gage steel panels may be used if agreed upon between the producer and the user.

8.2 Cure the coated panels under conditions of humidity and temperature agreed upon between the producer and the user.

NOTE 2—The thickness of the dry coatings should be measured in accordance with Test Methods D 1186.

9. Conditioning

9.1 Unless otherwise agreed upon between the producer and the user, condition the coated test panels for at least 24 h at 73.5 ± 3.5°F (23 ± 2°C) and 50 ± 5 % relative humidity. Conduct the test in the same environment or immediately on removal therefrom.

10. Procedure

10.1 Install the punch having the head diameter specified or agreed upon. Place the test panel in the apparatus with the

both the test areas and cloth for evidence of copper deposition or iron-rust staining respectively.

NOTE 3—The copper sulfate solution will not perform properly on zinc-phosphate-treated metal unless the conversion coating cracks.

10.3.3 To detect breaks in the film with a pin hole detector, first connect the ground lead from the instrument to the bare substrate and connect the instrument to an electrical power source. Moisten the probe sponge with tap water and slowly draw the probe over the impact area. The presence of cracks will be indicated by an audible alarm.

10.4 For each inch-pound (kilogram-metre) level, tabulate the number of times the coating passed or failed. The value where the results change from mainly passing to mainly failing is the impact failure end point.

11. Report

11.1 Report the following for each coating tested:

11.1.1 The inch-pounds (kilogram-metres) at the impact failure end point,

11.1.2 Whether intrusion or extrusion was used,

11.1.3 Diameter of the punch used,

11.1.4 Thickness of coating,

11.1.5 Substrate thickness and type of metal,

11.1.6 Method of panel preparation, and

11.1.7 Atmospheric conditions under which the coated panels were conditioned and tested.

NOTE 4—Because of the poor reproducibility of this method, the reporting of inch-pounds (kilogram-metres) in comparing coatings for impact resistance should be restricted to one laboratory. For interlaboratory comparisons, rankings of coatings for impact resistance should be coated side either up or down as specified or agreed upon. Be sure the panel is flat against the base support and that the indenter is in contact with the top surface of the panel. Lightly place the weight on the indenter and adjust the guide tube so that the lifting pin is at the zero mark. Raise the weight up the tube to a height where it is expected that no failure will occur. Release the weight so that it drops on the indenter.

10.2 Remove the test panel from the apparatus and observe the impact area for cracks in the coating. If no cracks are evident, repeat the procedure at a greater height, increasing 1 in. (25 mm) at a time. Once visible cracks are observed, repeat the test five times at each of three heights: slightly above, slightly below, and at that determined in the first trial. Test in a random fashion so that all impacts from one height are not made in succession or on one panel.

10.3 Examine the impacted areas for cracking by one of the following methods:

10.3.1 Use a magnifier to examine the area for cracks.

10.3.2 Hold a white flannel-type cloth saturated with the acidified copper sulfate ($CuSO_4$) solution (7.1) over the impacted areas for at least 15 min. Remove the cloth and examine

reported.

12. Precision and Bias

12.1 On the basis of [illegible] operators [illegible] laboratories [illegible] range of impact resistance [illegible] as follows:

	[illegible]	[illegible]
	%	%
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible] diameter punch)	[illegible]	[illegible]

12.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, bias cannot be determined.

13. Keywords

13.1 cracking; failure; [illegible]; deformation; impact [illegible]

D. Rover Engineering standard

ROVER ENGINEERING STANDARD

RES.30.CT.109

Resistance to salt immersion

Issue No. 1

Published September 1990

[illegible]	1 to 2
Issue	1

Implementation date 3 September 1990

1 SCOPE

This test method defines a procedure for assessing the corrosion resistance or paint adhesion loss after immersion in a heated salt solution.

It is designed specifically for the testing of organic coatings that are subjected to severely corrosive conditions in service, i.e. chassis and suspension items incorporating electrocoat or powder coat paint systems with phosphate pretreatments.

The test may be carried out on test panels or components in conjunction with the relevant paint material standard and incorporate any pre-test sample preparation requirements specified therein.

2 APPARATUS AND REAGENTS

2.1 5% ± 1% w/v salt solution (prepared by dissolving Sodium Chloride to BS 998 in distilled or de-ionized water).

2.2 A tank or container constructed from an inert material (e.g. glass or suitable plastics material) and capable of accepting the test panel/component with complete immersion in salt solution (see also clause 3.5).

2.3 A thermostatically controlled immersion heater capable of maintaining the salt solution at 55° ± 1°C.

2.4 A stirrer or other suitable means of circulating the salt solution to achieve uniformity of temperature.

2.5 A ball valve and reservoir of distilled/de-ionized water or other suitable means of maintaining salt solution levels throughout the test period

2.6 Specimen supports constructed from inert material (e.g. suitable plastics material).

ROVER ENGINEERING STANDARD

Resistance to salt immersion

RES.30.CT.109
Issue No. 1
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3 PROCEDURE

3.1 Condition the test panel/component in accordance with the relevant paint material standard.

3.2 Thoroughly clean/degrease all relevant surfaces on the test panel/component

3.3 Carry out any specimen marking (e.g. cross scribe to RES.30.CT.118) required by the relevant paint material standard.

3.4 Fill the tank with salt solution, switch on the circulation system and set the thermostat. Allow the solution to achieve a temperature of 55° ± 1°C

3.5 Totally immerse the test specimen in the salt solution ensuring it is at least 20 mm from other specimens and the sides/bottom of the tank.

3.6 On completion of the required test period remove the test specimen from the salt solution and thoroughly rinse it in distilled or de-ionized water.

3.7 Immediately assess the specimen for any degradation using the acceptance criteria specified in the relevant standard.

Note: The salt solution must be changed and the tank cleaned after each batch of test specimens, or if in continuous use after 500 hours.

4 REPORT

Report the nature of any degradation together with the duration of the test

Appendix 2 – Test procedures

A. Phosphate

B. Fe^{3+}

C. Aluminium

A. Determination of phosphate

Title: **The determination of orthophosphate by colorimetric macroscopic method**

Description: The reaction of orthophosphate with molybdic acid, followed by reaction yields molybdenum blue. This colour can be measured by spectrophotometer to determine concentration of phosphate. This method is suitable for orthophosphate determination in water, effluent streams, ponds and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 100ml flasks
3. 1g spoon
4. Water bath
5. Ring weights (for flasks when in water bath)
6. 5ml pipette
7. 2ml pipette

Standard Solution

Orthophosphate, di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm as P.

Reagents

1. Ascorbic acid 18g/l, this solution is stable for one week.
2. Potassium antimony tartrate 3.5g/l
3. Molybdic acid 40g/l
4. Sulphuric acid 140ml conc. This is used to make Molybdate reagent

5. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.
6. Sulphuric acid 50% conc.

Procedure

1. Take a 50ml sample and place in 100ml flask.
2. Add 3ml molybdate reagent.
3. Add 2ml ascorbic acid.
4. Make up to 100ml by adding deionised water.
5. Heat for 30 minutes to 35°C
6. Leave for 15 minutes.
7. Read absorbance at 889nm in visible
8. Calculate ppm

Title: **The determination of orthophosphate by microscopic colorimetric method.**

Description: The reaction of orthophosphate with molybdic acid, followed by reaction yields molybdenum blue. This colour can be measured by spectrophotometer to determine concentration of phosphate. This method is suitable for orthophosphate determination in water, effluent streams, ponds and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 10ml vial

3. Water bath
4. Vial rack
5. 2, 5ml pipette

Standard Solution

Orthophosphate; di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm.

Reagents

1. Ascorbic acid 18g/l, this solution is stable for one week.
2. Potassium antimony tartrate 3.5g/l
3. Molybdic acid 40g/l
4. Sulphuric acid 140ml conc. This is used to make Molybdate reagent
5. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.
6. Sulphuric acid 50% conc.

Procedure

1. Take 5ml of sample and place in vial
2. Add 0.6ml molybdate reagent
3. Add 0.4 ml ascorbic acid
4. Shake well
5. Heat to 35°C for 30 minutes
6. Read absorbance at 889nm
7. Calculate ppm

Title: **The determination of total phosphate by macroscopic colorimetric method**

Description: The reduction of polyphosphate by hydrolysis to orthophosphate is followed by the reaction of orthophosphate with molybdic acid. This reaction yields molybdenum blue colour. This colour can be measured by spectrophotometer to determine concentration of phosphate. This method is suitable for total phosphate determination in water, effluent streams, ponds and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 100ml flasks
3. 1g spoon
4. Water bath
5. Ring weights (for flasks when in water bath)
6. 3, 2 ml pipette

Standard Solutions

Pyrophosphate, tetra-Sodium pyrophosphate, $Na_4P_2O_7$ – (265.9/190)*100 = 0.1399g/l will give 100ppm.

Reagents

1. Ascorbic acid 18g/l, this solution is stable for one week.
2. Sulphuric Acid H_2SO_4, 30% concentrate ensure to add water to acid not vice versa.
3. Potassium persulphate $K_2S_2O_8$ Use in powder form.

4. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.
5. Phenolphthalein indicator solution.
6. Sodium hydroxide 2M NaOH.

Procedure

1. Take a 50ml sample and place in 100ml flask, by titrating sample into flask.
2. Add three, 1g spoons of potassium persulphate to each flask and shake well.
3. Add 2ml of sulphuric acid (b) 50%.
4. Heat to 90°C for 30 minutes.
5. Allow flask to cool.
6. Add one-drop phenolphthalein indicator.
7. Titrate sodium hydroxide until a faint pink develops.
8. Add 3ml molybdate reagent using automatic pipette.
9. Add 2ml ascorbic acid using automatic pipette.
10. Make up to 100ml with deionised water.
11. Heat to 35°C for 30 minutes.
12. Leave for 15 minutes
13. Read absorbance-using uv/visible at 889nm.
14. Calculate ppm.

Title: **The determination of total phosphate by microscopic colorimetric method**

Description: The reduction of polyphosphate by hydrolysis to orthophosphate is followed by the reaction of orthophosphate with molybdic acid. This reaction yields molybdenum blue colour. This colour can be measured by spectrophotometer to determine concentration of phosphate. This method is suitable for total phosphate determination in water, effluent streams, ponds and rivers.

