CORROSION AND LEACHING STUDY OF LOW COPPER (I) OXIDE PAINTS FOR ANTIFOULING APPLICATION

by

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ABSTRACT

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Global environmental concern/economy challenges necessitate innovation of AFP's with novel additives offering improved corrosion protection, and biofouling resistance. Dispersing large proportions (40-70%) of Cu/Cu_2O in paints although inexpensive produces excessive leaching & heavy accumulation of copper in marine.

This study aims at formulating AFP's with reduced Cu_2O levels along with novel additives, targeting controlled copper release around 15 ug/cm2/day.In the present study several formulations were prepared using Viscoplex (PAMA in mineral oil), Ionomer ED-SPAN and CuDDP. Substitute ocean water was prepared to simulate marine environmental conditions and perform leaching studies of different formulations. A variety of preliminary elimination tests monitoring; copper leach rates, corrosion and degradation of coating properties were used to eliminate those additive formulations which demonstrated poor feasibility of antifouling and corrosion protection. Formulations with viscoplex and ionomer demonstrated better control over leach rates both in terms of reducing burst release and sustaining constant release of copper.

In the second part of the study the selected additives (from part I study) were combined using the DOE approach to obtain an optimized combination which would exhibit good control over the leaching rates and an improved protection against corrosion. In this regard a blend series (with additives and biocide blended together in paint) and a top-coat series (with additives and biocide in separated coating layers) were examined and compared. ICP analysis was performed to quantify and compare copper release rates of different coatings. Nano-Mechanical studies, Optical microscopy, and scanning electron microscopy techniques were used to evaluate and characterize the mechanical properties and corrosion behavior of coatings.

The experimental findings suggest improved performance compared to commercial coatings in many regards. The blend series demonstrated better control on leach rate renewal while the top coat formulations had better control over the burst release. Long-term study with fouling species is desirable to substantiate the improved performance of the formulated coatings.

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INTRODUCTION

1.1 Biofouling and Antifouling

Ever since their first venture in the waters, mankind has faced the detrimental effects of biofouling. The problem of biofouling is particularly acute today due to the rapid transport of marine organisms across distant waterways. [1-10]All engineered structures such as ships and marine platforms, as well as offshore rigs and jetties, intakes of nuclear pressure vessels and power plants are under constant attack from the marine environment. These structures need to be protected from the influences of the key elements of the marine environment such as saltwater, biological attack and temperature fluctuations.[1-3, 10-12] Marine technology has progressed over the centuries and in pace with this technical progress there has been a steady improvement in the analysis and treatment of the fouling problem.[1, 11] Various approaches have been tried including coatings that have mitigated the fouling of marine and fresh water structures.

Origin and Characteristics of Biofouling:

Marine Biological fouling, commonly referred to as “biofouling” can be defined as the undesirable accumulation of marine organisms both plants and animals on any artificial surface immersed under sea water.[1-3, 5, 6, 9, 13-25] Biofouling is not restricted to sea-water alone but is prevalent even in fresh-water. An innumerable list of marine organisms populates different parts of marine habitat all over the world. Adaptation requirements in different parts differ widely and produces a whole range of biofouling types which can be classified not only by the types of organisms causing it but also on the kind of water body it occurs in, the climatic variations, salinity and pH conditions and finally based on the location where it occurs such as: cold water regions, warm water regions, off-shore oil platforms, cooling water conduits for power plants and so on.[1-5, 10, 12, 19, 28]

Some of the common problems associated with biofouling involve, increased weight of structures, enhanced viscous drag caused by morphological changes in the surface of the structures(for ships, pleasure crafts etc.) both leading to higher fuel consumption.This results in poor fuel economy. Biofouling also triggers consumption of resources due to requirements of frequent dry-docking & repainting, surface clean-up with the aid of expensive skilled divers and handling unseen damages of cracks/ faults in the vessels. Fuel demands coupled with enhanced consumption of resources; enhance the global economy challenges.[1-5, 8, 10, 11, 24, 26]

The primary task for prevention and or inhibition of biofouling require a thorough knowledge of the mechanism of fouling and the factors that play a key role in facilitating attachment, growth and colonization of marine species on man-made surfaces. Although there is a controversy regarding the process of biofouling in different environments under different conditions,[1, 2, 2, 3, 5, 9, 14, 16, 22] a unanimous opinion prevails about grouping the key stages into the following categories:

1. Conditioning film formation
2. Biofilm film formation by bacteria and microalgae
3. Macrofouling
4. Growth and colonization of macrofoulers

The use of toxic materials ("Antifoulants") on marine vessels for fouling protection has been historically the most popular means of antifouling protection. Different toxic agents like lead, tin, arsenic, antimony, mercury, copper etc. have been explored as antifoulants in different carriers.[1-3, 8, 12, 21, 24, 26, 29]The most popular carrier for toxins is paint traditionally called "Antifouling paints". [1-3, 7, 8, 15, 17, 21, 28, 30-38]Paints have a plethora of applications like aesthetics, concealing flaws, providing support and protection. Ever since the 1800s paints with all different toxins as mentioned above have been formulated and experimented for antifouling till organo tin compounds came into vogue.[1-3, 8, 26]These tin compounds were extremely toxic, prevented galvanic corrosion, could be easily formulated with paints and lasted over five years without dry docking requirements. However, the acute toxicity of these compounds threatened the safety of the marine environment, affecting the growth, fertility and existence of delicate non-target marine organisms. This led to the ban of organo tin compounds for antifouling purposes. [1-3, 5, 26, 39, 40]

Following the ban of organo tin compounds the antifouling industry witnessed a revolution with a number of biocidal and non-toxic/non-biocidal substitutes trying to fill the place of organo tin compounds. The most effective substitute to organo-tin compounds has been copper based antifouling paints.[1-3, 8, 38, 41] The key advantage of copper is its easy dispersion in paints and its potential toxicity to a wide variety of marine species, even in the absence of other biocides. In addition copper exists in high concentration, naturally in the marine environment and has been found to be benign to human beings.[1-3, 28, 41, 42] The Environment Protection Agency (EPA) is examining copper based AFPs because copper has been found to be lethal to marine invertebrates even at concentrations of 5-25ug/L.[28, 41-44] A part of the marine threat caused by copper is a result of inefficient formulation of AFPs, which rely simply on dispersing large proportions (almost up to 70wt %) of copper in the paint body. In the absence of suitable binding agent which can exercise control on the rate at which copper is released into the marine environment, burst and sustained release at high rates is possible. [1-3, 18, 36, 38, 42, 44, 45]

Table 1.1 List of Environmental Regulations relating to Antifouling Paints [46, 47]

Type of Toxic Element	**Restriction**	**Comments**
Organo Tin Compounds	Banned/ Registration Cancelled	From use on all vessels/hulls
Volatile Organic Compound(VOC) content	All AFP must contain less than 400g/L of VOLATILE ORGANIC HAZARDOUS AIR POLLUTANT (VOHAP)	AFPs subject to National Emission Standards for Hazardous Air Pollutants NESHAP rules
Copper based AFP	Restricted on pleasure crafts in Sweden & Netherlands	Low salinity, presence of delicate species and accumulation of copper from other sources

1.2 Drive for This Research

In an effort to produce AFPs that can survive severe marine conditions and exhibit prolonged durability even in severe fouling conditions, the marine industry uses heavy concentration of copper in current AFPs to generate a sustainable leach rate for antifouling for longer periods of time.[1-3, 8, 26, 28, 38, 41, 42] However, little attention has been paid to the use of a suitable binder which can control the leach rates of copper into the marine environment. This results in heavy and uncontrolled leaching of copper, following immersion of a freshly painted surface in water. Loss in significant amounts of copper in the early stages of water immersion, affect the life-span of the coating as well. It has been established long before that a leach rate of $15ug/cm^2/day$ is essential for antifouling action of copper biocide.[1-3, 14, 17, 26, 28, 36, 38, 42] Thus a significantly higher leach rate of copper (as found in the early stages of immersion in water) is essentially a waste and is instead of concern to the marine environment. The current EPA regulations limit all antifouling paints to a copper release not exceeding $40ug/cm^2/day$.[2, 3, 26, 38, 42] Thus, the current EPA regulations, lack of suitable substitutes for copper based AFPs and the limitations of current technology in using effective binding compounds for leach rate control serve as the motive for this research to examine the effect of certain additives and binders, novel to antifouling application in controlling the leach rate of copper in sea water. It would also be important and necessary to evaluate the effect of these additives on the morphology, physical, mechanical and chemical properties of the paint to have a bearing on their applicability.

1.3 Objective of This Research

The first task in this study would be to select suitable compounds which could be used as binders and or release aids in AFPs to promote controlled release of copper. The objectives for this research can be summarized as follows:

Formulation of AFP with the following additives:

Viscoplex: a high molecular weight polymer comprised of polyacrylicmethacrylate (PAMA) dispersed in mineral oil, commonly used as a viscosity modifier in engine oils. This polymer is likely to be easily blended with the paint matrix while its high viscosity would prevent rapid leach out of particulate matters like copper and its hydrophobicity would keep water away from the paint matrix and improve the corrosion resistance. Details of this compound have been discussed in the Chapter 3 and 4

Cupric Dialkyl Dithio phosphate (CuDDP): a high molecular weight copper complex, which contains ‘Cu an antifouling agent’ and ‘P’ an anticorrosion agent. It might be possible to obtain by synergism both of these above mentioned properties and improve the AFP performance. Also it is likely that as a complex CuDDP will retain the inherent individual properties of both Cu and P and exhibit both antifouling and anticorrosive character when immersed in water. Thus if the complex is incorporated as an additive in paint it may be possible that it will diffuse out of the paint at a slower rate because of its bulky nature and hence the release of copper from paint will be slowed and the anticorrosive properties of the paint improved.

Polyaniline Sulfonic acid: a water soluble conductive ionomer (ionic polymer) which gradually dissolves in water from the paint surface, generating pores facilitating controlled copper leaching. (Details have been discussed in Chapter 5)

Examine the effect of the above mentioned additives in controlling the copper release rate of AFPs

The primary objective of this research is to develop suitable formulations with additives (binding and or releasing) for controlling the copper release from paints. Hence, it is important to subject the formulated AFPs (with the chosen additives) to standard leaching tests and evaluate their ability to restrain the release of copper.

Study the effect on mechanical properties and morphology of the paint

The formulated AFPs should not deteriorate in properties or performance with the progress of leaching studies and should be resistant to corrosion even in severe conditions. Thus it would be interesting and necessary to study the influence of the additives on the morphology and mechanical properties and in controlling the degradation of the paint body upon exposure to drastic conditions. This would help to understand the corrosion-resistance of the paint and also predict its durability in regular and or severe exposure conditions.

Optimize the leach rate of the current AFPs by optimizing the additive ratios

The final stage of this research would involve an optimization of the chosen additives based on performance in leaching studies and mechanical tests to eventually formulate a suitable AFP that is capable of generating an adequate leach rate throughout its service life.

1.4 Structure of Thesis

This thesis comprises of nine chapters which can be briefly summarized as follows:

Chapter1 Introduction: This chapter introduces the concepts of biofouling and the need for antifouling paints that control the rate of biocide release and answer the antifouling needs. The structure of the thesis is also reviewed.

Chapter 2 Background: This chapter reviews the mechanism of fouling and the factors influencing it. A historical overview of the approaches used to address biofouling is provided together with examination of mechanism of antifouling action with each of these approaches. The advantages and shortcomings of the approaches to biofouling are detailed and a framework for a new approach developed.

Chapter 3 Approach: This chapter discusses the approach used in selecting additives to control the leach rate of copper biocide (most popular biocide) from antifouling paints designed for marine application. It also identifies the key experimental steps necessary for analyzing the performance of the chosen additives in achieving the targeted control.

Chapter 4 Experimental Procedure: This chapter describes the experimental procedure designed and the characterizing techniques adopted for discriminating different additives with respect to improving or deteriorating the performance of antifouling paints.

Chapter 5 Synthesis of Polyaniline Sulfonic acid: The synthesis & characterization of ED-SPAN

Chapter 6 Results and Discussion: The results for all experiments and characterization techniques have been summed up in this section.

Chapter 7 Design of experiments: The results for the optimization study are discussed in the light of the design method.

Chapter 8 Conclusion: The outcomes of this study have been summarized in this chapter.

Chapter 9 Future Work: This chapter provides an overview of further research that can be performed to supplement this study.

CHAPTER 2

BACKGROUND

2.1 What is Biofouling?

Biofouling is a term often used synonymously for ‘colonization’ or simply ‘fouling’ to implicate a process which involves spreading of some territory. This process depicts biological fouling as a specific kind of fouling proliferating on hard surfaces under water and distinguishes it from other accumulating deposits resulting from processes like corrosion, crystallization, chemical reactions etc. As such biofouling may be considered as “a biofilm reactor in the wrong place”. Biofouling usually doesn’t occur in a spectacular way but rather develops in a more subtle manner due to biological deposit-the biofilm. Thus marine biological fouling constitutes a special kind of colonization which forms on hard surfaces (both man-made and natural) in water or in constant contact with it and is caused by living organisms both plants and animals which attach to these surfaces regardless of human needs or convenience. Marine organisms are attracted to hard surfaces with a view to achieving anchorage and tend to grow, mainly at the expense of nutrients accumulated as organic film from the aqueous phase. The large diversity of marine kingdom and its organisms complicate the fouling process further for mankind as there exists a possibility of fouling from a huge variety of participating marine population starting from microscopic bacteria and diatoms to shelled invertebrates like barnacle, tubeworms etc.[1-4, 6, 8, 9, 11, 13, 14, 20-22, 26]

2.1.1 The Biofouling process; stages and influencing conditions

The biological fouling process involving attachment and growth of living organisms contributes to hygienic and functional problems on most of the man-made surfaces.[2-4, 14, 48] Owing to the large amounts of losses incurred from the fact that fouling disturbs appropriate functioning of artificial surfaces in aquatic conditions, it becomes vital to develop means of protecting them. It is apparent that theoretical analysis of protection of artificial structures against biofouling requires identification and understanding of the key processes leading to fouling, their complexities and the conditions influencing them.[4, 5]

Most researchers are unanimous in their opinion on the process and stages of biofouling.[3-5, 14]Sessile organisms which occur in shallow waters are the chief organisms that create concern of fouling. One of the primary steps in understanding the fouling process is to identify the species that attach and the stages and mechanisms by which they attach. A stumbling block lies here in identifying all the species, as there are about 4000 known species of the thousands of marine species likely to cause fouling.[1-5, 14]Besides, these organisms have different preferences of conditions for attachment, and also different mechanisms of attachment. The process of biofouling is traditionally believed to occur in four stages; conditioning film formation, microbial film formation, attachment of multicellular species and finally colonization of multicellular species.[1-5, 9, 13, 14, 49] The following figure (2) describes the time necessary for the different stages to complete, once a fresh foul-free surface is under water.

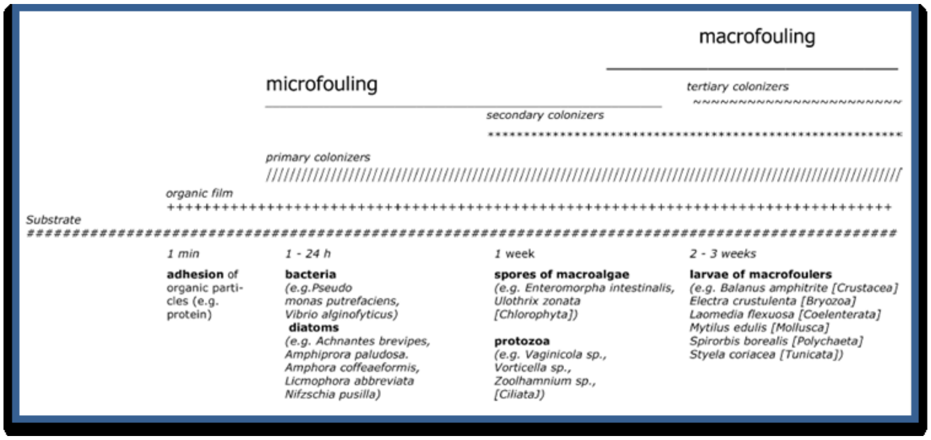


Figure 2.1 Stages of biofouling

The first step is initiated by the deposition and accumulation of organic molecules like polysaccharides, proteoglycans, proteins and possibly some inorganic compounds on a freshly immersed surface. These organic groups accumulate on the surface by Brownian motion and or Van der Waals forces, to generate a soft/spongy conditioning film which is very attractive for settlement.[2-5] Subsequent micro colonization of the surface depends on the nature and chemical composition of the conditioning film.[2]The second stage involves micro-colonization of the surface by single cellular diatoms like rod-shaped bacteria and micro-algae. These single cellular species adopt a process of reversal adsorption to attach to the surface to form a biofilm i.e. they first get adhered onto the spongy conditioning film and then exude extracellular polymeric substance (EPS) which is mostly composed of carbohydrates like glucose, fructose and polysaccharides to attach reversibly. The conditioning film has a high level of architectural symmetry and is equipped with water channels aiding transport of nutrients and metabolites to and out of the system.[2, 5, 14]It has been agreed upon that even with the highest level of antifouling protection it is almost impossible to protect a surface from biofilm-formation. Based on their ability of quorum, sensing and availability of nutrients, the microcolonisers progress to anchor, grow and loco mote to cover the entire surface.