Apparatus

7. Cary UV/visible machine or Hach colorimeter.
8. 10ml vials
9. 1/2g spoon
10. Water bath
11. 5, 2ml pipette

Standard Solutions

Pyrophosphate; tetra-Sodium pyrophosphate, $Na_4P_2O_7$ – (265.9/190)*100 = 0.1399g/l will give 100ppm.

Reagents

1. Ascorbic acid 18g/l, this solution is stable for one week.
2. Sulphuric Acid H_2SO_4, 30% concentrate ensure to add water to acid not vice versa.
3. Potassium persulphate $K_2S_2O_8$ use in powder form.
4. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.

5. Phenolphthalein indicator solution.
6. Sodium hydroxide 2M NaOH.

Procedure

1. Take 5ml sample and place in a vial
2. Add one half gram spoon of potassium persulphate
3. Add 0.1ml 30% concentrate sulphuric acid
4. Shake well
5. Heat to 100°C for 30 minutes
6. Allow flask to cool
7. Add one drop phenolphthalein indicator
8. Add sodium hydroxide drop-wise until pink colour forms.
9. Add 0.6ml molybdate reagent
10. Add 0.4ml ascorbic acid
11. Shake well
12. Heat to 35°C for 30 minutes
13. Read absorbance at 889nm

B. Determination of Fe^{3+}

Title: The determination of Fe^{3+} by macro colorimetric method

Description: The reaction of Fe^{3+} with ammonium thiocyanate forms a reddish colour in the presence of Fe^{3+}. This procedure is suitable for testing water streams, effluent, ponds, and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 100ml flasks
3. 50,5 ml pipette

Standard Solutions

Fe^{3+} Sulphate; Ammonium iron sulphate hexahydrate, $(NH_4)_2Fe(SO_4)_2.6H_2O$ – (392.14/55.8)*100 = 0.702g/l will give 100ppm.

Reagents

1. Hydrochloric acid HCl 6M.
2. Ammonium thiocyanate NH_4SCN, 100g/l.

Procedure

1. Take 50ml sample and place in a 100ml flask
2. Add 1 ml 6M hydrochloric acid
3. Add 5ml ammonium thiocyanate.
4. Make up to 100ml with deionised water.
5. Shake well.
6. Read absorbance at 464nm.
7. Calculate ppm

Title: The determination of Fe^{3+} by microscopic colorimetric method

Description: The reaction of Fe^{3+} with ammonium thiocyanate forms a reddish colour in the presence of Fe^{3+}. This procedure is suitable for testing water streams, effluent, ponds, and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 10ml vials
3. 2, 5ml pipette

Standard Solutions

Fe^{3+} Sulphate; Ammonium iron sulphate hexahydrate, $(NH_4)_2Fe(SO_4)_2.6H_2O$ – (392.14/55.8)*100 = 0.702g/l will give 100ppm.

Reagents

1. Hydrochloric acid HCl 6M.
2. Ammonium thiocyanate NH_4SCN, 100g/l.

Procedure

1. Take 5ml sample and place in a vial
2. Add 0.1 ml 6M hydrochloric acid
3. Add 0.5ml ammonium thiocyanate
4. Shake well
5. Read absorbance at 464nm.
6. Calculate ppm

C. Determination of aluminium

Title: **The macroscopic determination of alum by colorimetric method**

Description: The reaction of alum with eriochrome cyanide R forms an orange colour. This procedure is suitable for testing water streams, effluent, ponds, and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 100ml flasks
3. 50,5 ml pipette

Standard Solutions

Alum; Aluminium Nitrate, $Al(NO_3)_3.9H_2O$ – (375.15/26.9)*100 = 1.394g/l will give 100ppm.

Reagents

1. Ammonium acetate CH_3COONH_4, 50g/l.
2. Eriochrome cyanine R $C_{23}H_{15}O_9SNa_3$ 1g/l

Procedure

1. Take a 50ml sample and place in a flask
2. Add 5ml ammonium acetate solution
3. Add 5ml eriochrome cyanide R
4. Make up to 100ml with deionised water.
5. Shake well, read absorbance at 535nm.
6. Calculate ppm

Title: **The determination of alum by microscopic colorimetric method**

Description: The reaction of alum with eriochrome cyanide R forms an orange colour. This procedure is suitable for testing water streams, effluent, ponds, and rivers.

Apparatus

1. Cary UV/visible machine or Hach colorimeter.
2. 10ml vials
3. 2,5 ml pipette

Standard Solutions
Alum; Aluminium Nitrate, $Al(NO_3)_3.9H_2O$ – (375.15/26.9)*100 = 1.394g/l will give 100ppm.

Reagents

1. Ammonium acetate CH_3COONH_4, 50g/l.
2. Eriochrome cyanine R $C_{23}H_{15}O_9SNa_3$ 1g/l

Procedure

1. Take a 5ml sample and place in a vial
2. Add 0.5ml ammonium acetate
3. Add 0.5ml eriochrome cyanide R
4. Shake well, read absorbance at 535nm
5. Calculate ppm

Appendix 3 – Process trials

A. Removal Methods
    a. Electro-coagulation
    b. Precipitation
B. Cleaning effectiveness test
C. Coating weight measurement
B. Pre-treatment in-process control
    a. Cleaner
    b. Zinc Phosphate
    c. Iron Phosphate
    d. Silane
    e. Autophoretic

A. Removal Methods

a Electro-Coagulation

Title: **To determine ability of Electro-Coagulation to remove phosphorus**

Description: This procedure is suitable for testing water streams, effluent, ponds, river. It involves passing a current through a phosphate sample, causing a floc to form. The floc is filtered and the remaining liquid tested for phosphate.

Equipment:

1. Magnetic stirrer
2. AC transformer
3. DC power pack
4. Alum, brass, stainless steel, steel electrodes
5. Crocodile clips
6. Il beaker
7. 100ml flasks

Solution

Orthophosphate; di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm.

Pyrophosphate; tetra-Sodium pyrophosphate, $Na_4P_2O_7$ – (265.9/190)*100 = 0.1399g/l will give 100ppm.

Reagents

1. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.
2. Ascorbic acid 18g/l, this solution only lasts one week.

Procedure

1. Make up standard solution of 100ppm orthophosphate and place in beaker.
2. Connect electrodes to dc transformer (ac power pack), ensuring they are not earthed in any way.
3. Switch on power putting voltage at 30V for dc (ac set voltage 18V).
4. Add 10ml 2M sodium hydroxide.
5. Leave for 15 minutes.
6. Filter each beaker under gravity conditions using 540 filter paper.
7. Take 2, 50ml from beaker and place into two flasks.
8. Make up standard solutions and place in flasks.
9. Make up blanks.
10. To each flask add 3ml molybdate reagent.
11. To each flask add 2ml ascorbic acid.
12. Heat all flasks to 35°C for 30 minutes.
13. Read results at 889nm using uv/visible
14. Calculate amount of phosphate removed.

Conclusion

All phosphate was removed.

b. Precipitation

Title: To determine effectiveness of aluminum in the removal of phosphate

Description: This procedure is suitable for testing water streams, effluent, ponds, and rivers. The trial involved addition of aluminium sulphate to a phosphate solution, causing a floc to form. The floc was then filtered and the remaining solution analysed for phosphate.

Equipment

1. Centre glass crucibles
2. 125ml beakers
3. 100ml flasks
4. 540 filter paper
5. Water bath

Solutions

1. Orthophosphate; di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm.
2. Aluminium; Aluminium Nitrate, $Al(NO_3)_3.9H_2O$ – (375.15/26.9)*5000 = 69.7g/l will give 5% concentration.

Reagents

1. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.
2. Ascorbic acid 18g/l, this solution only lasts one week

Procedure

1. Wash all glassware with 2% sulphuric acid and rinse toughly with deionised water.
2. Make up the 100ppm orthophosphate solution.
3. Into 125ml beaker place 100ml of phosphate solution
4. Add 1.5ml, 5% alum to beaker.
5. Adjust pH to between 7 – 8.5 using sodium hydroxide and sulphuric acid.
6. Leave beaker to stand for 10 minutes.
7. Filter beaker under gravity conditions using 540 filter paper.
8. Divide solution between two 100ml flasks and label sample.
9. Make up orthophosphate standards of 2.5, 5 ppm.
10. Place 50ml of 5ppm standard in two 100ml flasks
11. Place 50ml of 2.5ppm standard in two 100ml flasks
12. Place 50ml deionised water in another two flasks
13. In all eight flasks place the following.
14. Add 3ml molybdate reagent.
15. Add 2ml ascorbic acid.
16. Make up to 100ml by adding deionised water.
17. Heat for 30minutes to 30°C
18. Leave for 15 minutes.
19. Read absorbance using uv/visible at 889nm
20. Using the absorbance obtained from standards calculate phosphate level for sample.

Conclusion

All phosphate was removed.

Title: To determine effectiveness of Fe^{3+} Sulphate in the removal of phosphate

Description: This procedure is suitable for testing water streams, effluent, ponds, and rivers. The trial involved addition of Fe^{3+} sulphate to a phosphate solution, causing a floc to form. The floc was then filtered and the remaining solution analysed for phosphate.

Equipment

1. Centre glass crucibles
2. 125ml beakers
3. 100ml flasks
4. 540 filter paper
5. Water bath

Solutions

1. Orthophosphate; di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm.
2. Fe^{3+} Sulphate; Ammonium iron sulphate hexahydrate, $(NH_4)_2Fe(SO_4)_2.6H_2O$ – (392.14/55.8)*5000 = 35.1g/l will give 5% concentration.

Reagents

1. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.