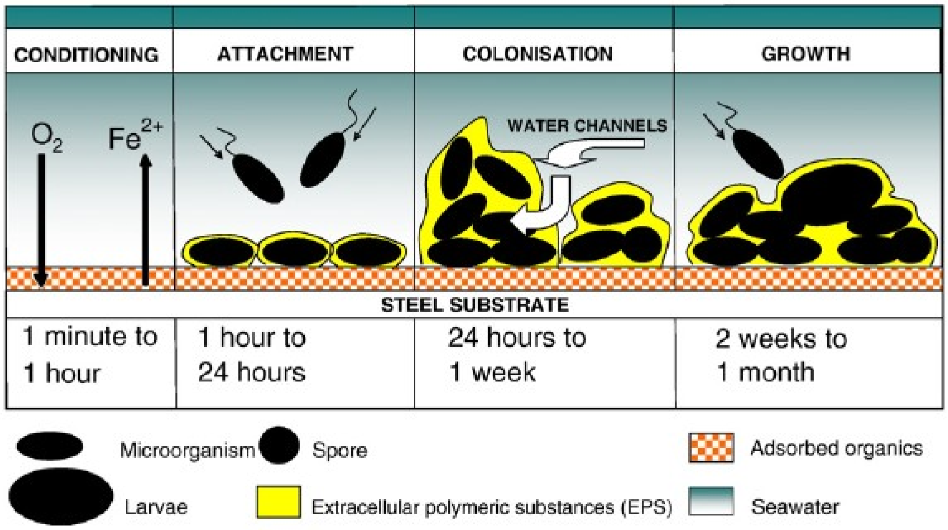


Figure 2.2 Attachment process of fouling organisms

The third stage involves settlement of the macro-fouling species like multicellular species like barnacles, algal-spores etc. the attachment of the multicellular species is encouraged by the enhanced surface roughness, nutrient rich EPS matrix and variety of microorganisms to predate. The fourth and final stage allows growth and colonization of the multicellular species as well as settlement of invertebrates so that every part of an exposed artificial surface is completely covered. The barnacles which are the most popularly known macro-foulers and also the most-studied; use a protinaceous glue for temporary attachment while a stronger cement protein for final attachment. The pertinent nature of this glue protects the larvae from being washed-off in the waters while they metamorphose and allow successful colonization of the surface.[past, enzyme, antifouling]. While the process of fouling starts within seconds of immersion of an object in fouling medium, the hard fouling is completed in several weeks.[2-5, 14, 35, 50]

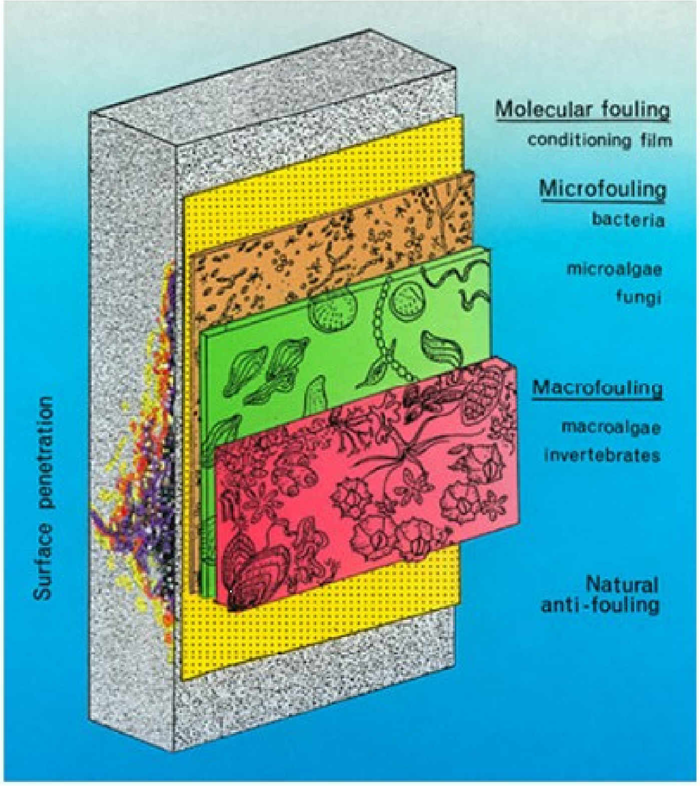


Figure 2.3 Organisms constituing the different stages of biofoiling

The study of the biofouling process is highly complicated by diversity in the marine kingdom and the impact of the geographical conditions in further varying it. The dynamic conditions of the marine environment coupled with variability of the parameters like water-temperature, water-chemistry, salinity level, pressure, shear stress etc. affect the extent and kind of growth on artificial surfaces. For example some species preferably grow in colder regions while others are abundant in warm equatorial or tropical regions. While some species of algae grow on stationary on-shore structures others pertinently grow in dynamic surroundings like off-shore ships, submarines etc.[1-5, 9, 13, 14, 20, 22, 51] Some of the highly developed species like barnacle, mussels, and some special types of algae possess the capability of adapting to any changes made by man to protect their artificial surfaces in water. Thus the antifouling technology is required to meet the challenges of adaptability of organisms as well as geographical diversity to specifically address different species in differing habitats.[2-5, 13, 14, 28, 43, 52]

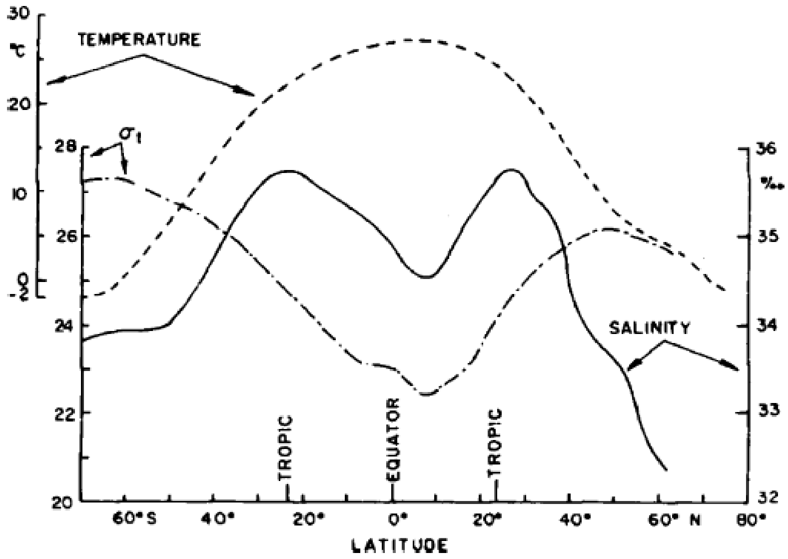


Figure 2.4 Variation of temperature, salinity and density-average for all oceans with latitude[3]

2.2 Classification of Biofouling

The local severity of biofouling depends on a large number of factors some of which include varying conditions of the sea-water, the geographical condition and the kind of application an artificial structure is subject to. Thus in order to design a suitable antidote to remediate and prevent biofouling, a modification and control needs to be exercised on these parameters. As discussed earlier, in the section above, the process of biofouling is complicated by a large number of variables that influence it. Biological fouling can be classified in several different ways based on the conditions that influence it. Although the sequence is unpredictable, the process of biofouling is broadly categorized into four growth stages as discussed in section 2.1.1. The first and second stages of fouling involving conditioning film and biofilm formation i.e. microfouling can also be referred to as soft-fouling, whereas the settlement and colonization of macro-foulers which is extremely irreversible and extremely difficult to remove is referred to as hard-fouling to describe the condition of a fouled substrate in terms of attachment, coverage and recovery requirements.

(a) (b)

Figure 2.5 (a) Fouling green algae (NERC 1995) and (b) massive Shell fouling (Clare, 1995)

Temperature is a major parameter influencing the kind and severity of biofouling. It has been realized after survey on fouling communities scattered all-over the world that, warmer regions suffer from greater intensity of fouling as compared to colder regions. There is also a contrast in the kind of growth viz. hard shell growth forms from top to bottom of surface in warm regions compared to bulky growth forms like mussels and kelps and cementing calcareous forms from top to bottom in the colder water regions. The variance with temperature can be understood from the fact that it influences the breeding and growth rate of organisms. Thus tropical and equatorial regions with less seasonal changes allow enough time for breeding and growth for fouling to continue without any obstructions.[1-3, 9, 53]A higher density of fouling population invades the coastal areas closer to the shore and diminishes with increasing distance and depth from the shore. While the kind and severity of fouling differs on-shore and off-shore, it also differs immensely between fresh-water bodies like estuaries, rivers, lagoons, lakes, ponds etc. and marine biofouling in sea or ocean water. It is known that primarily sea-water (3.4 % salt content) differs from fresh-water <1% salt content) in its salt content and also its pH (approx 7 for fresh water and 8.2 for sea-water).[3] Most common fouling forms exhibit malfunctioning and poor growth in low salinity environments. As a result, some of the more delicate forms cease to grow and foul surfaces in fresh-water while the more tenacious breeds like slime, algae, bryozoans, mussels etc. survive better in low-salinity waters. The available sunlight and salt nutrients may be reduced in polluted environments and acidic pH conditions of water render a substrate unsuitable for attachment of many forms. The condition of the water-flow bears its own impact on the severity of fouling; an analysis of the flow rates suggest that too slow flow rates slow down the uptake of nutrients while too fast flow-rates enhance the erosion risks of the attachments.[2, 3, 8] The kind of application area exposed to fouling hazards also creates a separate classification of biofouling. This is in keeping with the fact that the circumstances and conditions of exposure varies in most applications and hence the protection needs vary due to the variability in the fouling forms so that each application area requires separate focus and understanding.

2.3 Problems due to Biological Fouling

Marine Structures like jetties, oil-platforms, ship hulls as well as surfaces inconstant exposure to water as in cooling water conduits in power stations, drinking water pipeline etc. are subject to diverse and severe amount of biofouling. The damage on most marine structures is incurred to due to addition of weight by attachment and growth of the fouling organisms on the surface. The increased weight in case of oil-platforms designed for longer periods of contact with ocean water increases risks due to higher resistance to tidal and water flow. This added weight increases the hydrodynamic lag, thus slowing the maneuverability of the vessel (for ships, jetties, pleasure crafts etc.); in turn demanding higher fuel consumption which not only causes huge financial losses within the marine industry but also generates higher emissions of harmful compounds from the fuel combustion. Increased fuel consumption of almost 40% leading to extra voyage expenditure of almost 77% can accrue.[1-3, 5, 8] From the stages of biological fouling as discussed in section 2.2, it has be calculated that biofilm formation is almost impossible to control or avoid and alone contributes to about 18% spike in fuel consumption. The dry docking operations required for cleaning repairing and repainting the vessel are also elaborate, time consuming incurring additional expenses and generating toxic wastes in large quantities. The cleaning operation is difficult requiring skilled diving expertise to support the operation. The vessel is now further prone to corrosion and risks of accidental failures caused by hidden/unseen cracks and damages.

An important consequence of marine fouling accounted by several researches in different parts of the world is the presence of unwanted organisms and pathogens in ballast water, sediments and ship hulls, leading to their transfer all over the world.

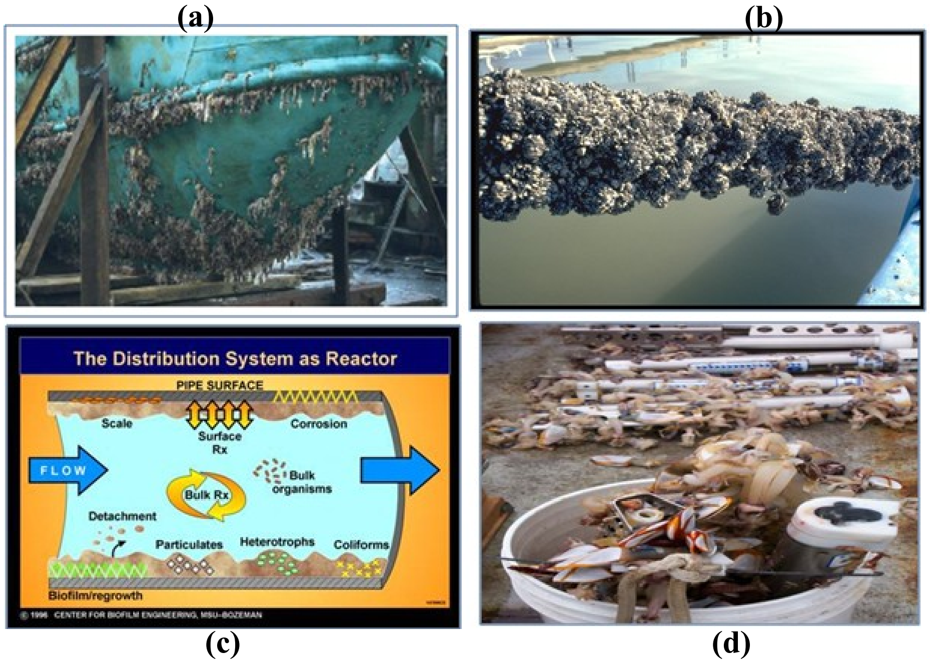


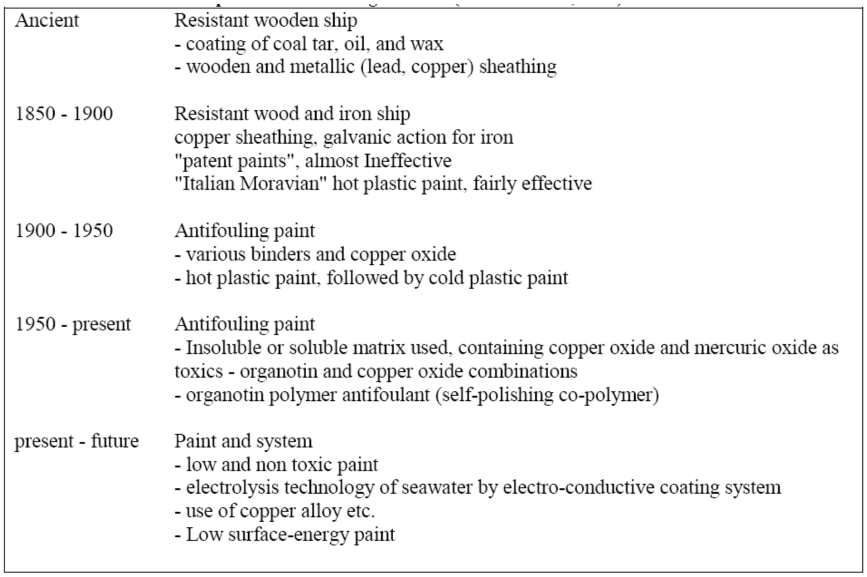
Figure 2.6 Problems of Biofouling affecting (a) ship hull (b) sewage pipe (c) cooling water pipe and (d) marine instruments

Some reports depict that about 12 billion tons of ballast water is transported all over the world annually involving the transfer of about 7000 different species daily. Examples include, the zebra mussel, a native of the black and Caspian Sea in Eastern Europe was introduced in North America in 1980's from ballast water. The survival of the organisms in the new environment depends on their ability to attach and the availability of food, sunlight, air, reproducibility and predators. Organisms successful in attaching and colonizing enhance population densities limiting the availability of food and space thus creating a competition for the natives from the encroachers. This threatens extinction of some of the delicate rare and endangered species.[1, 3, 8, 10, 14, 16, 19, 50, 52]

Biofouling incurs heavy penalties on on-shore engineered structures too. In case of heat exchangers biofouling can clog systems whereas cooling water conduits for power plants suffer enormous down times for cleaning of build-ups. Yachts and pleasure crafts look unsightly and turn slow in speed. Marine instruments and machinery suffer corrosion and loss of functionability on a permanent basis.[2]

2.4 History of Antifouling

As the name suggests, antifouling refers to counteracting or preventing the build-up of deposits on underwater surfaces of marine structures and other engineered structures constantly facing the attack from water bodies. The history of development of antifouling methods for protection of engineered structures dates far back to the ancient times but is the topic still continues to remain an important issue for research.[1-3, 8] The historical developments of antifouling systems were based on needs and technological progress in development of versatile biocides and foul-releasing method and the means for applying them.



Ancient	Resistant wooden ship - coating of coal tar, oil, and wax - wooden and metallic (lead, copper) sheathing
1850 - 1900	Resistant wood and iron ship copper sheathing, galvanic action for iron "patent paints", almost Ineffective "Italian Moravian" hot plastic paint, fairly effective
1900 - 1950	Antifouling paint - various binders and copper oxide - hot plastic paint, followed by cold plastic paint
1950 - present	Antifouling paint - Insoluble or soluble matrix used, containing copper oxide and mercuric oxide as toxics - organotin and copper oxide combinations - organotin polymer antifoulant (self-polishing co-polymer)
present - future	Paint and system - low and non toxic paint - electrolysis technology of seawater by electro-conductive coating system - use of copper alloy etc. - Low surface-energy paint

Figure 2.7 History of developments in antifouling

2.4.1 The first attempts in antifouling

The disadvantages of biofouling have been realized over 2000 years ago. In the third century B.C. the ancient Greeks used tar and wax to coat their vessels to protect them from fouling. Phoenicians and Carthaginians used copper and pitch sheathing on ship bottoms while wax and asphaltum was used by other cultures. In the 5th century B.C. historians reported the use of arsenic and sulphur mixed in oil for protecting ships from ship worms. Later in the 14th-

15th century pitch, tallow, oil and resin were applied as a means of protection. As mentioned by Morison in his life of Columbus;

All ships'' bottoms were covered with a mixture of tallow and pitch in the hope of discouraging barnacles and teredos, and every few months a vessel had to be hove-down and graved on some convenient beach. This was done by careening her alternately on each side, cleaning off the marine growth, repitching the bottom and paying the seams. In the following centuries wooden sheathing topped on animal hair and tar sheathing was a common practice in some places while lead sheathing was a more popular procedure in France, Spain and England. In fact a rolling mill was particularly designed in 1500 for making lead sheath by Leonardo da Vinci.[1-3, 26] Although it gave protection against the ship worms, it resulted in corrosion of the iron components of the hull. Following the problems faced with lead sheathing wooden sheathing coated with mixtures of tar, grease, sulphur, pitch and brimstone filled with iron and copper nails with large head to form a sort of metal sheathing was used.[3] The use of copper sheathing was improbable in the Greek and Roman times. The first use of copper was reported in 1618 by the Danish people only in the keel rudder of a ship. However an authenticated and widespread use of copper sheathing prevailed in 1780 by the British army. The popular use of copper sheathing for antifouling reigned until iron-hulls came to be used when problems of galvanic corrosion of iron became evident. It was only in the 19th century that Sir Humphrey Davis studying the effects of corrosion of copper established that it was the dissolution of copper in sea-water that contributed to its antifouling action. [past, antifouling] the failure of copper sheathings for protecting iron hulls paved the way for experimenting with a host of metallic and non-metallic sheathings which included zinc, galvanized iron, nickel, alloys of zinc, antimony and tin, felt , canvas, ebonite, cork, paper, glass, enamel and rubber. Attempts of preventing contact between copper sheathing and iron hull were made by soaking the hulls in tar or using rubber, cork etc.[2, 3] The above elucidation for ancient attempts on antifouling reveals the improvement that followed with antifouling methods based on problems faced and causes or requirements identified. Most of these ancient methods were partially effective in protecting the surfaces of ships and resulted in huge losses in property and lives. The sheathings were difficult to structure and cast and left defects or holes which led to drastic corrosion and failure. However the identification of toxic materials capable of resisting fouling on vessels led to the development of blends or mixtures and eventually antifouling paints.[1-4, 8, 12, 14, 15, 17, 18, 21, 26, 28, 35]

2.4.2 Antifouling Paints

The advent of antifouling paints added a level of advancement towards the protection of marine vessels. Paints are a mixture of several raw material each contributing to a special purpose; the major components include binder, pigment and solvent. The first antifouling paint was recorded as a British patent in 1625 by William Beale, and it was comprised of mixture of cement, copper compound and iron powder. Later 18th and 19th century developments include the use of varnish, tar and iron sulfide mixed with arsenic used as antifoulant. All of these paints like the modern antifouling paints used a toxic substance dispersed in a polymeric carrier such that the toxicant is released by some leaching mechanism.[1-3, 8, 26] Linseed oil, shellac, varnish and tar were the common resins and salts of copper , arsenic and sulfur popular toxicants for antifouling paints. Rosin was found to be an inexpensive and easily available replacement for coal-tar and shellac based paints. Hot Plastic-paints which required heating of the paint in the site of application were used for some time but based on the inconvenience of heating on shipping sites; cold-plastic paints were developed. Post World War II; technical progress brought in the use of synthetic resin with improved mechanical and application characteristics. The next step of progress in the antifouling technology was to tweak the chemistry of the resin and use solvents to improve the homogeneity of the dispersion and ease the application on the surface. The paints used at this time can be classified into insoluble and soluble matrix paints. [1-3, 18, 29]

The insoluble matrix paints comprise of high molecular weight polymer backbone such as epoxy, acrylates etc. which are insoluble in water but which contain soluble pigments. These pigments dissolve in sea-water penetrating through interconnecting pores and diffuse out similarly to generate antifouling action. Although these are mechanically robust and resistant to cracking and atmospheric degradation yet they lose their pigment/toxicant release capacity due to build-up of thick leach leached layers and have a very short life-span.

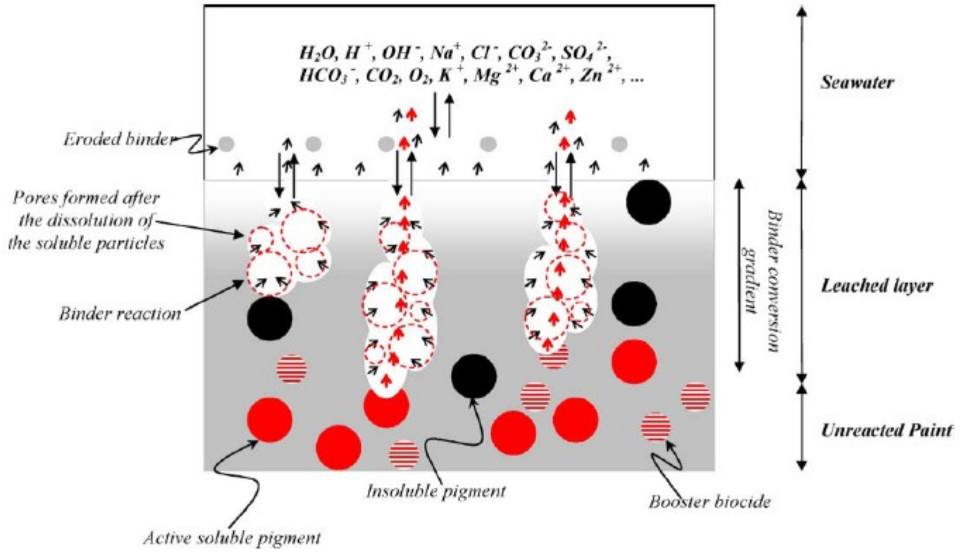


Figure 2.8 Behavior of biocide –based paint upon in immersion in water

The soluble matrix paints are designed to cope with the inefficiencies of the insoluble counterparts. These paints comprise of large proportion of Rosin (a natural extract of pine-tree). Rosin acts as a binder in the paint. A binder is the film forming component of the paint which determines its physical and chemical properties. Its role is to form a continuous film and its functionalities determine the paints resistance to the environment. Rosin is comprised of several unsaturated carboxyllic acid components; abietic acid being a major one. Once in contact with sea-water (alkaline), the carboxillic components react with sodium/potassium salts to form soluble resinates. [1-3, 7, 11, 15, 17, 21, 31, 35, 44, 45, 48, 53, 54]

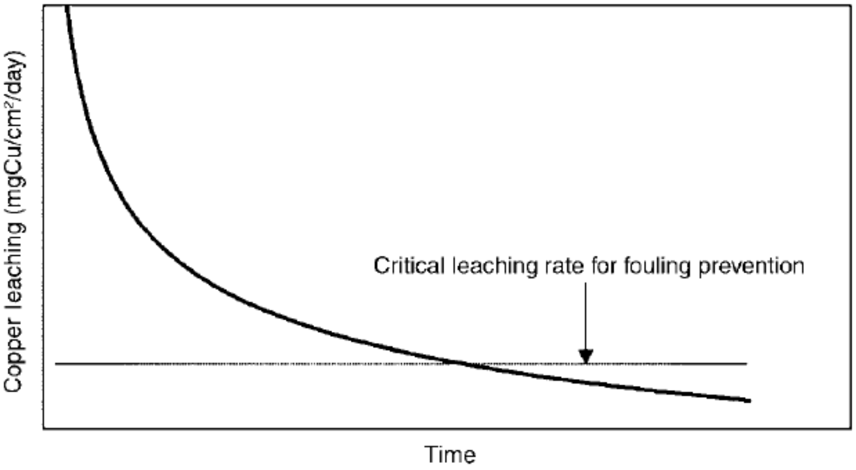


Figure 2.9 Critical copper Leach rate for antifouling action

This solubility of the paint matrix helps wash off diffusion barriers from leached layers so that the toxic pigments continue being released and the antifouling performance prevails. The rosin based paints although fairly effective but lose their toxic pigments early due to uncontrolled rate of dissolution of the matrix. Rosin being a natural component, there is no control on the number of carboxyllic functionalities leading to uncontrolled dissolution in the early stages of immersion. The rosin based paints contain unsaturation and are prone to ageing when exposed to UV-radiation especially during dry-docking periods. Also after the dissolution of the carboxyllic components, the remaining backbone is carbon-carbon straight chain, losing its flexibility in terms of bond stretching turning the matrix brittle. Thus rosin based paints necessitate the use of plasticizer components to prevent the brittleness of the matrix in the long-term. A comparison of the insoluble and soluble matrix paints can be made by comparing their toxicant release strategies from the schematic below:[1-3, 17, 21, 31, 48]

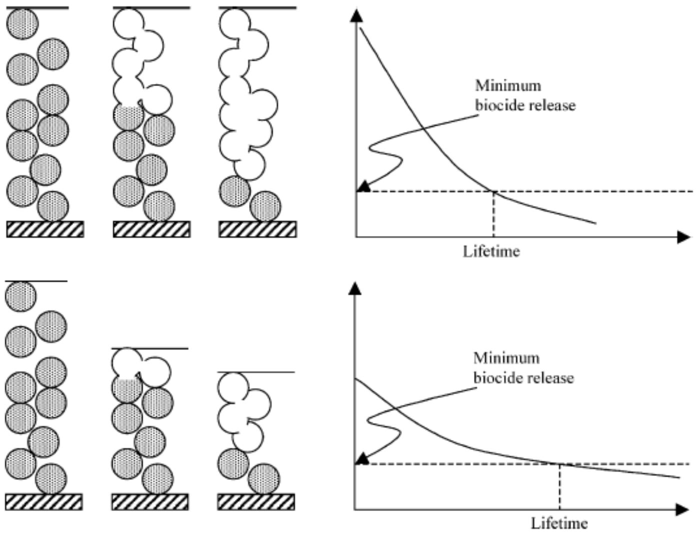


Figure 2.10 Schematic for biocide release rates of insoluble and soluble matrix paints

2.4.3 Biocides for Antifouling- the advent of TBT-compounds

In 1960s the organotin compounds were commercialized. Initially these compounds were used as co-toxicants in high performance copper based paints.[1-3, 12, 24, 26, 29, 39, 40] With the advent of Triorganotin derivatives, the antifouling technology was revolutionized. Tin compounds like TBTF, bis-oxide TBTO, TPTCl etc. have been explored to meet antifouling needs very effectively. These tin derivatives are resistant to vegetative and shell fouling, easily miscible in soluble and insoluble matrix paints, colorless, compatible with other biocides and cause no galvanic corrosion like copper derivatives so that they can even be used on aluminum hulls. These paints exhibited a service life of up to 5 years with the hull smooth and foul-free. The drawback for these compounds was their plasticizing action on the paint matrix limiting their concentration in paints and also the fact that they rapidly migrate to the surface of the paint leading to rapid depletion. Also it was discovered that the use of such tin compounds by themselves was a matter of concern for health and safety of those involved in manufacturing and applying such paints. Hence an increasing need for TBT-compounds chemically bonded to the polymer backbone was realized.[1-3, 10, 21, 26, 40]

A breakthrough in the antifouling systems came in the form of “self-polishing or ablative TBT-based” systems which were self sufficient in controlling biofouling through the life of the paint by controlling the rate of toxicant release.[1-3, 8, 26, 39, 40] The TBT-SPC contain acrylic co-polymer as the film-forming component of the paint where TBT is covalently bonded into the acrylic backbone by an ester linkage.[1, 3, 8, 10, 26, 40, 55, 56] Different pigment biocides such as ZnO and later Cu_2O were used as booster biocides and also to influence the polishing rate. The hydrophobic matrix of the TBT-SPC system prevents entry of water except through the inter-connecting pores which help dissolve soluble pigments and biocides.

$$\text{polymer–COO}^-\text{Na}^+ \text{ (s)} \rightarrow \text{polymer–COO}^-\text{Na}^+ \text{ (aq)}$$

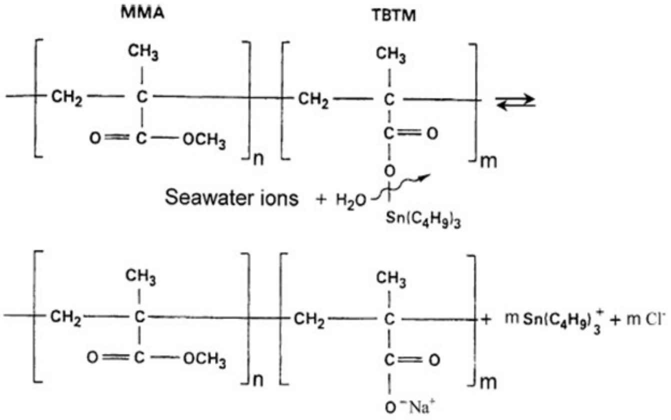


Fig. 7. Controlled release mechanism of TBT copolymer by hydrolysis (modified from [38], with permission of Kluwer).

Figure 2.11 Reaction scheme of TBT-SPC compounds

Apart from providing a long service life of over 5 years without dry docking needs, the possess the advantage of easy control on the release rate of the TBT groups at a time by controlling the esterification of the polymer backbone with TBT. The TBT-SPC systems are of high mechanically strength and shorter drying times.[1-3, 31, 48]

2.5 Impact of ban of TBT-compounds for use in antifouling-Current technologies

The biocidal potency and wide range of activity against a host of biofouling forms coupled with precisely controlled release of toxicants allowed a TBT-SPC system to remain foul-free for long durations and return for dry docking in satisfactory condition at the end of the expected lifetime. Records depict about 90% vessels exhibited superior performance in terms of biofouling resistance. The acute biocidal effects of TBT compounds were their key to success but unfortunately it was this that was responsible for their undoing. In 1980s it was realized that the slow release of organotin compounds in water poisoned not only the target fouling species but other non-target species as well and resulted in their malfunction and also extinction in some cases.[1, 2, 4, 5, 7, 8, 10-12, 14, 17, 18, 21, 24, 26, 35, 38, 39, 55, 56] TBT concentrations in parts per billion toxicated a host of marine species like mollusks, whelks and oysters.[1, 26, 40] Some of the problems resulting from tin accumulation in mammals and fishes caused shell deformities in oysters, development of imposex or male-characteristics in females, retardation of immunity in fishes and other adverse effects on marine life as a whole. The harmful effects were also detected in the vicinity of the dry-dock and repair areas.