2.Ascorbic acid 18g/l, this solution only lasts one week

Procedure

1. Wash all glassware with 2% sulphuric acid and rinse toughly with deionised water.
2. Make up the 100ppm orthophosphate solution.
3. Into 125ml beaker place 100ml of phosphate solution
4. Add 2.5ml, 5% Fe^{3+} to beaker.
5. Adjust pH to between 6 – 9.5 using sodium hydroxide and sulphuric acid.
6. Leave beaker to stand for 10 minutes.
7. Filter beaker under gravity conditions using 540 filter paper.
8. Divide solution between two 100ml flasks and label sample.
9. Make up orthophosphate standards of 2.5, 5 ppm.
10. Place 50ml of 5ppm standard in two 100ml flasks
11. Place 50ml of 2.5ppm standard in two 100ml flasks
12. Place 50ml deionised water in another two flasks
13. In all eight flasks place the following.
14. Add 3ml molybdate reagent.
15. Add 2ml ascorbic acid.
16. Make up to 100ml by adding deionised water.
17. Heat for 30 minutes to 30°C
18. Leave for 15 minutes.
19. Read absorbance using uv/visible
20. Using the absorbance obtained from standards calculate phosphate level for sample.

Conclusion

All phosphate was removed.

Title: To determine effectiveness of Calcium hydroxide in the removal of phosphate

Description: This procedure is suitable for testing water streams, effluent, ponds, and rivers. The trial involved addition of aluminium sulphate to a phosphate solution, causing a floc to form. The floc was then filtered and the remaining solution analysed for phosphate.

Equipment

1. Centre glass crucibles
2. 125ml beakers
3. 100ml flasks
4. 540 filter paper
5. Water bath

Solutions

1. Orthophosphate; di-Sodium hydrogen phosphate, $NaH_2PO_4.2H_2O$ - (156.01/95)*100 = 0.164g/l will give 100ppm.
2. Lime; Calcium hydroxide, $CaHO_2$ – (/)* = g/l will give 2% concentration.

Reagents

1. Molybdate reagent contains; 500ml Sulphuric acid H_2SO_4 (14% m/v), 50ml Antimony potassium tartrate (at 3.4375g/l), 150ml ammonium molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}.4H_20$ 40g/l, mixed together solution.

2. Ascorbic acid 18g/l, this solution only lasts one week

Procedure

1. Wash all glassware with 2% sulphuric acid and rinse toughly with deionised water.
2. Make up the 100ppm orthophosphate solution.
3. Into 125ml beaker place 100ml of phosphate solution
4. Add 2.5ml, 2% lime to beaker.
5. Adjust pH to between 7 – 8.5 using sodium hydroxide and sulphuric acid.
6. Leave beaker to stand for 10 minutes.
7. Filter beaker under gravity conditions using 540 filter paper.
8. Divide solution between two 100ml flasks and label sample.
9. Make up orthophosphate standards of 2.5, 5 ppm.
10. Place 50ml of 5ppm standard in two 100ml flasks
11. Place 50ml of 2.5ppm standard in two 100ml flasks
12. Place 50ml deionised water in another two flasks
13. In all eight flasks place the following.
14. Add 3ml molybdate reagent.
15. Add 2ml ascorbic acid.
16. Make up to 100ml by adding deionised water.
17. Heat for 30 minutes to 30°C
18. Leave for 15 minutes.
19. Read absorbance using uv/visible
20. Calculate phosphate level for sample.

Conclusion

All phosphate was removed

C. Cleaning effectiveness tests

White Glove test

This was a very simple test, and gave results immediately. The substrate was wiped with a white cloth or tissue while applying moderate pressure. This test determines the particulate removal, each time applying the same pressure and wiping the same number of times when the test was preformed.

Water break

Water break test determines the oil, fats and grease removal from the substrate. After the substrate was cleaned it was then rinsed. It was after rinsing that the visual water break was observed. If the oil was fully removed, then the rinse water flowed down the substrate without breaking. The substrate was rinsed in cool water as if warm water was used for rinsing this may have evaporated at the time the test was being performed, thus giving inaccurate results.

D. Coating weight measurement

Title: To measure coating weight of iron/zinc phosphate on mild steel

Description: The following procedure can only be used on mild steel, it can also be used to quantify the zinc coating on galvanised steel.

1. Make up 30% hydrochloric acid
2. Add 0.1g thiourea to solution
3. Weigh panel and then immerse in solution for 1 minute
4. Weigh panel and calculate mass in grams per meter squared

E. Pre-treatment process control

a. Cleaner

Title: **Cleaner preparation and control for immersion alkaline cleaner Novaclean 177D**

Description: The following procedure applies only to Novaclean 177D when used as by immersion.

Surfactant: Novaclean A

Make up for Thermo King plant

Half fill tank with water (4000litres) and bring to operating temperature (60°C). Turn on agitation, slowly add Novaclean 177D (250 litres). Fill the remaining volume of tank with water bringing total volume to 8000 litres.

Make up for pilot plant

Half fill tank with water (22.5litres) and bring to operating temperature (60°C). Turn on agitation, slowly add Novaclean 177D (1.4 litres). Fill the remaining volume of tank with water bring the total volume to 45 litres.

To determine concentration of cleaner

1. Get 10ml grab sample of working solution, ensuring to rinse out beaker several time with working solution.
2. Add a few drops of phenolphthalein.
3. Titrate with 0.05 M H_2SO_4.
4. The number of mls required to change colour from pink to clear is know as the pointage.

5. Make the following calculation:

   (number cm^3) $\ast$ (0.175) = Concentration (%v/v)

Additions

To increase pointage by one in Thermo King add 100 litres of Novaclean 177D

For pilot plant to increase pointage by one add 560ml

Operating conditions

Temperature	50 – 75°C
Concentration	1 – 5 %
Immersion time	5 – 25 minutes

Title: **Cleaner make up and control of Gardoclean TP10528 by both immersion and spray application**

Description: The following procedure applies only to Gardoclean TP10528

Surfactant: For spray – Gardobond additive H7352

For immersion – Gardobond additive H7375

Make up for Thermo King spray application

Three quarters fill tank with water (240litres) and bring to operating temperature (43°C). Turn on agitation, add Gardobond additive H7352 (20 litres). Add 25kg borax; fill the remaining volume of tank with water bringing total volume to 6843 litres.

Make up for Thermo King immersion application

Three quarters fill tank with water (6000) and bring to operation temperature (65°C). Turn on agitation, add Gardobond additive H7375 (56 litres). Fill the remaining tank with water bringing total volume to 8000 litres

Make up for pilot immersion plant GMIT

Three quarters fill tank with water (34 litres) and bring to operating temperature (65°C). Turn on agitation, add Gardobond additive H7375 (0.3 litres). Fill the remaining volume of tank with water bring the total volume to 45 litres.

Make up for pilot spray plant Chemetall

Three quarters fill tank with water (38 litres) and bring to operating temperature (65°C). Turn on agitation, add Gardobond additive H7375 (0.33 litres). Fill the remaining volume of tank with water bring the total volume to 50 litres.

Operating conditions

Temperature	50 – 75°C
Concentration	3 – 4 %
Immersion time	3 – 5 minutes

To determine concentration of tank

1. Get 10ml grab sample of working solution, ensuring to rinse out beaker several time with working solution.
2. Add a few drops of phenolphthalein.
3. Titrate with 0.05 M H_2SO_4.

4. The number of mls required changing colour from pink to clear is know as the pointage.
5. Make the following calculation:

   (Pointage) $*$ (0.286) = Concentration (%v/v)

Additions

To increase pointage by one in Thermo King 12.5 litres per 1000 of Gardoclean tp10528.

For pilot plant to increase pointage by one add 560ml

b. Zinc Phosphate test

Title: **Zinc phosphate make up and control for Gardobond Z3480 A**

Description: The following applies only to calcium modified zinc phosphate, Gardobond Z3480 A

Nitrite Accelerator: Gardobond additive H 7004

Make up Thermo King immersion

Fill tank ¾ full (6000 litres) with water and heat to operating temperature add 264 litres of Gardobond Z 3480A. Fill the rest of the tank up with water. Add 2.4 litres of Gardobond – Additive H 7004.

Make up pilot plant GMIT

Fill tank ¾ full (34 litres) with water and heat to operating temperature add 1.45 litres of Gardobond Z 3480A. Fill the rest of the tank up with water. Add 0.0135 litres of Gardobond – Additive H 7004.

Operating conditions

Temperature	60 – 70°C
Concentration	3.3 – 5 %
Immersion time	3 – 5 minutes

To determine total acid pointage

1. Get 10ml grab sample of working solution, ensuring to rinse out beaker several time with working solution.
2. Add a few drops of phenolphthalein.
3. Titrate with 0.05 M H_2SO_4.
4. The number of mls required to change colour from clear to light pink is know as the pointage.
5. Make the following calculation:

   (pointage) * (0.165) = Concentration (%v/v), pointage should be maintained between 19 and 22

To determine phosphate free acid

1. Get 10ml grab sample of working solution, ensuring to rinse out beaker several time with working solution.
2. Add 50ml of deionised water and 25ml of 30% potassium oxalate.

3. Add a few drops of phenolphthalein.
4. Titrate with 0.1 M NaOH, until a faint pink appears.
5. The number of mls required to change the colour is know as the pointage.
6. Make the following calculation:

   (pointage) ∗ (0.206) = concentration (%v/v), pointage should be maintained between 15 and 18.

To determine accelerator pointage

1. Take a 50ml grab sample of working solution, ensuring to rinse out beaker several times with working solution.
2. Add a 3ml 30% H_2SO_4
3. Titrate with 0.2 M $KMnO_4$ until a pink colour persists for at least 20 seconds.
4. The number of mls required to maintain the pink colour is know as pointage.
5. This pointage needs to be maintained between 1.0 and 2.5.

Additions Thermo King

Total acid pointage add 13.6 litres Gardobond Z 3480 A, to increase pointage by one. Free acid in add 16.8 litres Gardobond Z 3480 A, to increase pointage by one. Accelerator pointage in add 1.04 litres of Gardobond H 7004, to increase pointage by one.

Additions pilot immersion plant GMIT

Total acid pointage add 0.0765 litres Gardobond Z 3480 A, to increase pointage by one. Free acid in add 0.0945 litres Gardobond Z 3480 A, to increase pointage by one.

Accelerator pointage in add 1.04 litres of Gardobond H 7004, to increase pointage by one.

c. Iron phosphate test

Title: **Iron phosphate make up and control for Gardobond LMH**

Description: The following is only for the use of Gardobond LMH, when used by spray application.