The International Maritime Organization established in 1958 set up an antifouling group in 1990 to understand and evaluate the problem better. The organization anticipated that bioaccumulation of tin compounds in the food-chain would eventually threaten the health and safety of man-kind. The IMO conference in 2001 resulted in a declaration of a ban on the use of TBT-compounds on any vessel smaller than 25m in length with a leach rate not exceeding 4ug/cm2/day. This was done as an interim measure to reduce the widely spreading hazard and the environmental threat by the high usage of tin compounds. The Environmental Protection Agency (EPA) working in communion with the IMO- has attempted to phase out TBT-compounds by cancelling all registration and implementing stricter regulations. The present day situation is such that all tin compounds have been banned from use as biocides (from 1st January 2008). The ban of tin compounds led to significant investments in research and development of tin-free technologies; the industry benchmark for performance of all current and future antifouling paints being the TBT-SPC system.[1-3, 26, 38-40, 55, 56]The post TBT developments can be broadly categorized as below:

2.5.1 Alternative Biocide based antifouling paints

With the anticipated demise of TBT-SPC large concentration of research was concentrated to the development of alternative biocides to produce tin-fee SPC where the alternate biocides like copper, zinc; silicon etc. was covalently bonded to an acrylic backbone for release in water by alkaline hydrolysis.

TBT Acrylate: $\mathrm{Polymer{-}COO{-}Sn\ (Bu)_3 + NaCl \Leftrightarrow Polymer{-}COO{-}Na + Sn\ (Bu)_3{-}Cl}$
Copper Acrylate: $\mathrm{Polymer{-}COO{-}Cu{-}R + NaCl \Leftrightarrow Polymer{-}COO{-}Na + R{-}Cu{-}Cl}$
Zinc Acrylate: $\mathrm{Polymer{-}COO{-}Zn{-}R + NaCl \Leftrightarrow Polymer{-}COO{-}Na + R{-}Zn{-}Cl}$
Silyl Acrylate: $\mathrm{Polymer{-}COO{-}Si\ (R)_3 + NaCl \Leftrightarrow Polymer{-}COO{-}Na + (R)_3\ Si{-}Cl}$

Figure 2.12 Reaction scheme for alternative biocide based afps

Apparently none of these tin-free SPC's were as successfully as the original TBT compound; the primary reason being difficulty in striking a balance between the dissolution of the pendant groups by hydrolysis and the property damage/change of the remaining matrix.[1-3] Besides, these systems fail to protect vessels from fouling in stationary conditions as the pores get blocked –up and require the eroding effect of water to generate a nascent surface to renew the antifouling action.

Another alternative to TBT-SPC systems include the controlled depletion polymer systems (CDP). These paints are based on an up gradation of the traditional soluble matrix paints. They include large proportions of rosin to solubilize the matrix and allow controlled release of biocides like copper (I) oxides.[1-4, 7, 8, 10-12, 14, 24, 26, 31, 37, 39, 40] When seeking a biocidal substitute to tin cuprous oxide (added as a pigment) turned out as the common choice for formulators, in view of its proven efficacy in antifouling. To counterbalance the brittle nature of rosin and its uncontrolled release of biocide; modern reinforcing polymers like acrylates, polyesters, vinyl, polyamides etc. were employed to retard excessive dissolution of matrix and exercise some control over the release of the toxicant. This method is currently being used by several formulators with large doses of copper (upto-70%) to serve longer periods in water. The CDP systems still suffer development of thick diffusion barriers from leached layer due to uncontrolled burst release on immediate immersion in water. In addition since the biocide release is not constant throughout the life-time, there is very little activity during idle periods.[1-3, 8, 15, 17, 18, 26, 29, 31, 45, 48]

The improvement in the performance of present biocidal paints is assisted by additional biocides which help complement and bump up the performance of the biocidal paints. These biocides are known as booster biocides because of their action and the key to their activity is their low solubility in water so that they last longer in the paint. These booster biocides are designed to specifically attack a class of fouling species. Some of them like Irgarol, Diuron, and Zinc Pyrithione etc. are very commonly used. Although very effective there prevails question and concern on the environmental impact of these booster biocides. Ideally booster biocides are desired to have rapid degradation rates so that once released in water and after serving the purpose of repelling the fouling species they are decomposed by light or other bacteria etc. so that they do not accumulate in the environment to raise any concerns. This situation is further complicated by the fact that the fate of decomposition of all biocides is not clearly known and there are insufficient analytical techniques currently available to detect and monitor them and their degradation products and ascertain their bioactivity and toxicity to non-target species.[1, 3] All of these uncertainties coupled with the fact that these compounds have not been able to demonstrate promise equivalent to the bench-mark TBT compounds limits their commercial success. In addition with stricter regulations from EPA due to environmental concerns, the cost of registering a new biocide is extremely high about 4 Million U.S. Dollars, thus , limiting the prospects of research and development in this field.[1-3, 5, 6, 8, 10, 12, 26, 38-41, 56]

The toxicity problems and severe restriction by EPA on environmental release of toxicant has channelized research to identify natural metabolites, repellants and toxicants which are completely safe from bioaccumulation or eco-toxicity aspect and are specifically targeted at toxic to fouling forms. The interest in this area was developed from other marine bodies which also suffer from fouling but are capable of liberating their surfaces from it by generating special metabolites which discourage attachment of such species.[3, 5] In this regard enzymes have also been proposed as a viable option. Enzymes which have been already explored for bio-catalysis in a variety of applications were first suggested for use in antifouling coatings in 1983. Enzymes are bio-molecules (proteins) that catalyze (increase the rate of) chemical reactions by lowering the activation energy Ea. They are an important development in the field of non-toxic/natural biocides which are aimed at interfering with the process of attachment or breaking down the adhesive components of the anchoring species and thus inhibiting fouling.

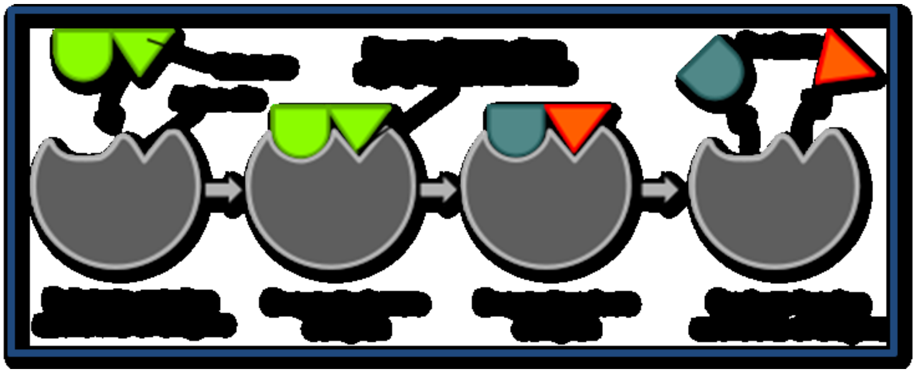


Figure 2.13 Mechanism for enzyme lock and key action

As discussed in section 2.1. all fouling forms in general adopt the process of releasing an EPS which forms as an adhesive bed on the substrate and creates a suitable surface for attachment. This extracellular polymeric substance (EPS) is comprised of lipids, proteins, carbohydrates and fatty acids. Thus depending on their nature enzymes can be effective in deterring settlement or attachment by decomposing the adhesive used for attachment.

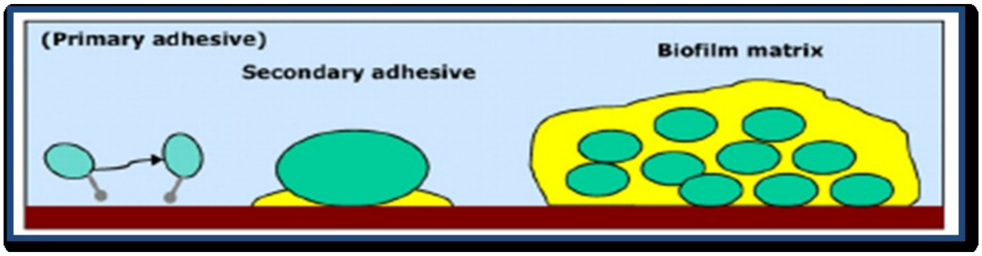


Figure 2.14 Attchment of foulants through EPS adhesive

A combination of enzymes may also be effective in decomposing a biofilm by breaking and hydrolyzing the polymer composing the biofilm. Some enzymes may act like secondary metabolites; these are called biocidal enzymes and their function is to leach out to the surface of the coating due to their different polarity from the rest of the paint matrix and repel species aiming attachment.

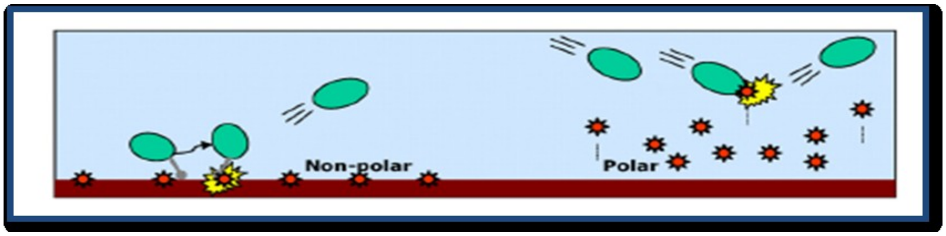


Figure 2.15 repelling action of polar and non-polar metabolites

Although encouraging the key challenges limiting the popularity of the enzymatic approach to antifouling lie in developing coatings such that enzymes retain their activity even in the coating system, are compatible with the other additives,, do not react with the rest of the caoting system and retain their activity in dry paint as well as after immersion in water. The most important challenge is in developing enzymes/combination effective towards a wide range of fouling species for generalised usage.[1, 3, 5]

Apart from enzymes several other natural biocides products which are extraced from plats, herbs etc. have been identified as strong herbicides, algicides and seem to possess bioactivity towards a wide-range of fouling forms. Most of these compounds are only partially effective in preventing and inhibitng biofouling on a small scale like pleasurecrafts and are effective only against a limited number of target species so that the desired control is not achieved. Also, a large scale extraction and development of these products as commercial antifouling coatings is fairly difficult and hence limited.

2.5.2 Non-Toxic-Foul Release Antifouling Coatings

An awareness of the harmful effects of biocides used for antifouling divert the attention to develop non-toxic alternatives as it was realized that the best possible approach in controlling biofouling would be not to rely on the release of toxic biocides to control the problem. Thus keeping in mind the environmental perspective several non-toxic antifouling concepts were conceived but only few attained commercial success. Two winners in this category include the silicone coatings and the PTFE's both of which rely on 'foul-release' or 'non-stick' principle to minimize the attachment of the fouling forms and achieve this by modifying the surface characteristics in creating a very low energy surface which deters adhesion.[1-3, 8, 11, 12, 18, 21, 24, 26, 29, 30, 38, 41, 55, 57]

The non-stick coatings must satisfy the following requirements in order to inhibit attachment:

The polymer matrix should comprise of a linear-backbone to avoid any extra-interactions. Also, the material should be of low-modulus and have additives which can tailor the surface energy to create a smooth surface whose irregularities are ironed out so as to disallow any scope for adhesive interlocking with surface. In addition, the material should possess high flexibility of the molecular chains and should be stable both physically and chemically. Fortunately the silicones and PTFE's both satisfy the above mentioned criteria to a great extent and hence have been explored for non-toxic foul-release coatings.

The concept of fouling control by low adherence was developed in the 19th century but was practiced only after the discovery of the foul-release properties of silicones. These compounds have been in vogue since 1990's after the ban on tin compounds. Silicones such as Poly dimethyl siloxanes (PDMS) are low surface energy compounds which do not completely eliminate attachment of fouling forms but prevent strong adhesion of the latter due to smooth low energy surface so that the hydrodynamic forces of water are sufficient in washing off the attachments. These compounds are soft as compared to current copper-based coatings so that they can be deformed with application of very little force and in the process detach and release the fouling adhesive attachment.[1, 5, 30, 48, 57] The advantage of the silicone coating comes from the high flexibility of the Si-O-Si bond which allows the attainment of a low energy conformation and a very low glass transition temperature (Tg). The coating can also be combined with low molecular weight oils which migrate to the surface to generate enhanced smoothness and increase the deterrence for species attempting to settle on the surface.

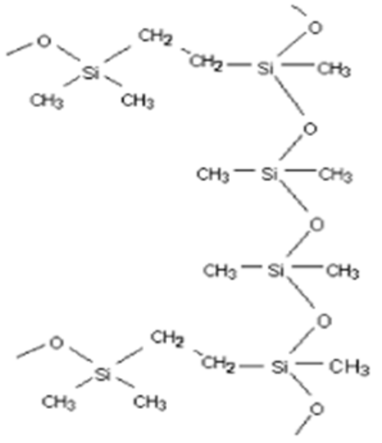


Fig. 13. Molecular structure of a cross linked poly(dimethylsiloxane).

Figure 2.16 Structure of cross-linked poly(dimethylsiloxane)

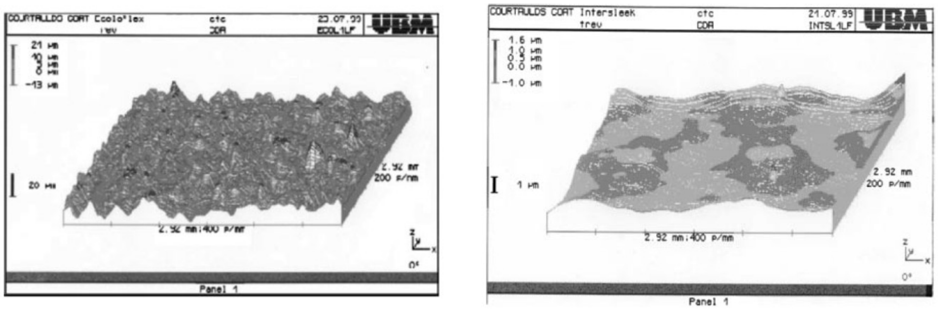


Figure 2.17 Comparison of topography of SPC coatings and silicone coatings

Again in contrast to the SPC-coatings which have a more rugged topography comprising of peaks and troughs as seen in Fig 2.16, the silicone coatings have more rounded and gentle hills with shallow valleys as the surface topography which further reduce friction and interlocking sites. Despite all the attractive aspects, the silicone coatings have a limited market capture because of the very high price, poor mechanical properties, poor substrate adhesion and the longevity of these coatings.[3] Another reason for the limited commercial success of the silicone coatings is that majority of the world's fleets and bulk carriers do not operate at very high speeds and do not allow enough scope for the silicone coatings to deliver their best performance[1-3, 5, 55, 57]

Fluoropolymers like PTFEs are compounds which produce non-porous and non-stick surfaces that are hydrophobic and resist diffusion & or attachment/ fouling adhesion. The C-F is smaller and hence stronger to allow close packing of the perflouro moieties in the polymer chains, forming a close-knit non-porous surface that is hydrophobic and very low surface energy. This low surface energy doesn't favor formation of biofilm or spread of EPS and attachment of marine organisms. The benefits from the strong C-F bond create problems too. The short length C-F bond increases the stiffness and modulus. Hence if there is any attachment onto the surface, the force required to break the adhesive attachment is also very large and is not possible to break the substrate-adhesive bond without damaging the coating. Thus once fouled there is very little that can be done to recover the Fluoropolymer coated surfaces and huge investments are required.

Attempts are being made to combine the properties of fluoro-compounds and silicones by developing fluoro substituted silicones. As technology evolves, it is likely that products capable of operating at both low and high speeds will be developed.[1, 3]

2.5.3 Alternative technologies for antifouling

Based on the level of toxicity of variety of different compounds and different concepts were used to prevent and inhibit biofouling. The most widely practiced of these ideas include applying alternating current on surface to repel and kill attaching species. This technique consumes a lot of energy and other resources and may be difficult to set up on large systems. Also voltage drop across surfaces of large system could generate corrosion damage and coating damage.[2, 3, 5, 12, 25, 27, 28, 34, 40, 55, 58-60]

A lot of pipe-systems for cooling water supply and other pipe linings rely on passing chlorine through the water to prevent fouling of the pipe linings. These are very effective but generate health hazards owing to the acute toxicity of chlorine and also problems of local concentration gradients, corrosion, localized pollution etc. To avoid these problems, electronically generated ozone bubbles, copper ions, peroxides, Pt-complexes etc. have also been explored. Conductive coatings like Polyaniline have also been reported to possess weak but synergistic antifouling performance by virtue of their conductivity. [3]

Another set of ideas for antifouling include radioactive coatings (e.g. those containing Thallium compounds), piezoelectric coatings, and application of external vibrations, glass-flake coatings have also been attempted with some success and are deserve mention. Most of these techniques are limited to practice on a very small scale to limited marine organisms so that uncertainties about real scenario performance exist. The greatest drawback to most of these concepts is that the set-up and application requirement of these are very expensive and they outweigh the benefits obtained.

While efforts continue to be made in the development of coatings suitable under all environments, application conditions, surfaces and organisms the copper based systems continue to dominate the market and can be foreseen to do so till superior non-toxic replacements surge the market.[3]

2.6 Shortcomings of current technologies-need for immediate replacement

The current IMO & EPA regulations in use of antifouling paints worldwide include the following:

- All antifouling compounds need registration prior to use.
- Organo-tin compounds have been banned all over from use
- Specific procedures and guidelines have been defined to the use of toxic compounds both for manufacturing to applying.
- Scientific and technical research for non-toxic alternatives is being promoted
- The use of volatile organic compounds has been limited.

Despite resistance from the ship-owners and environmentalists on the viability of the available substitutes, the ban has been implemented. This overall legislation seems to have had a positive impact as the TBT levels in water, shellfish and sediments has dropped as compared to prior assessment values. The alternatives for organo-tin compounds as discussed in section 2.5 biocide based or biocide free have been able to offer some benefits but are unable to surpass the performance of the TBT-SPC systems due to several drawbacks as discussed above. The present day scenario is such that non-tin alternatives have been able to support the antifouling industry but only at the cost of being more expensive, low in life-span and durability and unable to deliver the same satisfactory antifouling performance. To aggravate the situation, the time periods required for scientific research to come-up with a material capable of performing under stagnant and dynamic conditions using natural materials providing comparable performance as the tin compounds is too long and time consuming. The need for proper understanding of the working mechanisms of the products, screening of compound based on laboratory studies, industrial and academic collaboration, infrastructure requirements, expensive and time-consuming environmental assessments, government registration and the availability of cheaper toxic substitutes slow down the infiltration of newer non-toxic alternatives in the market.[1-3, 14, 26, 38-40]

Copper is the biocide of choice for present day antifouling paints, but according to many sources it is also a source of additional copper loading into the marine environment.[3, 28, 38, 41, 44, 53]Copper based systems continue to reign the market till the environmental pressure prohibits use of toxic compounds. The popular usage of copper after the ban of tin compounds is owing to the fact that it is one of the oldest explored biocide for over 200 years that is toxic in most forms and treats a wide range of fouling species. The antifouling efficiency of copper is high due to the intrinsic toxicity of its ions and its solubility of its corrosion products in sea-water.[1-3, 11, 28, 38, 44] Another advantage of using copper is that it is a naturally occurring element with typical concentrations of about 0.03-0.23 ug/L in sea-water and 0.2-30ug/L for freshwater. In its natural form it serves as a trace element essential for uptake and nutrition for plants and animals. Also copper compounds like cuprous oxide are easily available commercial and can be synthesized in the form of very fine powder (particle size <5micron), so that they can be easily dispersed into paints and easily applied by spraying, brushing etc. Apart from the ease in handling copper similar to organo-tin compounds provides the flexibility of combining other co-biocides or booster biocides as discussed in section 2.5 which broadens the target range of fouling species. In this manner copper compounds can be used to offer wide-range long-term antifouling activity in most environments and at a lower price compared to some of the expensive non-toxic technologies like silicone coatings, PTFE's, enzymes based afps. etc.

Of the two ionic forms of copper Cu+ and Cu 2+, the latter is more toxic and the toxicity of copper is accountable to the bioavailability of the cupric ions. Most quality assessments acknowledge the fact that of the numerous reasons for adding copper to marine systems antifouling paints contribute only a small amount and they aren't the potential source. The Toxic release Inventory for copper in 2001 estimated that about 211022 kg of copper and its compounds constitute the surface water discharges, but most of these inputs are not from antifouling paints. Some studies also confirm that a lot of copper accumulation is brought about by the irresponsible use of copper while manufacturing and applying antifouling paints. Several studies recommend that a reduction in the harmful ecological impact of copper can be achieved without compromising the interests of the boat and marina owners by promoting marina education to encourage sensible use of copper compounds and also by incorporating changes in the afps used. While economic, efficient non-toxic alternatives that address all issues and concerns with marine biofouling and antifouling seem far away in time; the use of copper compounds seems inevitable. However continued research and development of reduced copper based antifouling paints can contribute to reducing the copper loading in the environment and prevent TBT-type of binding regulations.

CHAPTER 3

APPROACH

3.1 Leach Rate Control for Antifouling Paints

Antifouling Paint's have a long history behind their development involving tremendous technological progress and research.[1-4, 14, 21, 26, 28, 29] Although the list of accomplishments in the field of antifouling is significant, the EPA regulations are being tightened in response to the environmental hazards and inefficiencies of the current antifouling technology as discussed in Chapter 2. An understanding of the formulation process and reasoning behind present antifouling paints can project a clearer picture of this grave problem. The current paints are formulated with increasingly higher percentages of biocides to provide better protection for longer periods of time.[1-4, 11, 14, 18, 26, 38, 42, 44, 48, 53] This practice partially addresses the problem and instead promotes uncontrolled burst release of biocides resulting in increased concentrations at locations such as harbors and estuaries.[1-3, 26, 41, 42] To aggravate the situation; the burst release of biocides results in rapid development of diffusion barriers and a drop in antifouling efficiency until a fresh surface is regenerated to renew release of fresh supplies of biocides for antifouling. Thus based on the above discussion, paints should be formulated to promote sustained release of biocides and limit burst release upon the immersion of a new painted surface in water. [1-3, 15, 18, 29, 31, 42, 44, 45, 53]

3.2 Materials for Controlled Release

The selection of materials for this research was governed by the current need of finding suitable additives which help in preventing burst release and at the same time encourage nascent surface generation by paint matrix degradation. After careful study of literature[1-4, 8, 12, 14, 24, 26, 28, 37, 38, 42, 44, 45, 52], and a comprehensive understanding of properties requirements for additives in an antifouling formulation; like high viscosity for binding, water solubility for controlled release, low modulus for fouling detachment, resistance to corrosion and compatibility with other additives and conditions of operation(e.g. Different temperature zones, salinity levels, pH levels, structure and application of substrate to be coated, kind of species that populate the area etc.), the following materials were shortlisted for formulation of antifouling paints for this research:

Viscoplex 6-954: This is a product of Rohmax Oil Additives. It is a multifunctional dispersant popular as a viscosity index improver for both gasoline and diesel engine oils.[61] It’s a pale yellow to amber colored slightly hazy liquid which has an excellent combination of low and high temperature viscometric properties. Viscoplex is comprised of a solution of polyalkyl methacrylate (PAMA) in refined mineral oil.

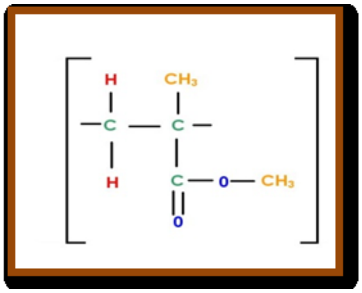


Figure 3.1 Structure of PMMA

The plausible benefits of adopting PAMA as an additive in paint chemistry for antifouling lay hidden in its viscoelastic properties. The molecular weight of PAMA added to the paint recipe can be controlled as a wide range of Viscoplex series is commercially available with varying density and viscosity to suit all application needs. The composition of PAMA in mineral oil appears to be encouraging in terms of achieving good compatibility with an antifouling paint formulation which is frequently epoxy or acrylic in nature.

Table: 3.1 Properties of Viscoplex

Typical Physical Properties of Viscoplex 6-954	
Visual Appearance	Clear to slightly hazy, pale yellow to amber
Color (ASTM D1500)	3
Viscosity at 100C,mm^2/s (ASTM D445)	1250
Flash Point, C (ASTM D 3278)	0.90
Shear Stability Index(P-SSI), ASTM (D 6278)	170
Density at 15C,g/cm3 (ASTM D 4052)	45

It is known that polymers follow the general rule of "like mixes easily with like".[62-64]Being polymers with similar polarities (owing to their hydrocarbon backbone) and in addition having the presence of carboxylic acid groups (-COOH) and epoxy ring moieties there is easy blending even at room temperatures[62-64] .Additionally it follows from the viscosity vs. temperature relationship as well as density vs. temperature relationship that the additive possesses very high viscosity and density at room temperatures or for that matter at operation temperatures of marine paints in sea/ocean/fresh water bodies.[sea temp ref from past, anti, others]. Hence under such working conditions, it is reasonable to expect that Viscoplex shall due to its high viscosity aid in binding the components of the paint chemistry and prevent them from diffusing out due to the turbulent/corrosive/erosive attack of water. In other words, a reduction in the burst release rate of copper/cuprous oxide biocide (fine powder) from paint and a consequential increase in the performance and durability of the same antifouling coating can be expected. In addition to these, the hydrocarbon (hydrophobic) nature of mineral oil could be capable of enhancing the hydrophobocity of the paint formulation itself[62-65]. This could act as an supplementary aid in improving the corrosion resistance and also the life-span of the coating; since diffusion of water in paint pores is known to be primarily responsible for causing corrosion (electrolyte) as well as leaching out additives and other hydrolysable/soluble components (causing advanced degradation) of the paint film[2, 3, 31, 42, 48]. Thus based on review of the above mentioned properties, Viscoplex was selected for formulating antifouling paints in this research.

- Cupric dialkyl dithiophosphate (CuDDP): The structure for CuDDP can be seen below. CuDDP is a long chain copper complex obtained by the reaction of copper compound with phosphorus pentasulfide and a long chain alcohol. The length of the alkyl chain desired on the complex can be controlled by the alcohol used in the synthesis. These compounds have been explored as antioxidant and antiwear additives in engine oils.

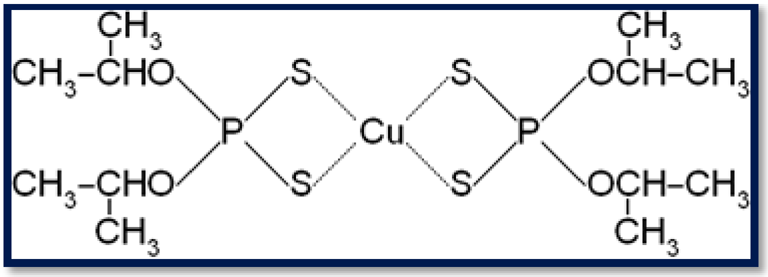


Figure 3.2 Structure of CuDDP

Two important properties to be considered when formulating antifouling paints for this study were controlled leaching of copper and corrosion resistance of the paint. The reason for selecting CuDDP for this study come from the above mentioned properties required for antifouling. CuDDP is a copper complex which is bulky in size and has a larger molecular weight than small copper compounds like cuprous oxide or chloride. It is known that the release of copper biocide from paints is by diffusion of sea-water. Hence if a larger molecule like CuDDP is used as an antifoulants it might be slower in terms of diffusing out from paint (since larger molecules require ,larger time for diffusion). Thus in this manner it may be possible to control the release rate of copper and reduce the burst release. In addition the presence of phosphorus in the complex might be able to introduce some anticorrosive properties in the paint retarding the corrosion of the coatings in water. Also the hydrocarbon chains on the phosphate groups would be helpful in achieving compatibility with the paint which also has a hydrocarbon backbone. The key challenge here would be to explore whether Cu and P would be retaining their antifouling and anticorrosive properties in the complex form.

- Ionic Polymer- Externally doped Sulfonated Polyaniline (ED-SPAN): the use of an ionic polymer is fairly unique to antifouling application. The rationale behind using ED-SPAN as an additive for controlling the leach rate of copper biocide from antifouling paints arrives from the high water solubility of Sulfonated Polyaniline in water. As result of its water solubility a formulation containing ED-SPAN when immersed in water would dissolve the same throughout the surface creating pores which could act as pathways for copper release. Details of the plausible benefits of using ionomer ED-SPAN for antifouling have been discussed in chapter 5.

3.3 Antifouling Properties Experimentation Criteria

After the selection of additives for antifouling formulations, the next step required design of appropriate experiments for evaluating the influence of the above additives on the paint chemistry and discriminating their effect in controlling copper leach rate and generating sufficient antifouling efficiency even at relatively low rates of loading.[66, 67]

Two crucial parts of this research can be identified as follows:

1. Determining the ability of an additive/combination of additives in controlling copper leaching in simulated marine conditions of the laboratory as well as in actual marine environment. However, along with leach rate study; fouling resistance studies must be

performed and correlated to the leach rate study results in order to get a complete picture of the paint formulation capabilities.

It has recently been shown that chemical reactions and diffusion phenomena are key mechanisms dictating the performance of biocide-based A/F paints, and that these can be markedly affected by sea water conditions.[1-3, 5, 15, 18, 24, 42] The current antifouling paints are based on the ability of sea-water to penetrate the paint matrix, build-up of diffusion channels and hence generation of pathways for the biocides to be delivered to the surface for antifouling activity.[1-3, 15, 17, 18, 26, 28, 29, 31, 42, 44, 45, 60] In this case, the build-up of diffusion barriers which block biocide release pathways and hence decrease their release rates is a crucial phenomenon and is directly influenced and controlled by the sea-conditions of salinity, pH, temperature, velocity, geographical location and dynamic environment.[1, 3, 48] Unlike the laboratory experiments where all release rates calculations are performed on a certain controlled volume of simulated sea/ocean water; the actual environment is more dynamic, augmenting the setting-up of localized concentration gradients of released biocide in a large volume of the water body. Unfortunately in simulated conditions, in spite of maintaining an air-flow, the lack of replacement of biocide rich water with biocide scarce sea-water results in rapid arrival of a steady state of biocide concentration in water, thus affecting accuracy of data generated.

It may be best to make a case that laboratory experiments are much more effective for screening purposes and to develop a mechanistic understanding of the process of leaching and once that is developed we can always conduct marine experiments. It is also critical to eventually compare the performance of the formulated paint with other similar paints, and on the type of the vessel and under conditions under which it is designed to operate.

2. Calculating the fouling resistance of the additive/combination of additives under laboratory conditions.

Biological test which examines the fouling resistance of the paint formulations can be considered as one of the oldest yet most popular and frequently used testing method for antifouling. This test generates two types of information which help predict the potentiality and viability of the paint formulation as antifouling; first it helps to configure the ability of the paint to prevent fouling and second it highlights the physical performance of the paint-film /system when exposed to natural conditions.

This research is based on designing experiments with all formulations under laboratory conditions (simulating the marine environment). The time-period required for experimentation in ocean water with antifouling paints as well as the infrastructure requirements for such experimentation, restricted this research so as to focus on biocide leach rate determination as the governing factor in predicting suitable and competent antifouling behavior and generating optimized antifouling chemistry.

3.4 Formulation of Antifouling Paints

Antifouling paints are known to be comprised of a toxic material dispersed in a polymeric carrier for application on surfaces under constant corrosive attack from the water bodies. These paints are formulated with different base resins like epoxy, acrylic, urethane, siloxanes, PTFE etc. which are blended with toxic biocides varying in concentration from 30-80%.[1-3, 38, 41, 42] The formulation of antifouling paints is very crucial for achieving good control over leach rates of biocides. The purpose of this study is to formulate antifouling paints that are effective in generating sustained release of toxicant at lower concentrations of the toxicant to reduce environmental risks and hazards resulting from the use of such paints

The schematic diagram shown in Figure 3.1 shows the experimental approach used in this study.