Iron phosphate: Gardobond LMH

Make up Thermo King spray

Half fill tank with water (3125 litres), add 156.25 litres Gardobond LMH. Fill the remaining tank with water.

Make up pilot spray plant Chemetall

Half fill tank with water (25 litres), add 1.25 litres Gardobond LMH. Fill the remaining tank with water.

Operating conditions

Temperature	45 – 50°C
Spray time	1 – 3 minutes
Total acid pointage	6 – 8
Acid Consumed	1 – 2

To determine total acid pointage

1. Take a 10ml grab sample of working solution, ensuring to rinse out beaker several times with working solution.
2. Dilute with 25ml distilled water.
3. Add a few drops of phenolphthalein.
4. Titrate with 0.1N NaOH until solution colour changes to pink.
5. The number of mls required to change the colour is know as the total acid pointage.

To determine the acid consumed pointage

1. Take a 50ml grab sample of working solution, ensuring to rinse out beaker several times with working solution.
2. Add 3 – 5 drops bromocresol green
3. Titrate with 0.1N H_2SO_4 until colour changes from blue to green.
4. The number of ml required to change the colour of the solution is known as the acid consumed pointage.

Additions Thermo King spray

Total acid pointage, add 24.4 litres Gardobond LMH to increase pointage by one. Acid consumed pointage, to reduce the pointage by one add 0.16 litres Gardobond additive 38.

Additions pilot spray plant Chemetall

Total acid pointage, add 0.1952 litres Gardobond LMH to increase pointage by one. Acid consumed pointage, to reduce the pointage by one add 0.0013 litres Gardobond additive 38.

d. Chromium – free post rinse passivation

Title: **Post rinse make up and control for Gardolene D6800**

Description: The following is only for the use of Gardolene D6800, when used by spray and immersion application.

Non – chrome post rinse: Gardolene D6800

Operating Conditions

Temperature spray	ambient - 40°C
Temperature immersion	65 - 70°C
Total acid	1.5 – 3
PH	4.2 – 4.8

Make up Thermo King immersion

Half fill tank with water, add 10.4 litres of Gardolene D6800. Fill the reminded of the tank with water.

Make up Thermo King spray

Half fill tank with water, add 6.4 litres of Gardolene D6800. Fill the reminded of the tank with water.

Make up pilot immersion plant GMIT

Half fill tank with water, add 0.06 litres of Gardolene D6800. Fill the reminded of the tank with water.

To determine total acid

1. Get a 50ml grab sample of working solution.
2. Add a few drops of phenolphthalein indicator.
3. Titrate with 0.1M sodium hydroxide until a faint pink colour develops.
4. The number of mls should be maintained between 1.5 and 3.

Additions Thermo King immersion

To increase the total acid by one point 0.8 litres must be added.

Additions Thermo King spray

To increase the total acid by one point 0.6 litres must be added.

Additions pilot immersion plant GMIT

To increase the total acid by one point .0045 litres must be added.

d. Silane

Title: **Silane make up and control for Oxsilan mm702 and Oxsilan mm705.**

Description: The following is only for the use of Oxsilan mm702 and Oxsilan mm705, when used by spray and immersion application.

Make up Thermo King Immersion Oxsilan mm702

One-third fill tank water deionised water. Slowly add 1600 litres of Oxsilan mm702. Fill the reminder of the tank with deionised water.

Make up Thermo King Spray Oxsilan mm705

One-third fill tank water deionised water. Slowly add 940 litres of Oxsilan mm705. Fill the reminder of the tank with deionised water.

Make up pilot immersion plant GMIT

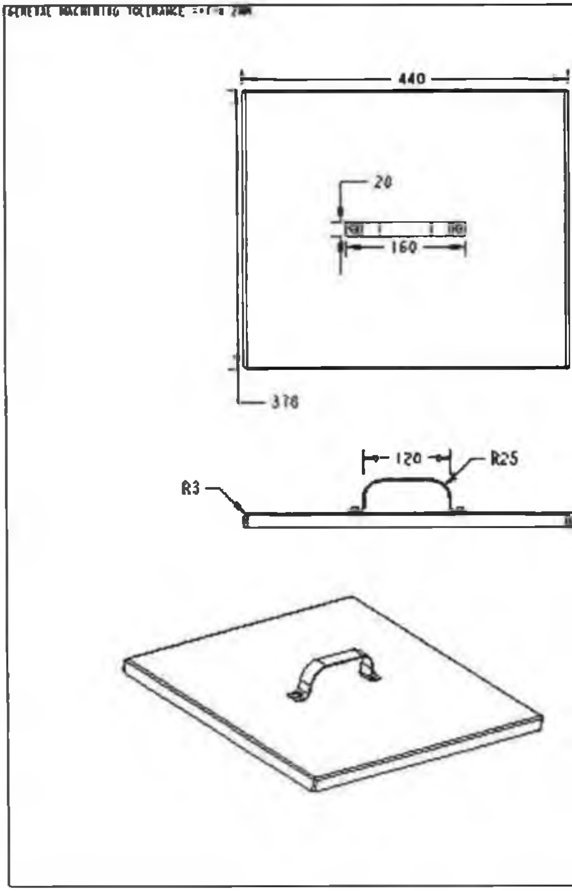
One-third fill tank with deionised water. Slowly add 9 litres of Oxsilan mm705. Fill the remainder of tank with deionised water.

To maintain concentration of both Oxsilan mm702 and Oxsilan mm705

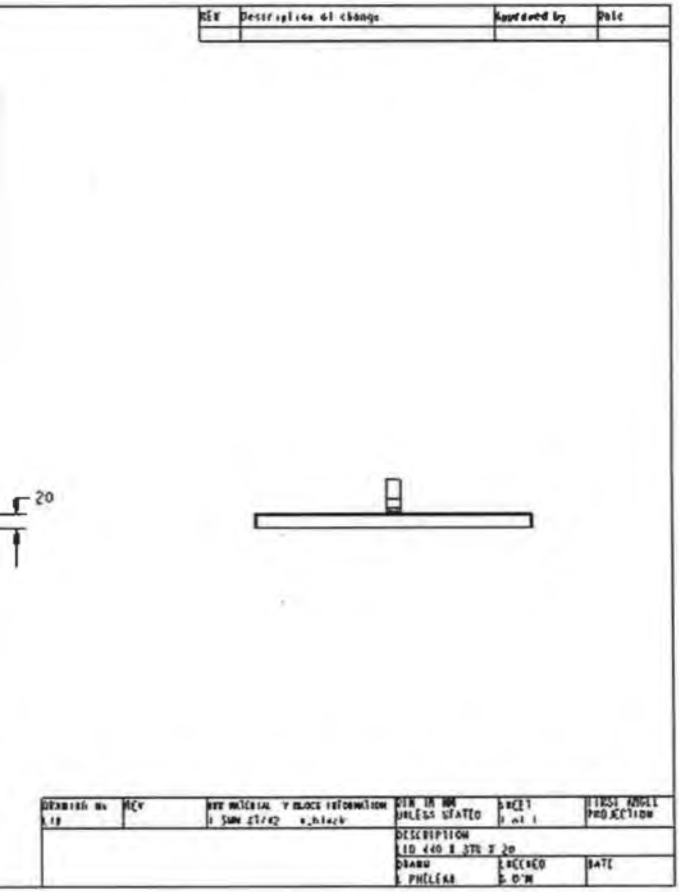
Appendix 4 – Pilot Plant and Design Drawings

A. Pilot plant systems
   a. Jig design for immersion
   b. Lid design
   c. Tank
      I Tank
      ii. Tank with element
   d. Immersion assembly drawing
   e. Proposed pilot spray plant
B. Proposed Silane plant
   a. Immersion plant Thermo King
   b. Spray plant Thermo King

A. Pilot immersion plant



Appendix 4


REV
Description of change
Approved by
Date
20
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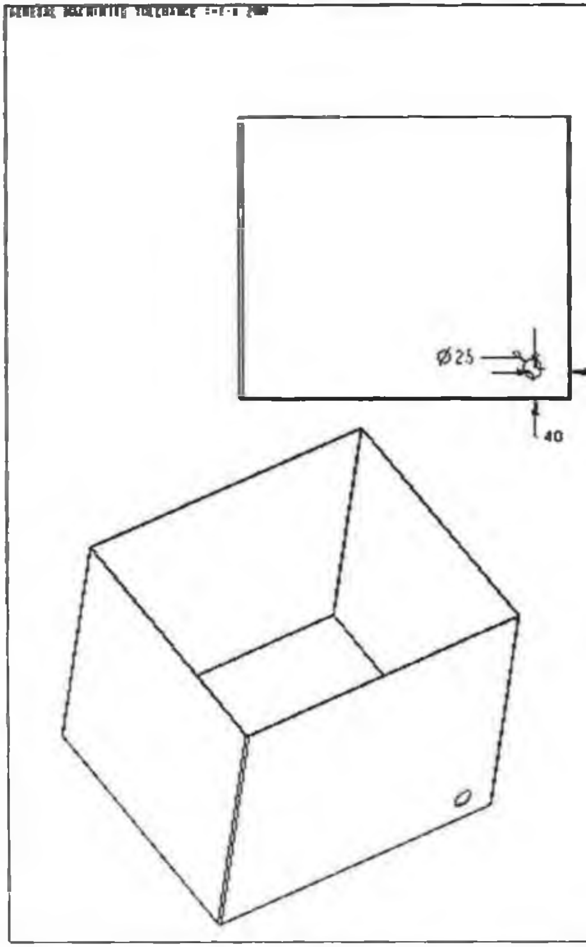
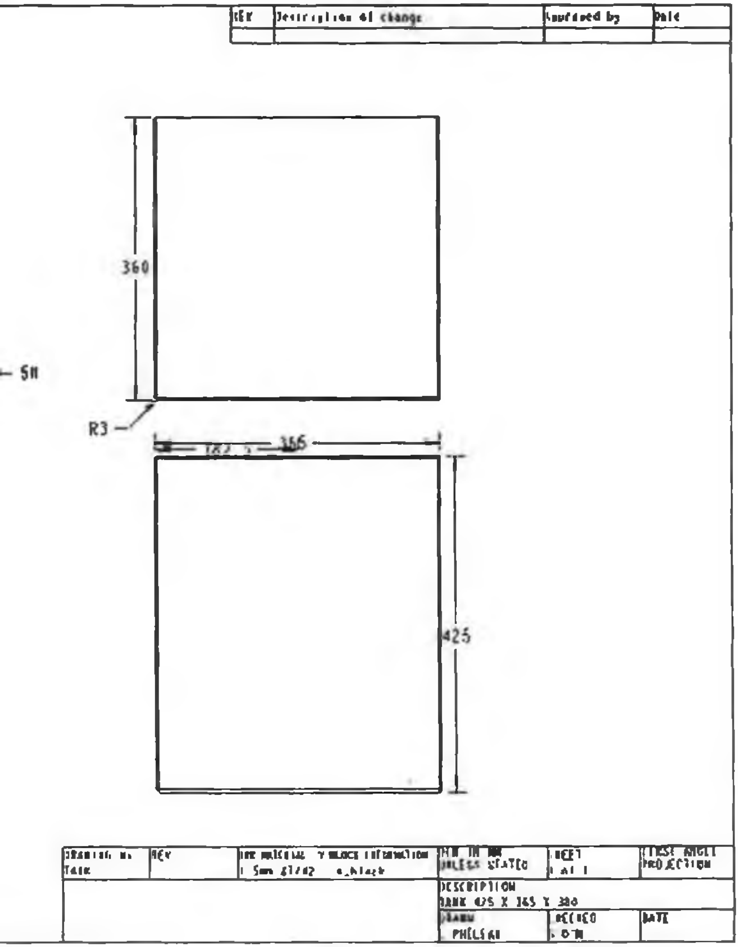
REV
QTY MATERIAL / BLOCK INFORMATION
DIM IN MM
UNLESS STATED
SHEET
1 of 1
FIRST ANGLE
PROJECTION
DESCRIPTION
LID 440 X 370 X 20
DRAWN
L PHELAN
CHECKED
DATE