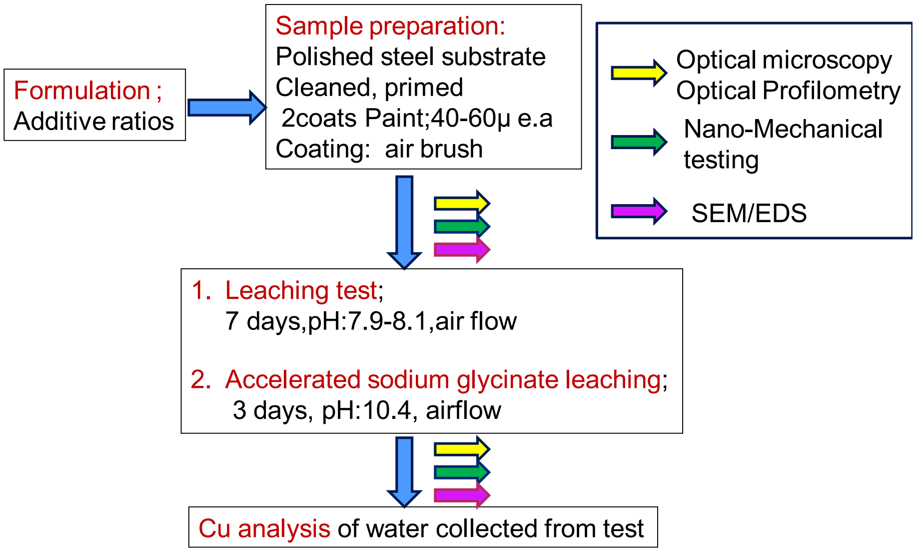


Figure 3.3 Experimental Approach for this study

3.5 Achieving an optimized composition for antifouling

The paints were formulated with the chosen additives individually or in combination and were subjected to a series of tests to evaluate performance and short list candidate for further analysis. The preliminary analysis was dictated by results of the following experiments:

- Paint Synthesis and application was a very crucial point with regard to preliminary elimination of inappropriate candidates. An additive which cannot be easily blended into the paint chemistry or which demonstrates poor compatibility with the complex components of the paint body had to be discarded at the very beginning. Factors such as reactions with the paint chemistry, excessive solvent (VOC) /other special condition requirements for formulation, ease of applicability and effect on the dried paint-film texture, morphology (including surface features, texture, topography etc.), mechanical properties such as hardness and reduced elastic modulus (which could have a bearing into the final application) were taken into consideration at each stage of experimentation.

- Cuprous oxide leach rate study was conducted both for preliminary elimination as well as optimized blend preparation. A modified ASTM Standard D 6442-06 [68]was used to examine leach rates keeping in mind the limited time-period and resources available for study. The formulations which under-performed in the leaching study in terms of being unsuccessful in generating an adequate leach rate for antifouling or failing the durational requirements were discarded as failures.
- Characterization Techniques were an important means of discriminating the performance of different coatings and accordingly justifying the choice of additives. To complement the leach study analysis, techniques capable of scrutinizing and characterizing changes in paint morphology (as discussed above), mechanical properties like hardness and reduced elastic modulus, composition, topography, corrosion resistance etc. before and after exposure to severe marine conditions (capable of promoting and accelerating biofouling and corrosion) were carefully selected and designed, this included ICP-chemical analysis for Cu leach rate determination (done from an external source), SEM-EDS, Nano Indentation, Optical Microscopy, Optical Profilometry, FTIR, UV-VIS Spectroscopy and Polarization Studies details of which are provided in the experimental procedure section.
- Optimizing performance of the promising formulations was the last step based on the results of all prior experimentation and characterization. Additives demonstrating extraordinary performance alone or in conjunction with other additives require further optimization. It is essential to ascertain the threshold concentration for additives in a formulation, compatibility, surface-application and performance. Combining additives which retarded biocide release with those that regenerated release, is extremely challenging and involves extensive formulation of

different combination ratios based on all the prior mentioned criteria for formulation, characterization and experimentation.

Finally after evaluating the additives based on the above mentioned experimental/elimination steps, a formulation comprising of an optimized ratio of (leach rate retarding & accelerating) additives, also capable of generating a constant-controlled biocide release and at the same time which passed the criteria for commercial viability would be considered as a successful antifouling paint – and a test candidate for evaluation in an actual marine environment.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Materials for Antifouling

A detailed and comprehensive study of the literature on current and past developments involving antifouling, related mechanisms, limitations and commercial interests help procure ideas for material selection for this research.[1-5, 8, 9, 11, 14, 21, 22, 26, 31, 35, 41, 45, 48, 57] The hypothesis as described in Chapter3 (section3.2) requires the use of two kinds of additives for this study; those which bind the paint matrix components preventing rapid burst release of toxicant and those which assist the restoration of biocide release by regenerating newer surfaces for diffusion. The following materials were selected for formulating paints for antifouling:

1. Viscoplex 6-954
2. Cupric Dialkyl Dithiophophate (CuDDP)
3. Ionomer-ED-SPAN

The reasons behind the choice of the above additives for controlling the release rate of copper from the antifouling paints have been described in section 3.2 of chapter three.

4.2 Formulation

The toxic pigment for biofouling control chosen in this study is cuprous oxide. The reasons for selecting cuprous oxide have been discussed in chapter 2 in section 2.6. Following the ban on the use of tin or any organotin compounds for antifouling, a plethora of alternatives have flooded the market; the most popular and successful toxicant of choice being copper more particularly its oxide i.e. cuprous oxide. The commercial products available presently in the market reveal that the present day usage of copper/cuprous oxide in antifouling paints ranges from about 30-70% by weight.[1-3, 15, 26, 28, 41, 42] As discussed earlier, the ideology behind such high proportions of toxicant being to let the paint survive longer. This lies in the inherent necessity of the toxicant to be dissolved and depleted slowly in water in order to be effective.[1-3, 15, 17, 42, 48, 67] Also the present paint technologies have insufficient control over the rate at which the toxicant is leached out of the coated object. Hence in order to compensate for the unavoidable need to allow erosion of the paint and its active ingredients for antifouling; the current manufacturers rely on loading paints with higher proportions of toxicant, to start with in order to to serve longer periods of time.[15, 38, 42, 48]

The present study is oriented at overcoming the above mentioned inherent drawback of formulating the antifouling paint inefficiently, with absolutely no control on performance. The manner in which this can be achieved is to utilize additives/ingredients in the paint recipe which exercise control over the performance of the critical/active components in the system. In this way the ideal situation would be to arrive at a formulation which offers protection without consuming the coating. The additional benefits of using such ingredients would not only be achieving control over performance but to achieve longer life-spans of coating life while consuming smaller fractions of active ingredients and appeasing environmental concerns to some extent.[2, 42, 48]

The formulations were prepared using the following concentrations:

- A commercially popular antifouling paint was chosen for establishing a baseline comparison. This paint belongs to a common brand called Interlux (Akzonobel Paints). The product is called *Interlux Fibreglass Bottomkote-part code INT-0669BQ.* This is a modified epoxy one-part paint which is loaded with 42.75% cuprous oxide as the active ingredient. The paint is blue and gives a matte opaque appearance based on its fast drying effect. The paint also contains o, m, p-xylene isomers and about 1-10% Rosin which helps paint matrix disintegration upon time to overcome diffusion barriers and renew blocked pores on paint surfaces. The product is suitable for application on steel, wood and even fiberglass. This product was selected to compare the performance of the paints formulated in this research.[47]

- In-order to formulate paints for antifouling, a paint devoid of any antifouling agent viz. a toxicant but comprising of other ingredients necessary and suitable for under-water applications (eg. solvents, pigments, abrasion resistant additives etc.) and most importantly comprising of a similar hydrocarbon backbone as the commercial baseline material i.e. Epoxy had to be selected. After careful review of the commercial products available; the paint selected was *Amercoat 238* from Ameron International.[69] This product is comprised of hard epoxy resin and reinforcing minerals so that it is designed to protect surfaces exposed to severe abrasive and wear conditions like those encountered in heavy-duty marine under water operations. It is a two-part system, so that an amine based hardening converter Amercoat 238 converter needs to be used in a fixed ratio of 4:1.The product is recommended for application on under-water hulls, working decks, cargo loading areas etc. It is suitable for application on steel, concrete, masonry, aluminum etc. and is compatible with antifouling paints. Based on properties and application requirements, this product appeared to suit the criteria for base paint and was selected as the base paint for all formulations involved in this study.[69]
- One of the purposes of this research was to derive improved performance from paint by exploiting all benefits achievable from additives so as to formulate paints with lower concentration of toxicant but with no compromise on efficacy.[2, 15, 28, 42, 48]The use of such additives should allow formulating paints with a reduced concentration of *cuprous oxide* while addressing all functional needs. This would be extremely critical in order to alleviate the marine environmental concerns of toxicant bio-accumulation and overcome the crisis/in-competencies in producing effective non-toxic technologies for

antifouling.[3, 42] After conducting some preliminary experiments with regard to preparing a formulation, applying it and performing leaching studies; the cuprous oxide concentration in all formulations was selected to be 30% by weight. The reason behind this selection being, preliminary results supporting the fact that 20% loading rate was insufficient for antifouling. This coupled with that reduction from 43% Cu_2O to 30% Cu_2O would serve as a substantial reduction in expenses involving the overall usage of cuprous oxide for antifouling and also a significant reduction in the release and accumulation of cuprous oxide in water.

- The loading concentration for *Viscoplex* in paint was selected to be 5% by weight. This was decided after conducting similar preliminary study as mentioned above. Formulations were prepared using 5%, 10%, and 15% of Viscoplex in the paint recipe. The formulation with 15% concentration had issues with drying due to high viscosity of Viscoplex. The one with 10% concentration although dried performed as too strong a binding additive, reducing leaching rate of cuprous oxide drastically. Thus 5% was selected as the concentration in paint formulations for the leaching/corrosion study and was further optimized in the second part of the study (as discussed in chapter 6).
- *CuDDP* is solid in nature and it required dissolution in hexane before blending with paint. Keeping in mind the miscibility requirement of the additive with the rest of the paint recipe and at the same time avoiding use of excessive VOC in form of solvent; the loading concentration for Cu-DDP was selected to be 5% by weight for the first part of this study.
- *ED-SPAN (Externally doped Sulfonated Polyaniline)* concentration in paint can be very critical and was dictated by several factors. The additive is a low density light but coarse granular (small agglomerates) material. Hence, small weight additions cumulate to a large proportion/volume of additive; generating issues with blending the formulation. The details of these formulation and application issues correlating to

additive concentration are discussed in the following section [section 4.3.1]. The role of this additive can turn out to be crucial in controlling the leach-rate of cuprous oxide by regenerating blocked diffusion pores on paint surface and also protecting the surface against corrosion.[15, 31, 42, 48, 65, 70] Based on the above mentioned criteria, the concentration of ED-SPAN was selected to be 15% by weight of the formulation for the leaching study and was further optimized in the second part of this study. [Discussed in chapter 6].

As discussed in Chapter 3, this study has been divided into two parts;

1. The first part of the study involving a leach and corrosion study through a series of experiments for preliminary elimination of those additives which demonstrate poor performance and produce an overall low expectancy in terms of providing antifouling and or corrosion protection of marine systems.
2. The second part of the study involving optimization of the overall paint formulation with control on the additive concentrations to produce a constant leach rate of copper at a desired value.

The series of antifouling chemistries designed for the first part of this research have been listed in the following table.

Table 4.1 Formulations for Part I of the Study

Formulation	Composition/ Chemistry	Type	Group
Sample 1 (IRCUFIB)	42.75 % wt. Cu_2O (Interlux Fiberglass Bottomkote)	Commercial Baseline	Group 1
Sample 2 AM42CU	42.75 % wt. Cu_2O in Base Paint	Internal Baseline	
Sample 3 AM30CU	30.0% wt. Cu_2O in Base Paint	Control	

Table 4.1 - *Continued*

Sample 4 AM30CU5DDP	30.0 % wt. Cu_2O + 5 % wt. CuDDP in Base Paint	Additive	Group 2
Sample 5 AM30CU5VIS	30.0 % wt. Cu_2O + 5% wt. Viscoplex in Base Paint	Additive	
Sample 6 AM30CU15IO T	30.0% wt. Cu_2O +15 % wt. ED-SPAN in Base Paint Top coat	Additive	Group 3
Sample 7 AM30CU15IO B	30.0% wt. Cu_2O +15 % wt. ED-SPAN in Base Paint Blend	Additive	
Sample 8 AM30CU5DDPVIS15IO B	30.0% wt. Cuprous oxide + 5 % wt. CuDDP + 5% wt. Viscoplex + 15 % wt. ED-SPAN in Base Paint Top Blend coat	Additive	

The properties of externally doped Sulfonated polyaniline (ED-SPAN) are discussed in details in Chapter 5. An important characteristic and reason for selecting the ED-SPAN for this study is the water solubility of the Ionomer. Varying concentrations of Ionomer distributed in paint along with other additives and copper oxide, can by dissolving in water generate pores in the paint film and aid disintegrating the paint film, overcoming the diffusion barriers and renewing the dwindled leach rate of copper by generating a nascent surface. Another line of thought is that if applied as a separate coat with no copper additive but just Ionomer in paint as the top most coat; and having an underlying coat of paint containing copper oxide additive, it would be likely that the Ionomer from the top coat would create pores on the surface by its dissolution on immersion in water. These pores would in turn create pathways for controlled release of copper from the underlying coat. The release rate would be dependent on the amount of Ionomer dissolution and matrix degradation and hence would be highly controlled. In both cases, the Ionomer concentration could be easily adjusted to adjust the matrix dissolution and hence set-up a desired leach rate of copper in water. Hence based on these two lines of thought; two set of samples for the optimization study had to be prepared; a Blend series where all additives would be blended in paint and a Top Coat series where the layers containing copper oxide and Ionomer /other additives were separated. The schematics for the formulations for optimization study are given below.

Figure 4.1 Schematic for samples with all additives in a blend Part-I and Blend Series

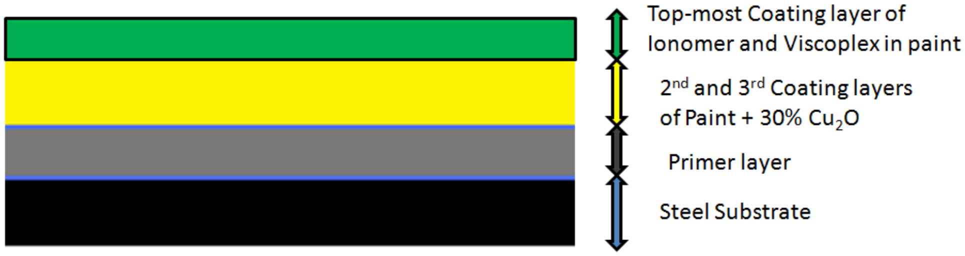


Figure 4.2 Schematic for Top Coat Series with separated additive layers

The series of antifouling chemistries designed for the second part of this study have been listed in the following table.