GENERAL MACHINING TOLERANCE ±0.1 MM
Ø25
40

Appendix 4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Date
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R3
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1 of 1
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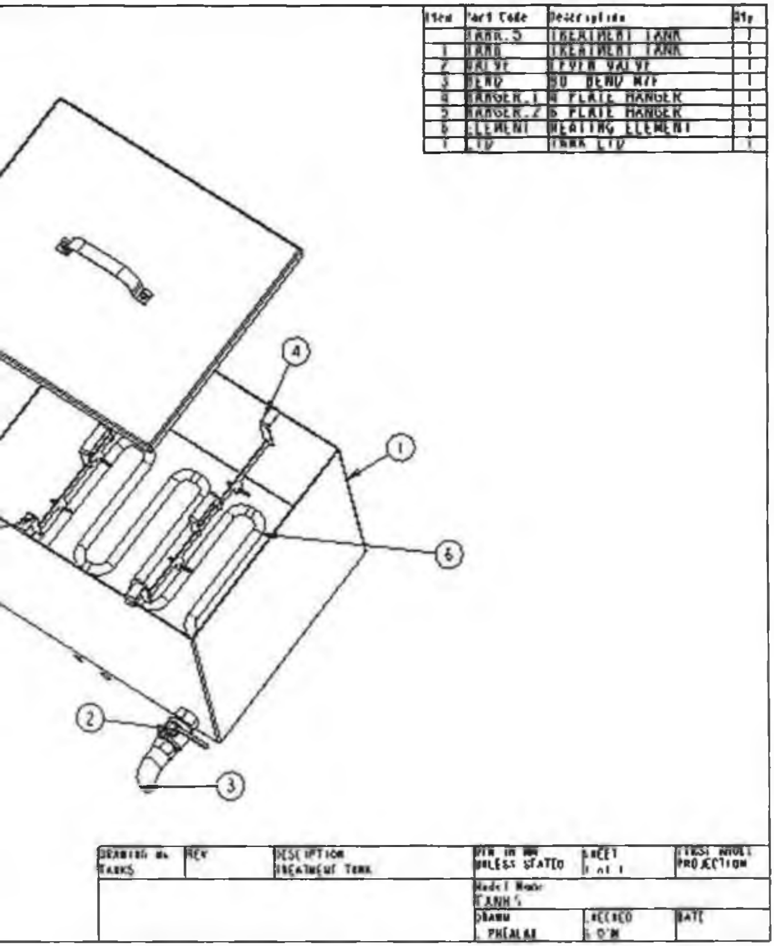
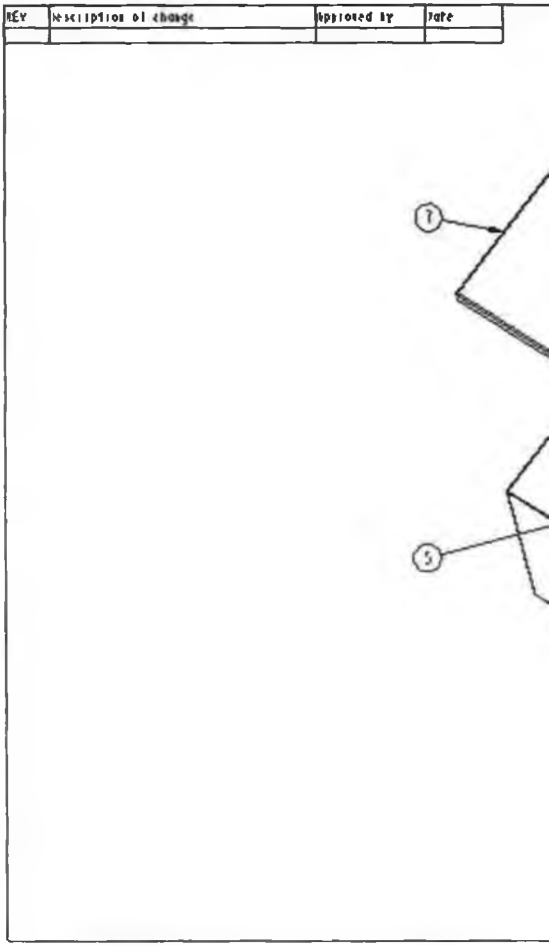
DESCRIPTION
TANK 425 X 365 X 360
DRAWN
CHECKED
DATE

Appendix 4

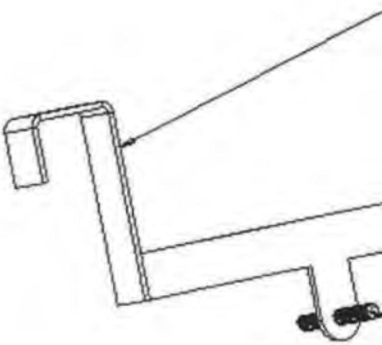


Item	Part Code	Description	Qty
	TANK.5	TREATMENT TANK	1
1	TANK	TREATMENT TANK	1
2	VALVE	LEVER VALVE	1
3	BEND	90 BEND M/F	1
4	HANGER.1	4 PLATE HANGER	1
5	HANGER.2	6 PLATE HANGER	1
6	ELEMENT	HEATING ELEMENT	1
7	LID	TANK LID	1