Table 4.2 Formulations for Part II of the Study-Blend Series

Formulation	Composition/ Chemistry	Group
Sample 1B	30.0% wt. Cu_2O +15 % wt. ED-SPAN+ 5% wt. Viscoplex blended in base paint	Group 1 Blend Series
Sample 2B	30.0% wt. Cu_2O +15 % wt. ED-SPAN+2% wt. Viscoplex blended in base paint	
Sample 3B	30.0% wt. Cu_2O +10 % wt. ED-SPAN+ 5% wt. Viscoplex blended in base paint	
Sample 4B	30.0% wt. Cu_2O +10 % wt. ED-SPAN+ 2% wt. Viscoplex blended in base paint	
Sample 5B	30.0% wt. Cu_2O +12.5 % wt. ED-SPAN+ 3. 5% wt. Viscoplex blended in base paint	

Table 4.3 Formulations for Part II of the Study-Top Coat Series

Formulation	Composition/ Chemistry	Group
Sample 1T	15 % wt. ED-SPAN+ 5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cu_2O in base paint as undercoat	Group 2 Top Coat Series
Sample 2T	15 % wt. ED-SPAN+ 2% wt. Viscoplex in base paint as Top coat 30.0% wt. Cu_2O in base paint as undercoat	

Table 4.3 - *Continued*

Sample 3T	10 % wt. ED-SPAN+ 5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cu_2O in base paint as undercoat	
Sample 4T	10 % wt. ED-SPAN+ 2% wt. Viscoplex in base paint as Top coat 30.0% wt. Cu_2O in base paint as undercoat	
Sample 5T	12.5 % wt. ED-SPAN+ 3.5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cu_2O in base paint as undercoat	

4.3 Formulation Conditions &Coating technique

The coating technique for any application bears a huge impact on the performance of the coating and its success/failure history.[1, 67] Depending on the application, the coating thickness requirements, the surface finish, the area/volume to be coated, the allowable VOC content, drying condition requirements, batch preparation and ease of application the coating technique must be cautiously selected. The parameters considered for this research were implemented after extensive experimental trials so as to arrive at the most suitable formulation and coating approach. The issues addressed in the development of an appropriate coating technique included the following:

4.3.1 Formulation and Processing Issues

1. *Influence of Nature/Physical state/ Blending capacity of additives*

    - The toxic pigment for biofouling control chosen in this study is cuprous oxide. Cuprous oxide is a fine powder (less than 5 um particle size for this study). Since it was blended at a concentration of 30 wt. % in the paint formulations, extensive homogenization of the paint mix was required. Also to avoid thickening of the recipe, paint thinner (Interlux 216) which is a mixture of o, m, p-xylenes and is well compatible with the solvent-based paints was used.
    - Viscoplex although used in a small proportion of 5% required careful mixing to ensure a homogenous composition and uniform distribution to coat all particulates.
    - CuDDP was also used in small concentrations but needed some crushing (particle size reduction), prior to mixing with paint recipe due to its solid structure. In order to facilitate easy mixing the CuDDP for the recipe was first dissolved in minimum volume of hexane and then the solution was immediately added to the paint and homogenized by hand stirring. Care was taken to immediately mix the dissolved CuDDP into the recipe, due to very high volatility of hexane and solidification tendency of CuDDP.
    - The Ionomer ED-SPAN was the most challenging additive in terms of blending and coating. The additive was an amorphous material in the form of semi-rigid agglomerates of very large particle size (several hundred microns) of low density. Hence the % weight additions required a huge quantity of the material. The paint volume was relatively small to harbor such high percentage of solids. Hence in order to create dispersion a suitable quantity of thinner was necessary (while remembering to not exceed the VOC limits or alter the recipe weight fractions by excessive dilution).

Thus the choice of a coating technique had to be such as to accommodate and allow homogeneous and continuous application of the coating in a conformal manner and minimize any pin holes and discontinuities and minimize possibilities of pitting corrosion. The significance of adopting a proper coating technique as well coating procedure can be well understood from the literature and referenced from the ASTM D6442-06[68] prescribed procedures.

2. *Issues with Small scale of production*
    - The present research involved experimentation within laboratory set-up. Hence the painted sample sizes were small to accommodate them into a relatively smaller volume of simulated sea-water. The over-all paint consumption for such small samples is very small.
    - Some of the additives (ionomer) used in this research required chemical synthesis in the laboratory. Due to limitations on the availability of raw-materials and to avoid unnecessary wastage of raw materials/additives/ solvents etc. the batch preparation was restricted to small quantities of 20-50gm approximately for each coat.
    - The small-batches of paint–mix required accuracy in additive concentration to avoid magnification of errors. The coating technique had to be consistent. Several techniques had to be eliminated owing to not being able to satisfy the above conditions. The discrimination between the coating techniques can be better understood from the following section.

4.3.2 Coating Application Problems

Over the years a large number of coating techniques have been developed to suit all kinds of application needs. Each technique has a characteristic of its own which may be good or bad for various applications. For example, very thick coatings are easy to apply but consume a lot of resin and provide poor adhesion; similarly thin coatings provide strong adhesion but often lack in offering sufficient protection and need several layers. At each stage of its advancement, coating technology has been able to answer some needs if not all. In this study several popular coating techniques were attempted and based on difficulties encountered, the most feasible technique was opted. The following techniques were tried to attain uniform coatings:[1, 67]

i. Brush Coating: This is one of the simplest coating techniques which is not only simple but also economic and time efficient. This technique was attempted with a trial of large variety of brushes ranging from; camel hair brush which is very soft with fine bristles to synthetic nylon brushes with fine but harder bristles. This technique could not be adopted for coating all experimental samples because, the finished samples had a rough & uneven texture with bristle marks on the surface and also the method lead to high variations in coating thickness. The coating thickness is very critical for this study and the coating method needs to generate a uniform surface upon drying. Despite all adjustments on thinners, paint consistency and brushes; the brush coat method failed to provide desired level of uniformity for small sized samples used in this research.

ii. Dip Coating: is a very useful tool in achieving smooth surface finish and good aesthetic quality coatings. As the name suggests, the method relies on dipping (and then taking out and drying) or holding a sample immersed in a large bath of paint/coating for a pre-calculated length of time (usually 24 hours or more, followed by drying). In this case the solvent/thinner requirements were critical with regard to coating consistency, coating thickness, immersion and drying time. Although very attractive for smooth surfaces, this technique had to be rejected for this research because it required large volume (bath) of coating /paint material which in this case wasn’t possible to prepare due to such a large number of experimental formulations. It also leads to huge wastage of raw materials and solvents and more critically suffers from the inherent drawback of producing samples thinner at the centre and thicker at the edges due to viscous flow of paints.

iii. Rollers: are extensively used for uniform thin coatings on a variety of surfaces. However this application applied a very narrow criterion for choice of applying aids. The samples used for all experimentation were limited to the small size of 2” x 2”. Rollers capable of painting such small samples are difficult to attain. Attempts were made to use foam and fiber rollers left fine fibers and or fiber prints on the surface while the foam roller did not wet enough to absorb paint and coat the surface well.

iv. Cast Film Method: is a common method used for both small and large sized samples. The method generates relatively thick films due to the absence of any draw-down on the coating. This method was practiced for some samples and was found to work fairly well with short sampling time. The method led to defects in coatings due to improper spreading and also suffered from large variations in thickness with no control on the viscous flow of paint. Due to these imperfections the cast-film technique was not considered a reasonable choice for formulations pertaining to this research.

v. Spin Coating: is the popular choice for achieving very thin and uniform defect-free coatings. The technique itself requires several adjustments of critical parameters like velocity of spin, sample weight, paint/coating consistency and spin time; which controls the final coating output. This is one of the fastest techniques for great quality coatings for a wide range of sample size. It also leaves the flexibility of controlling the coating thickness by adjusting the spin-time or the coating consistency. The spin approach for coating samples for this research was explored and several limitations were realized. The technique is very sensitive to time-temperature, spin-rate and consistency. It would be very challenging to adjust all the above, mentioned parameters constant for all the differing formulations based on their solid/particulate matters content. Also any adjustments in the formulation to comply with the coating condition requirements would leave the formulations incomparable. The greatest difficulty encountered was to achieve uniform coatings to cover all surfaces and sides of 2” x 2” steel samples used in this study. The instrument available was capable of coating only one surface at a time so that any attempt to coat the remaining surfaces would only be possible at the cost of damaging/ destroying or creating defects on the paint film on the previously coated surface. Thus with a view to the above mentioned complications, the spin coating technique could not be employed in this research.

vi. Air- Brush Spray Coating: is useful in achieving coatings of controlled thickness, great uniformity along with attractive features like coating as thin a line as 0.05” –as thick as 3”. In other words any sample size can be well coated with very small volumes as low as 5ml of coating. This method besides being very fast offers the benefits of working with very small volumes/weights of formulations. Keeping in mind, the large number of formulations prepared and experimented in this study, the air-brush seemed a feasible option. It also provides the option of controlling spray thickness by easy adjustments of solvents/thinners, the air flow and fluid flow nozzles. The method was practiced on a large number of samples and a thickness variation of (+/-) 0.0004”could be achieved. From a cleaning and maintenance standpoint too, the method seemed feasible. Thus based on all the beneficial features, and practical observations and the inapplicability of the above discussed techniques, the air-brush spray coating technique was adopted as the standard method for sample preparation for all formulations.

4.4 Sample Preparation

Sample preparations comprise of one of the most critical and elaborate steps in any research involving paints and coatings. As understood from the foregoing discussions the kind and nature of the coating and the technique used can have a tremendous impact on physical, mechanical and eventually chemical nature so as to affect the overall performance. Antifouling applications demand very resilient, abrasion resistant, defect-free, uniform coatings which allow continuous additive release but disallow aggravation of corrosion under drastic conditions.[1, 2, 28, 29, 54, 67] Sample preparation for this study was realized to be critical in terms of its influence on the experimental results and interpretations. Thus all parameters affecting or likely to affect the sample preparation process were carefully weighed out and accordingly an optimized procedure was adopted. The sample preparation was accomplished in the following manner:

i. Material Selection: Most of the on-shore or off-shore vessels requiring antifouling protection comprise either of a steel or aluminum body; the former being more popular. Steel was chosen as the base material for all experimental samples. In this case 1010 steel comprising of 0.01% carbon was chosen. The samples were ordered from Meta Spec Co. as pre-cut 2” x 2” square steel coupons which were 0.06” in thickness and had a small hole 1/16 “ in diameter drilled on one edge-centre (in order to facilitate sample suspension in water). The steel was highly polished by the use of 600 grit sandpaper.

ii. Surface Preparation: Prior to painting it was necessary to ensure that the samples were cleaned and made free of grease, dirt, dust or any contamination. The surface was checked to be highly polished and free of scratches as scratches could play a major role in accelerating corrosion of the substrate. In the event of a scratched surface the sample was polished once again to get rid of scratches & achieve a smooth mirror-finish. In order to degrease the steel-coupons, an etching process was followed. In this case, the steel coupons were immersed in a large bath (approximately 300ml) of hexane and ultra-sonicated for 20 minutes. After sonication, the sample coupons were carefully pulled out with tweezers, completely dried in house air and carefully stored in plastic sample boxes.

iii. Priming: is a very important process performed to achieve good adhesion between the coating and the metal substrate. A polished, bare metal-surface has all its irregularities ironed out. When a coating is directly applied onto a metal-substrate, the former fails to establish a very strong bond with the metal. Primers however, are carefully designed bridging materials, that specially contain metal oxides or active metal which generates strong polarities to form strong bond with the metal substrate on one end and the polymeric coating on the other. Thus all metal surfaces require priming to ensure strong coating coverage of the bare metal surface and improved protection from corrosion. In this research the Interlux brand primer PRIMOCON (grey)[47] recommended primer for steel-substrates and antifouling paints was used. The primer was thinned with Thinner 216 (about 8-10% thinner volume) to prepare the right consistency for spraying. Prior to priming, the steel coupons were weighed and their thicknesses were measured (average of three measurements from different locations). The primer was carefully sprayed to cover the entire surface of the steel-coupons and leave no area uncovered and to keep the thickness as uniform as possible. The primed samples were allowed to dry in air at laboratory temperature for about 24 hours to allow enough time for solvent evaporation. Thereafter the weight and thickness of the primed samples were carefully measured and recorded in order to calculate the amount of primer applied. Care was taken to ensure no damage was caused to the coating while measuring its thickness. Hence the sample was lightly held between plastic transparencies (of measure thickness) and then their thicknesses were determined with the aid of a micrometer. All weights (grams) and thicknesses (inches) were record correct to four decimal places.

iv. Painting: The next step after priming was painting the sample with the respective formulations. The formulations as listed in Table I & II (for the Part I & Part II of the study) were prepared meticulously in the following manner.

  - Based on the formulation ratios, the weight percentages of the additives required to make 25 gm of a coating were calculated. A recipe of about 25gm of paint with added solvents was more than sufficient for a single coat. The order of addition was as described below: for convenience and homogeneous mixing.

1. All <u>*non-Ionomer formulations*</u>: For all formulations containing only cuprous oxide with or without additives (i.e. SAMPLES 1-5; Table 4.1) of Part one of this study, the procedure for formulation included the following:
    a) Weighed amount of base paint was taken and to it a recipe weight of Cuprous oxide was added; viz. 42.75% for Sample 2 and 30% for all other samples.
    b) The cuprous oxide –paint mix was stirred well to homogenize and 2 ml thinner 216 was added to achieve better mixing. Cuprous oxide used was a fine powder (<5 micron particle size) and needed homogeneous blending in paint
    c) For formulations containing additives like Viscoplex and /or CuDDP, the weighed additive (5% recipe weight) was added and blended with the paint mix. Viscoplex being highly viscous needed vigorous stirring prior to solvent addition. As discussed in section 4.3.1. , the CuDDP was dissolved in hexane and the solution was added to the recipe.
    d) Finally paint converter was added in the proportion (4:1, paint: converter) and after proper mixing to prepare a homogeneous blend was allowed 15-20 minutes of induction time before coating. The converter helps cure the epoxy paint and harden it.
    e) Before spraying the coating with air-brush it was diluted with 5-7ml of Thinner 216 to facilitate ease in spraying. Once diluted and homogenized, the formulation was sprayed quickly with the air brush on a primed sample to cover all surfaces uniformly.

f) All weights were calculated as per the formulation percentages listed in Table 4.1 and Total recipe weight was 25.0 gm.

2. All *Ionomer-Blend formulations*: For all formulations containing cuprous oxide with Ionomer ED-SPAN with or without other additives in a blend (i.e. SAMPLES 7-8; Table 4.1 & SAMPLES 1B-5B; Table 4.2) of Part I & Part II of this study, the procedure for formulation included the following:

a) Weighed amount of Ionomer (as per recipe) was taken. The Ionomer was coarse and had large particle size so that it had to be crushed and then dissolved in minimum volume of water to attain a paste.

b) To the Ionomer paste, weighed amount of base paint was added and to it a recipe weight of cuprous oxide was added. The cuprous oxide-Ionomer–paint mix was stirred well to homogenize and 2 ml thinner 216 was added to achieve better mixing. Cuprous oxide used was a fine powder (<5 micron particle size) and needed homogeneous blending in paint

c) For formulations containing additives like Viscoplex and /or CuDDP, the weighed additive (as per recipe weight) was added and blended with the prepared mix. Viscoplex being highly viscous needed vigorous stirring prior to solvent addition. As discussed in section 4.3.1. , the CuDDP was dissolved in hexane and the solution was added to the recipe.

d) Finally paint converter was added in the proportion (4:1, paint: converter) and after proper mixing to prepare a homogeneous blend was allowed 15-20 minutes of induction time before coating. The converter helps cure the epoxy paint and harden it.

e) Before spraying the coating with air-brush it was diluted with 5-7ml of Thinner 216 to facilitate ease in spraying. Once diluted and homogenized, the formulation was sprayed quickly with the air brush on a primed sample to cover all surfaces uniformly.

All weights were calculated as per the formulation percentages listed in Table 4.1 and 4.2 and Total recipe weight was 10.0 gm due to small quantity of Ionomer available for use.

3. All *<u>Ionomer-Top Coat formulations</u>*: For all formulations containing cuprous oxide with Ionomer ED-SPAN with or without other additives in a blend (i.e. SAMPLES 6; Table 4.1 & SAMPLES 1B-5B; Table 4.3) of Part I & Part II of this study, the procedure for formulation included the following:

a) On the primed sample a 1st coat of paint with 30% copper prepared and applied as per 4.3.iv.1 described above for all non-Ionomer samples. After the coating dried for 24 hours the sample was weighed and its thickness measured. The next coat formulation was prepared and applied as below.

b) Weighed amount of Ionomer (as per recipe) was taken. The Ionomer was coarse and had large particle size so that it had to be crushed and then dissolved in minimum volume of water to attain a paste.

c) To the Ionomer paste, weighed amount of base paint was added The Ionomer–paint mix was stirred well to homogenize and 2 ml thinner 216 was added to achieve better mixing.

d) For formulations containing additives like Viscoplex, the weighed additive (as per recipe weight) was added and blended with the prepared mix. Viscoplex being highly viscous needed vigorous stirring prior to solvent addition.

e) Finally paint converter was added in the proportion (4:1, paint: converter) and after proper mixing to prepare a homogeneous blend was allowed 15-20 minutes of induction time before coating. The converter helps cure the epoxy paint and harden it.

f) Before spraying the coating with air-brush it was diluted with 5-7ml of Thinner 216 to facilitate ease in spraying. Once diluted and homogenized, the formulation was sprayed quickly with the air brush on a primed sample to cover all surfaces uniformly.