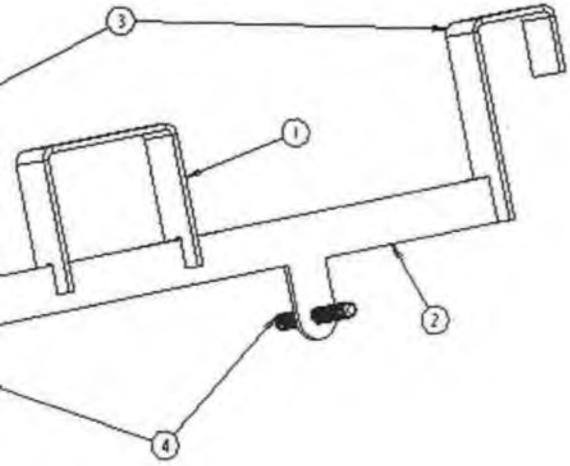


REV	Description of change	Approved by	Date

REV	Description of change	Approved by	Date

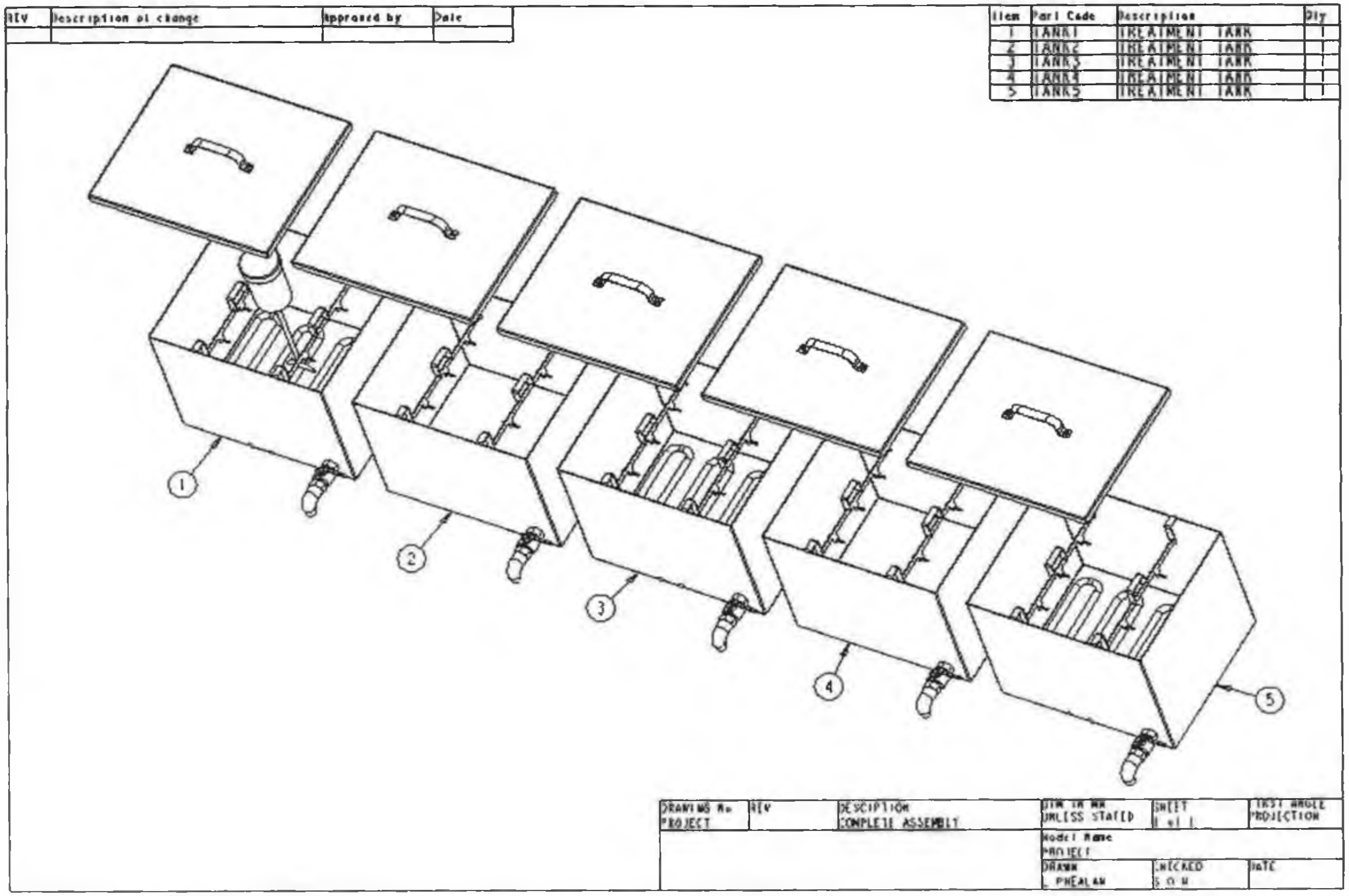


Item	Part Code	Description	Qty
	HANGER_1	4PLATE HANGER	1
1	HANGER2	2NM L PLATE ST742	1
2	HANGER3	2NM L PLATE ST742	1
3	HANGER1	2NM L PLATE ST742	2
4	STUD	5NM STUD BAR	2



DRAWING No HANGER_1	REV	DESCIPTION 4PLATE HANGER	DIM IN MM UNLESS STATED	SHEET 1 of 1	FIRST ANGLE PROJECTION
			Model Name HANGER_1		
			DRAWN L PHEALAN	CHECKED S O'M	DATE

Appendix 4

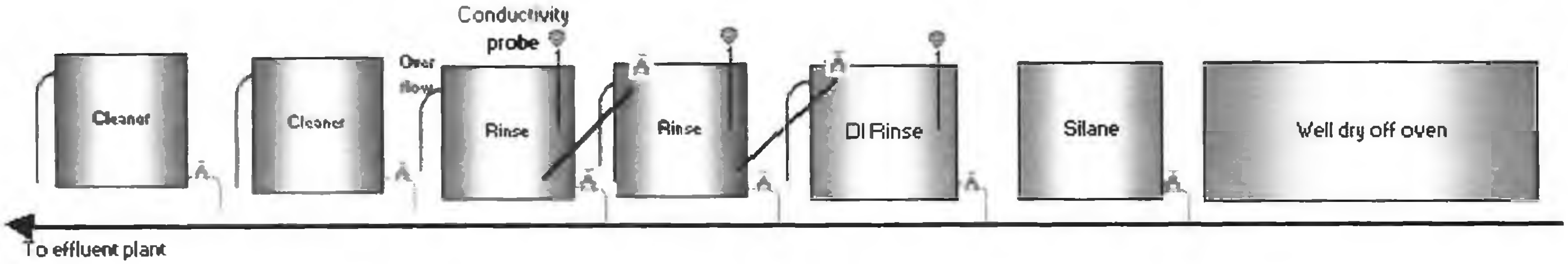


REV	Description of change	Approved by	Date

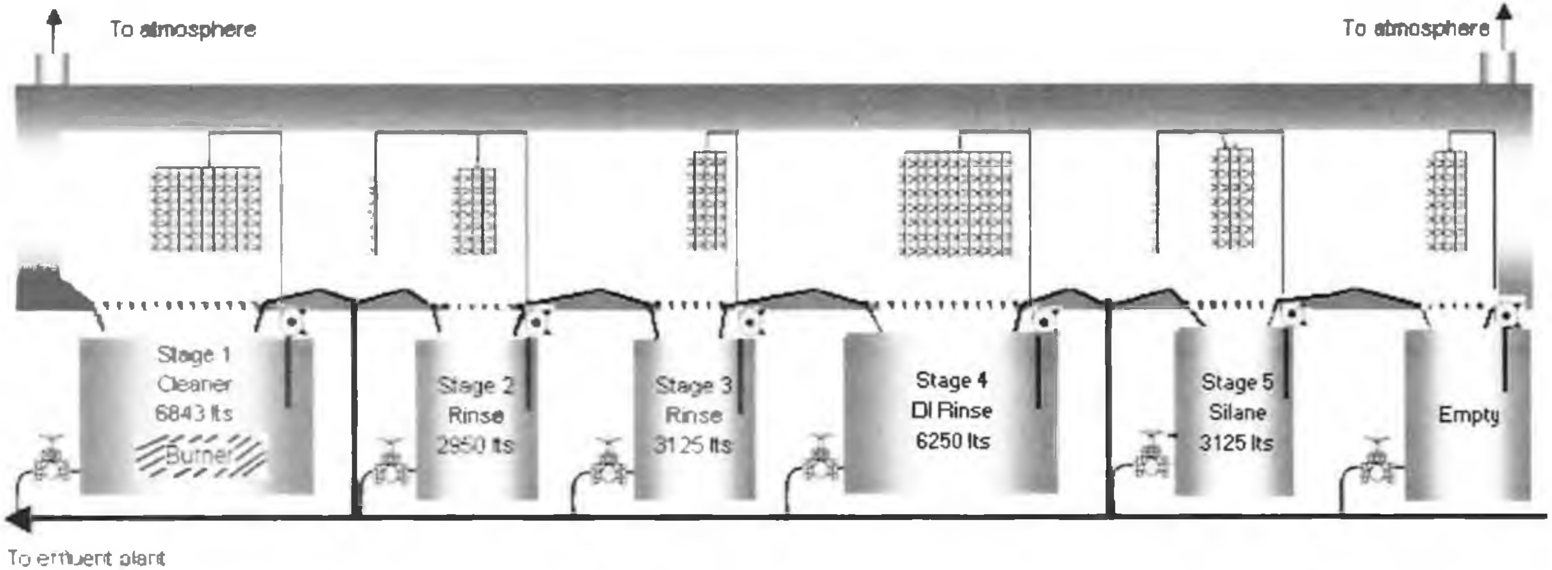
Item	Part Code	Description	Qty
1	TANK1	TREATMENT TANK	1
2	TANK2	TREATMENT TANK	1
3	TANK3	TREATMENT TANK	1
4	TANK4	TREATMENT TANK	1
5	TANK5	TREATMENT TANK	1

DRAWING No PROJECT	REV	DESCIPTION COMPLETE ASSEMBLY	DIM IN MM UNLESS STATED	SHEET 1 of 1	FIRST ANGLE PROJECTION
			Model Name PROJECT		
			DRAWN L PHEALAN	CHECKED S O N	DATE

B. Proposed Silane Plants for Thermo King



Immersion Plant Silane plant Layout



Spray Silane Plant layout

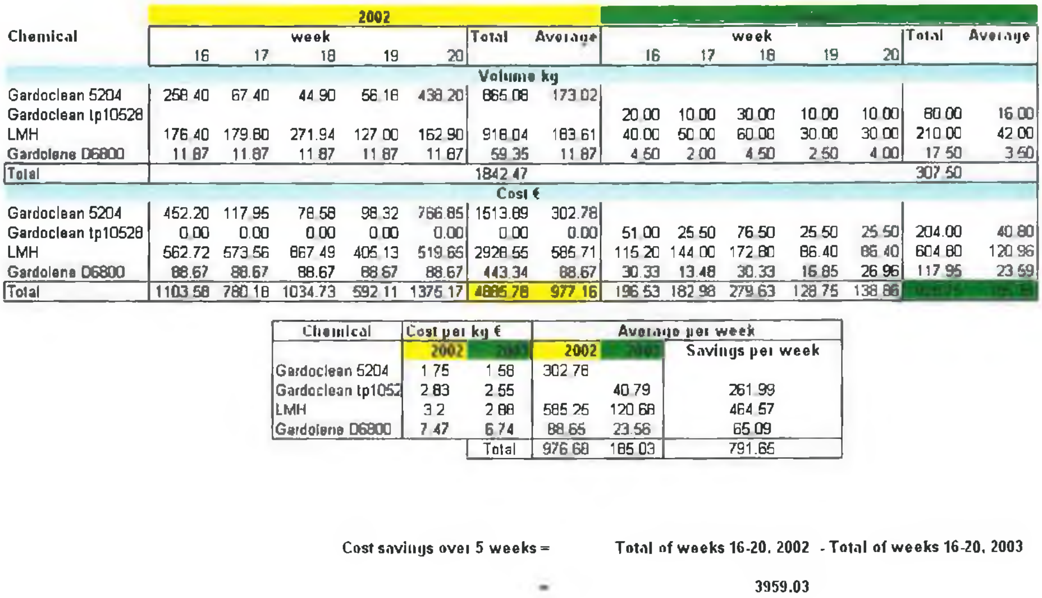
Appendix 5 – Coat saving figures

A. Spray line cost savings

B. Water conservation cost savings

Spray line cost savings

Chemical consumption and related costs

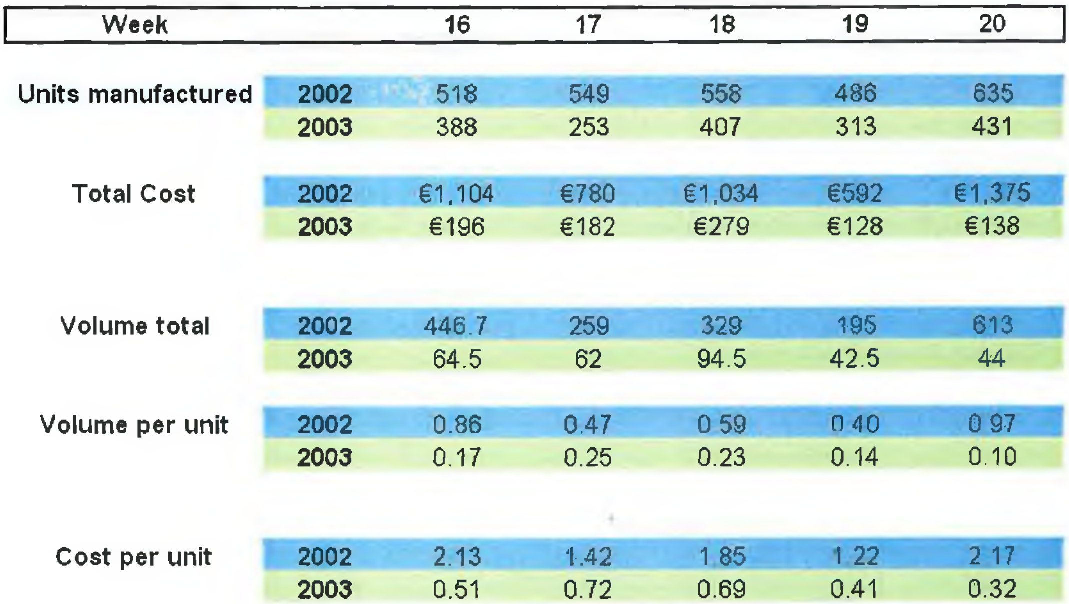


Chemical	2002												
	week					Total	Average	week					Total	Average
	16	17	18	19	20			16	17	18	19	20		
						Volume kg								
Gardoclean 5204	258.40	67.40	44.90	56.18	438.20	865.08	173.02							
Gardoclean tp10528								20.00	10.00	30.00	10.00	10.00	80.00	16.00
LMH	176.40	179.80	271.94	127.00	162.90	918.04	183.61	40.00	50.00	60.00	30.00	30.00	210.00	42.00
Gardolene D6800	11.87	11.87	11.87	11.87	11.87	59.35	11.87	4.50	2.00	4.50	2.50	4.00	17.50	3.50
Total						1842.47							307.50	
						Cost €								
Gardoclean 5204	452.20	117.95	78.58	98.32	766.85	1513.89	302.78							
Gardoclean tp10528	0.00	0.00	0.00	0.00	0.00	0.00	0.00	51.00	25.50	76.50	25.50	25.50	204.00	40.80
LMH	562.72	573.56	867.49	405.13	519.65	2928.55	585.71	115.20	144.00	172.80	86.40	86.40	604.80	120.96
Gardolene D6800	88.67	88.67	88.67	88.67	88.67	443.34	88.67	30.33	13.48	30.33	16.85	26.96	117.95	23.59
Total	1103.58	780.18	1034.73	592.11	1375.17	4885.78	977.16	196.53	182.98	279.63	128.75	138.86	[illegible]	[illegible]

Chemical	Cost per kg €		Average per week		
	2002	[illegible]	2002	[illegible]	Savings per week
Gardoclean 5204	1.75	1.58	302.78		
Gardoclean tp1052	2.83	2.55		40.79	261.99
LMH	3.2	2.88	585.25	120.68	464.57
Gardolene D6800	7.47	6.74	88.65	23.56	65.09
		Total	976.68	185.03	791.65

Cost savings over 5 weeks = **Total of weeks 16-20, 2002 - Total of weeks 16-20, 2003**

= **3959.03**



Week		16	17	18	19	20
Units manufactured	2002	518	549	558	486	635
	2003	388	253	407	313	431
Total Cost	2002	€1,104	€780	€1,034	€592	€1,375
	2003	€196	€182	€279	€128	€138
Volume total	2002	446.7	259	329	195	613
	2003	64.5	62	94.5	42.5	44
Volume per unit	2002	0.86	0.47	0.59	0.40	0.97
	2003	0.17	0.25	0.23	0.14	0.10
Cost per unit	2002	2.13	1.42	1.85	1.22	2.17
	2003	0.51	0.72	0.69	0.41	0.32

Appendix 5

Water conservation cost savings

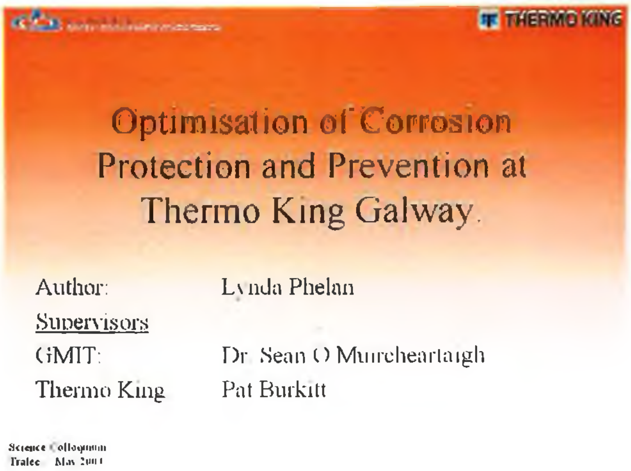
	Total Units produced	Total volume (1000 gallons)	Cost per 1000 gallons (€)	Total cost (€)	Cost per unit (€)	Volume per unit (gallons)
1st Qr. 2002	5467	4683.7	€2.60	€12,177.62	€2.23	856.72
2nd Qr. 2002	6161	2916.9	€2.60	€7,583.94	€1.23	473.45
3rd Qr. 2002	9380	1902.2	€2.60	€4,945.72	€0.53	202.79
4th Qr. 2002	4682	2383.9	€2.60	€6,198.14	€1.32	509.16
1st Qr. 2003	5178	1716	€3.75	€6,435.00	€1.24	331.40
2nd Qr. 2003	4748	1339	€3.75	€5,021.25	€1.06	282.01

Appendix 6 – Presentation

to

Annual Institutes of Technology Computing and Science Research colloquium,

Tralee May 2003



Optimisation of Corrosion Protection and Prevention at Thermo King Galway.

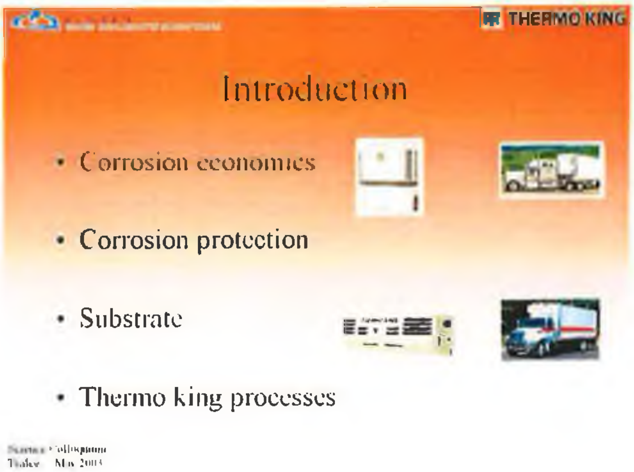
Author: Lynda Phelan

Supervisors

GMIT: Dr. Sean O Muircheartaigh

Thermo King Pat Burkitt

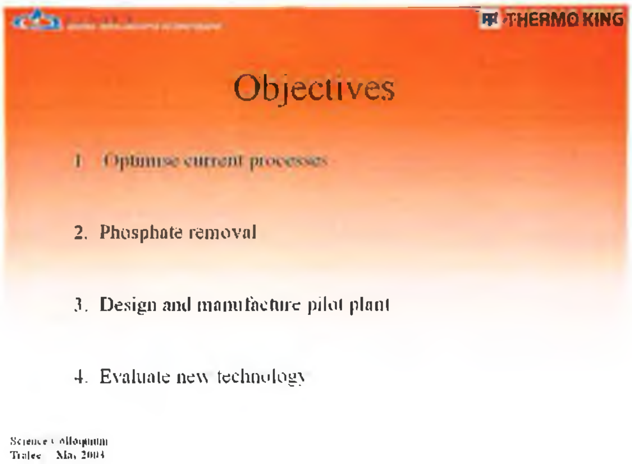
Science Colloquium
Tralee May 2004



Introduction

- Corrosion economics
- Corrosion protection
- Substrate
- Thermo king processes

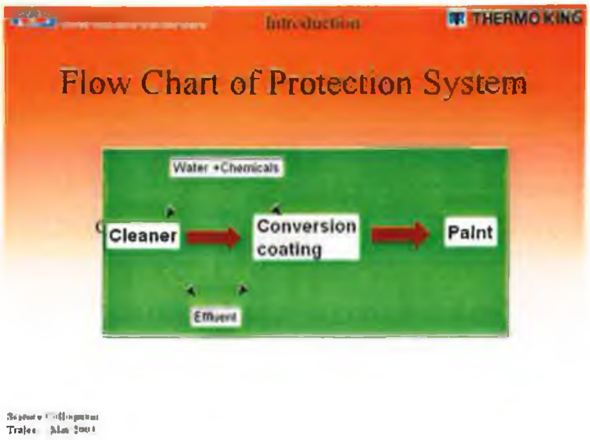
Science Colloquium
Tralee May 2004



Objectives

1. Optimise current processes
2. Phosphate removal
3. Design and manufacture pilot plant
4. Evaluate new technology

Science Colloquium
Tralee May 2004



Introduction

THERMO KING

Flow Chart of Protection System

Water +Chemicals

Cleaner

Conversion coating

Paint

Effluent

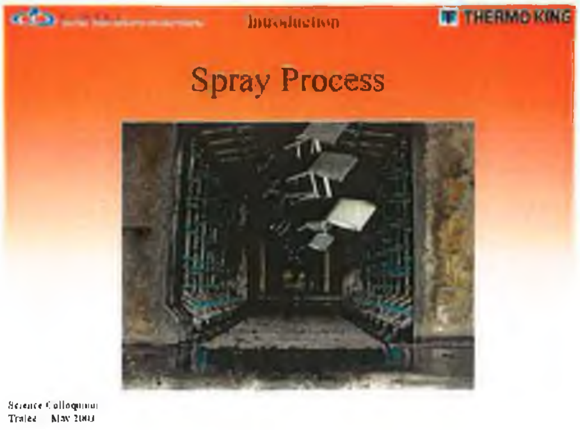
Science Colloquium
Tralee May 2003

Introduction

THERMO KING

Immersion Process

Science Colloquium
Tralee May 2003



Introduction

THERMO KING

Spray Process

Science Colloquium
Tralee May 2003

Introduction

THERMO KING

Powder Paint

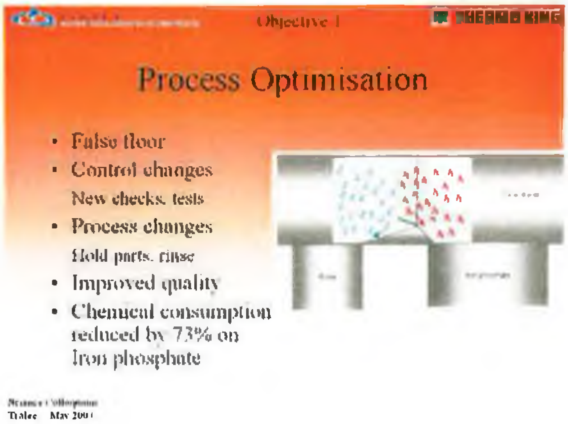
Science Colloquium
Tralee May 2003

Introduction

THERMO KING

Effluent treatment plant

Science Colloquium
Tralee May 2003



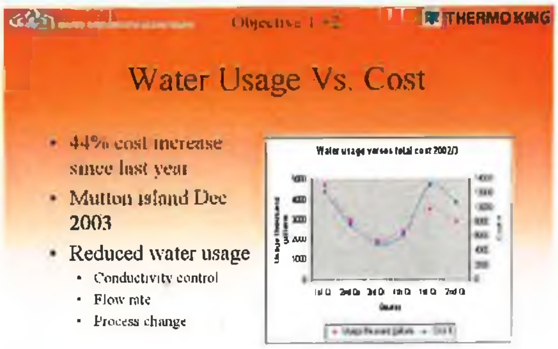
Objective 1

THERMO KING

Process Optimisation

- False floor
- Control changes
  New checks, tests
- Process changes
  Hold parts, rinse
- Improved quality
- Chemical consumption reduced by 73% on Iron phosphate

Science Colloquium
Tralee May 2003



Objective 1 +2

THERMO KING

Water Usage Vs. Cost

- 44% cost increase since last year
- Mutton island Dec 2003
- Reduced water usage
    - Conductivity control
    - Flow rate
    - Process change

Objective 2

THERMO KING

Phosphate Removal

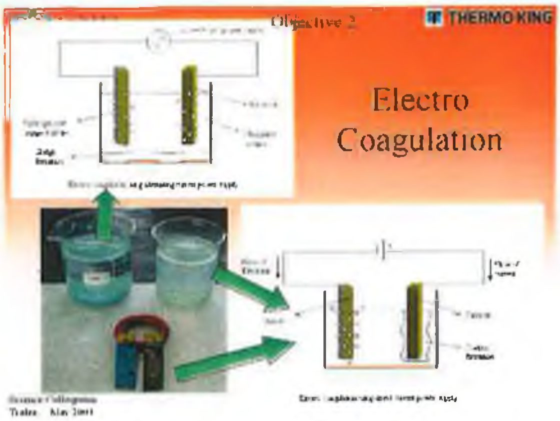
- Development of analytical techniques

  Macro + micro orthophosphate, total phosphate, alum, sulphate, ferric
- Development of removal methods

  Participation, electro-coagulation
- Laboratory trials

  Effluent samples, mass balance
- Plant trials

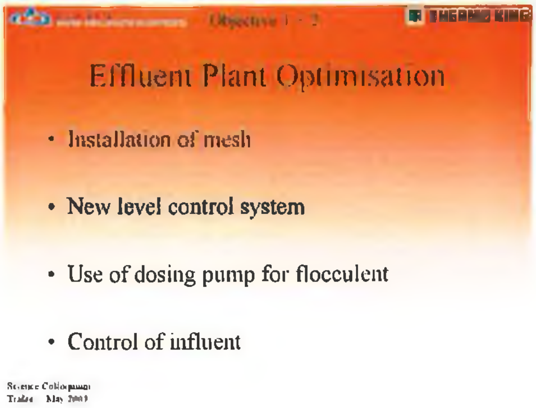
  One month, monitoring



Objective 2

THERMO KING

Electro Coagulation

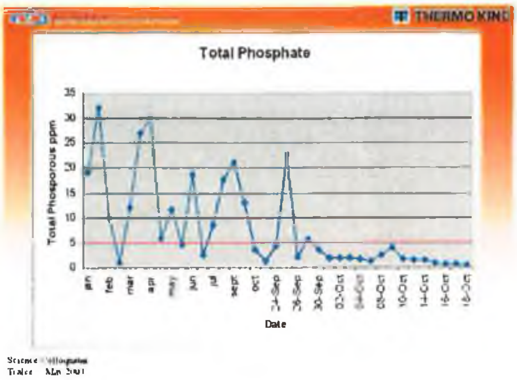


Objective 1 - 2

Effluent Plant Optimisation

- Installation of mesh
- New level control system
- Use of dosing pump for flocculent
- Control of influent

Science Colloquium
Tralee May 2001



Science Colloquium
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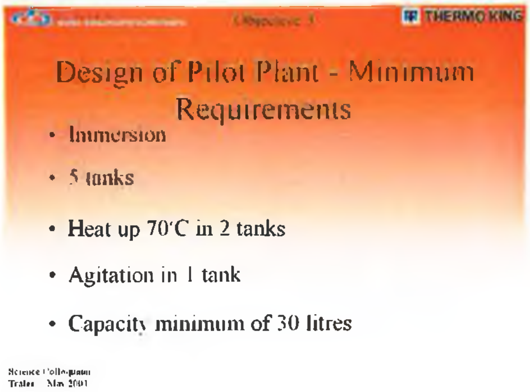
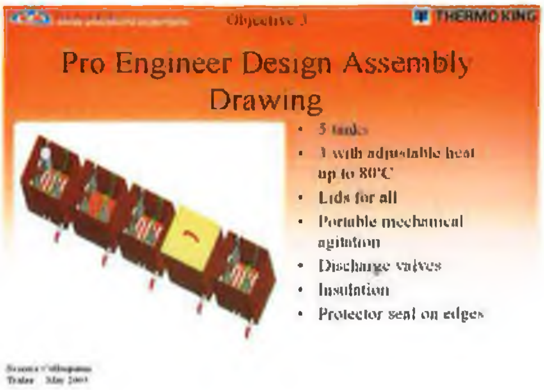


Objective 3

Design of Pilot Plant - Minimum Requirements

- Immersion
- 5 tanks
- Heat up 70'C in 2 tanks
- Agitation in 1 tank
- Capacity minimum of 30 litres

Science Colloquium
Tralee May 2001



Objective 3

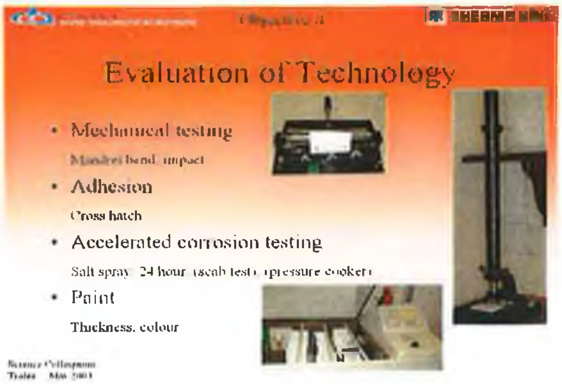
Pro Engineer Design Assembly Drawing

- 5 tanks
- 3 with adjustable heat up to 80°C
- Lids for all
- Portable mechanical agitation
- Discharge valves
- Insulation
- Protector seal on edges

Science Colloquium
Tralee May 2003

Pilot Plant in Operation

Science Colloquium
Tralee May 2003



Objective 4

Evaluation of Technology

- Mechanical testing

  Mandrel bend, impact
- Adhesion

  Cross hatch
- Accelerated corrosion testing

  Salt spray: 24 hour (scab test) (pressure cooker)
- Paint

  Thickness, colour

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Objective 4

THERMO KING

New technologies

Autodeposition	Silane
Autophoretic*	Oxsilan*
Corrosion resistant wet paint low solvent one layer	Conversion coating
Minimum 7 stages	Dry in place
Black only	Minimum 7 stages
If required subsequent powder/wet paint	No heavy metals
Steel only	Needs either powder/wet paint
	Alum/steel/galvan

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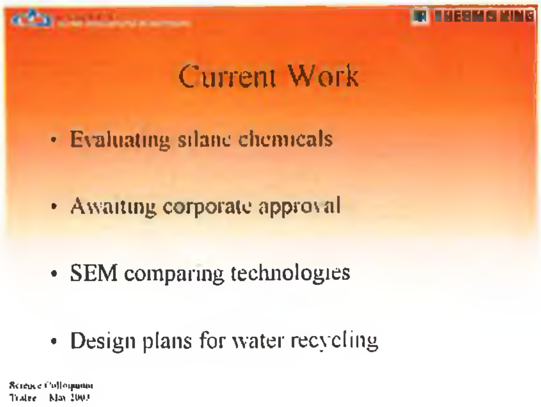

THERMO KING

Current Work

- Evaluating silane chemicals
- Awaiting corporate approval
- SEM comparing technologies
- Design plans for water recycling

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THERMO KING

Future Work – Type Report

Any Questions ?

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Award

Below is a photograph of the Johnny Dwyer Memorial award for excellence received by this project as the best overall chemistry postgraduate project at the Institutes of Technology Seventh Computing and Science Research Colloquium 2003. This specially commissioned bronze representing Mnemnosyne, the Greek Mother of the Muses, the muse of memory and knowledge, was designed, modelled and cast at AGB by sculptor John Coen.