All weights were calculated as per the formulation percentages listed in Table 4.1 and 4.3 and Total recipe weight was 10.0 gm due to small quantity of Ionomer available for use.

- The painted samples were allowed to dry in open-air by suspension from a rod, under laboratory conditions of temperature and pressure. Five samples were prepared for each formulation to allow all experiments.
- The samples were dried for about 24 hours and then a second coat of the same recipe prepared by using the same procedure as described in table 3,4 or 5(depending on the formulation) was applied. Before application of the second coat, the painted sample weights and thickness were recorded as described in procedure for priming.
- After the second coat the samples were dried for another 72 hours in air and then their weights and thicknesses were measured and recorded. The dried samples were either stored carefully in plastic boxes or used for experimentation.

4.5 Leaching and Corrosion Study

The rate at which a toxicant or biocide is released from an antifouling paint - i.e. the "leach rate" plays a major role in deciding the efficacy of the formulation for antifouling.[1-3, 18, 26, 28, 31, 44, 66, 67] The leach-rate study is very important not only because it helps in understanding and predicting the performance and durability of the formulation in actual conditions but in addition it also assists in determining the approach to be adopted and the modifications to be implemented in the formulation so as to achieve the desirable performance.[1-3, 26, 29, 41, 42, 44, 48, 49, 57, 67]Leach-rate determination methods have not been developed for all toxicants but for antifoulants like copper, mercury etc. the periodic release of toxicant can be monitored accurately by chemical methods so that they have been extensively used to interpret and predict the behavior of formulated antifouling paints in simulated laboratory conditions as well as actual environments.[15, 28, 38, 42, 52, 67] The leach-rate tests however generate no knowledge on the efficacy of the formulation in detaining fouling growth after long periods of time i.e. on the service life of the paint. The paint needs instead to be tested in actual environment for years to predict life-span of coating.[67]

4.5.1 Leach Rate determination procedure

The leach-rate study has a well defined procedure set-up as a guideline for marine industry by ASTM. It allows for laboratory as well as actual marine environment testing and calculations of copper leaching rate from candidate formulations. The coating procedure has been defined in ASTM procedure D 6442-06[68]. The painted samples after proper conditioning and drying need to soaked in sea-water/ fresh water (for actual environments) or artificial sea/ocean water (for simulated sea-conditions within laboratory). In this research all experiments were conducted within the laboratory using simulated sea-water conditions.

The painted panels need to be immersed/ suspended in a bath of simulated sea-water prepared as per ASTM procedure D 1141-98[71]. The bath must be well aerated and must have dynamic conditions of water flow to mimic the sea-environment as encountered for under-water ship hulls. The experiments need to be conducted under controlled conditions of temperature of 23 +/- 2 ˚C, salinity or chlorine content of 34ppm and pH of 7.9 – 8.1. The painted panel size should be such that the ratio of immersed area to sea-water should be between1:5 – 1:7. Water samples for copper concentration measurements; need to be collected at intervals like 1, 3, 5,7,11, 15, 22…..43 days. Based on the copper concentration calculated for each interval, the leach rates for the entire test period should be summed up and averaged to calculate an average leach rate (ASTM D6442-06). However, close monitoring of the leach-rate in the early stages is desirable to estimate the burst release-rate and to calculate the drop in leaching efficiency as steady state upon build-up of diffusion barriers is reached.[1-3, 17, 18, 29, 42, 44, 48, 67] Extensive studies on leach-rate and antifouling efficiency have demonstrated and confirmed that a copper leach-rate of15 ug/cm^2/day is ideal and sufficient to deter and inhibit fouling while no antifouling capability is seen below 10ug/cm^2/day of copper release. Thus the range between 10-15ug/cm^2/day of copper can be regarded as the marginal zone permitting some attachment especially as the lower limits are reached.[2, 17, 42]

To study the early stages of leaching in this study, the following procedure was adopted by simulating marine conditions (in the laboratory), conducting a leach-rate study and predicting the antifouling capability of formulations based on the generated copper leach rates:

i. The painted panels prepared for all formulations as described in section 4.2 and 4.4 were taped with electroplating tape to cover a width of ¼" on all four corners so as to have an effective exposed surface area of 29.33 cm^2. The taping was done to prevent acceleration of corrosion (which masks up the actual leaching behavior) on the corners and have uniformly exposed surface.

ii. A painted panel of each formulation was suspended in 300ml of substitute ocean water prepared as per ASTM procedure D 1141-98. The panels were kept completely immersed at all times with the help of an insulating wire which was attached to the cover for the 1-litre mason jar used for holding each sample bath. Each experimental sample required a separate mason jar for accurate determination of copper leaching from each formulation. Through some trials, it was realized that the sampling baths had to be kept covered at all times to minimize evaporation losses and also to avoid losses, due to water spurting out of the containers in response to the vigorous agitation caused by air-bubbling. The experiment was conducted at a constant temperature of 25˚C in a temperature controlled furnace. This temperature was selected in agreement with the ASTM D 6642-06 standard conditions and the constancy was maintained keeping in mind that every 1 ˚C rise or fall in temperature can affect the pH and salinity by affecting evaporation and fouling growth rates, so that a correction factor needs to be incorporated into calculations for any change of temperature.[3, 28, 67]The pH was monitored with a portable pH meter to ensure that it was always in the alkaline range of 7.9 - 8.2. Attempts were made to keep all variables constant throughout the experimental run to avoid influencing results and performance.

iii. To achieve dynamic conditions of air and water flow, small PVC-tubes ¼" in diameter were inserted into each sample bath from a manifold, which in turn was connected to a flow-meter – dessicator - house-air outlet. House air was used to allow air flow. The dessicator helped to remove the high moisture from the air, and the flow meter kept the air flow at a constant flow-rate of 480ml/min. The manifold uniformly distributed the air-flowing at 480ml.min to six PVC-tubes entering 6 sample baths to generate a constant air-flow rate of 60ml/min in each bath. This air-flow rate furnished a fresh supply of air and also caused vigorous agitation in water necessary to simulate the actual sea-water conditions as encountered by ship-hulls. A schematic of the leaching study set-up can be seen below.

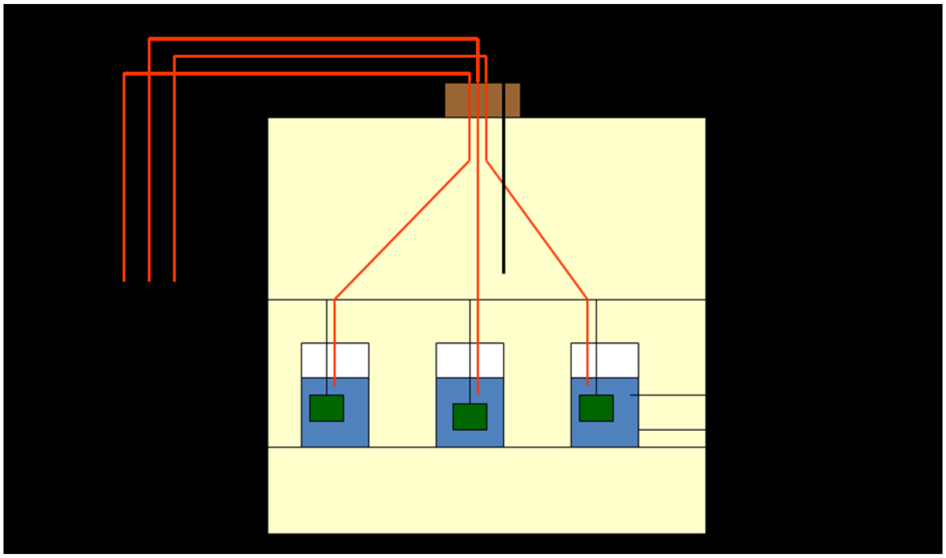


Figure 4.3 Schematic for leach study experimental set-up

iv. The leach-samples were collected as 10ml aliquots after the 1st, 4th, 7th day and analyzed by chemical analysis to calculate the copper concentration. A time-frame of seven days was selected to make a careful study of the burst release rate, track the buildup of diffusion barriers and drop in leach rate so as to critically examine the performance of the formulations in optimizing the leach rates by overcoming those barriers. Also from a time availability stand point, a 7 day experimental time-frame seemed suitable for examining such a large number of formulations. The copper concentration measured by chemical analysis was used to evaluate, leach rates. In actual sea-water environment, the volume of water is extremely large so that, the leached copper concentration although high in the immediate vicinity of the vessel gets distributed avoiding build up of concentration gradients to affect leaching rate. In this case, due to the small size of the sample bath, experimental trials revealed that copper concentration built up around the sample in the bath, dropping the driving force for further leaching so that the leaching rates dropped drastically following the 1st day of immersion. This phenomenon led to rapid attainment of steady-state concentration of copper in water which in turn caused misleading interpretations of the leaching rates and hence antifouling efficiency of the formulations. Thus to avoid such problems of complicated interpretations, a fresh stock of simulated sea-water was used after each sampling for the next sample collection. Hence the sample bath was replaced after the 1st and 4th day. This procedure also in agreement with the actual dynamic nature of the marine environment where concentration gradients are less likely to affect the leach behavior or rate of copper from paint. There was some water loss from evaporation. To make-up for the lost water, distilled water was used to re-fill the water level up to the original mark on the jar. Distilled water was used to avoid variation in the ion concentration.

v. The chemical analysis of copper for the samples solutions is used to evaluate the leach-rate and hence predict the antifouling efficiency of the paint based on the literature knowledge that 15ug/cm^2/day is necessary to preventing fouling by deterring attachment and inhibiting growth. The leach rate for copper can be calculated by using the following formula:[28, 67]

   LEACH RATE = {(mg/L) x VOLUME (ml.) x 24 hrs.} / {AREA (cm^2) x TIME (hrs.)}

   (ASTM D 6642-06)

vi. Corrosion plays a very important role is destroying under-water coatings and structures in general. Sometimes, the accrual of biological decay and metabolic wastes of the fouling organisms augments corrosion of the underlying coating and or surface; while at other times, corrosion and surface roughness created due to it may open further attack from the fouling organisms. Thus when doing a leach-rate study, it would also be valuable and important to monitor the corrosion behavior of the experimental formulations so as to have a comprehensive picture on the commercial applicability of the formulations. In this research, corrosion of the test panels was monitored by determining the mechanical properties like hardness and elastic modulus as well as the topography and surface features like, pitting, surface roughness, rusting etc. before starting, during and after completion of the leach study. Thus, the above mentioned characteristics for the test panels prepared of all experimental formulations were individually determined before, during and after the leaching experiments and their results were used to decipher the influence and or control - attained on corrosion by the use of the selected additives for antifouling formulations. The results from the corrosion study were meaningfully correlated to the additive properties and their chemical compositions. The characterization techniques used to study corrosion behavior of the test formulations are described in the last section 4.8 of this chapter.

4.6 Accelerated Leaching and Corrosion Study

The accelerated leaching tests are a part of the preliminary elimination test procedure to discard wasteful formulations which demonstrate a minimum possibility of surviving the aggressive marine conditions while providing a copper leaching rate sufficient to sustain the antifouling action of the formulation. Thus based on these tests, those formulations which are unable to release toxic sufficiently to prevent fouling are eliminated by a series of rapid physical and chemical-tests. These tests are designed to determine whether the copper-based paints are capable of releasing toxic material retained within the film.[67]

In this case acid-solutions or those capable of forming complexes with copper are used to accelerate the dissolution of copper from the paint into the sea-water. One such test devised for copper-based antifouling paints is the glycine test and is not applicable to paints containing other toxicants/biocides.

4.6.1 Accelerated Glycine test Method [67]

In this test, sodium glycinate solution at a highly alkaline pH is used to dissolve copper/cuprous oxide and paint matrix from an antifouling formulation. The dissolved copper remains in solution as copper glycinate complex and the highly alkaline nature of the solution accelerates matrix dissolution. A good antifouling formulation should be capable of releasing several milligrams of copper in solution in just three days irrespective of the release mechanism of the paint. Whether the paint releases copper by soluble matrix decomposition or by diffusion and transport of copper/cuprous oxide with sea-water; the highly alkaline glycinate solution should be capable of releasing a large quantity of copper in three days of the test. The concentration of copper from the retrieved test solution can be determined by suitable chemical methods. From the literature a correlation between the copper leached in three days in a glycinate test and the average leach-rate from a leaching study on several paints can be obtained. This correlation can be used to predict the life-span of an antifouling paint of the proposed formulation in actual environment as follows:

- A paint releasing less than 1.3 mg/cm^2/day copper in three days in the glycinate is not capable of surviving the actual marine conditions for six months and needs to be discarded.
- Paints releasing 1.3 - 2.5mg/cm^2/day may or may not succeed.
- Paints releasing over 2.5mg/cm^2/day of copper in three days demonstrate a fair chance to survive longer than six months in sea and need further testing.

4.6.2 Glycine Test Procedure

The sodium glycinate test for accelerated leaching of copper was performed in the same experimental set-up as used for the leaching study described in section 4.5.1. but with some different testing conditions. The test solution was prepared as follows:

i. A representative sample for each formulation as prepared by procedure in section 4.2 was immersed in 350ml of sodium glycinate (from the prepared stock solution) solution filled in each sample containers. The sodium glycinate stock solution was prepared as per the recipe provided in the literature[67]. The following materials were taken in a 1litre capacity volumetric flask.

    20ml of 1.25N NaOH
    1.875g of glycine
    28g NaCl
    Volume make-up to 1 litre with distilled water

ii. The immersed samples were subjected to testing conditions of 25˚C temperature, highly alkaline pH of 10.5 and air flow-rate of 60ml/min. The test was allowed to run continuously for 72 hours. At the end of 72 hours, the air flow was stopped and liquid aliquots were collected and analyzed chemically for copper concentration. The copper concentration was used to predict the life-span of the coating and also compared to the standard leach test data for further interpretations.

iii. Similar to the leaching study; the test samples for this study were evaluated for corrosion by visual examination as well as using optical characterization tools like optical microscopy (details of which will be discussed in section 4.8). Apart from the copper concentration for different formulations, their corrosion behavior was also used as a guiding parameter for selecting the right combination of additives.

4.7 Corrosion Study

Aqueous corrosion can be disastrous for marine coatings especially when combined with galvanic or other corrosion types. Historically, a variety of different forms of corrosion like aqueous, pitting, galvanic etc. have been detected in case of artificial structures in constant contact with water, such as encountered in marine applications like antifouling coatings on under-water steel hulls for ships, yacht's, motor boats etc. Hence, it is desired and necessary that the antifouling paints provide protection not only from biofouling but also from corrosion. As explained earlier, deposits from decaying organic matter, metabolic wastes from fouling organisms can combine to aggravate corrosion of the underlying steel or aluminum substrates of the above mentioned artificial structures. Coating discrepancies like discontinuity, cracks, pores, pin-holes etc. can expose the metal-surface to water, to set-up local galvanic cells with corrosion products/oxides which can trigger an accelerated corrosion mechanism.[2, 3, 30, 66] The accumulation of corrosion products, oxides etc. may create a favorable roughened surface attractive for settlement. Thus additional settling of the marine organisms may be encouraged, destroying the painted surface and worsening the whole problem. Hence along with exercising control on fouling prevention, measures should also be taken to inhibit corrosion and eliminating all fouling triggering elements.

The candidate formulations for antifouling were also examined for corrosion-resistance. Apart from the study of topography, surface features, morphology and mechanical properties of the painted samples before and after the leaching study; an additional separate corrosion study was performed on each of the formulations. This corrosion study was accomplished with help of scribed samples. The experimental procedure can be described as follows:

i. A painted sample for each formulation (from Table 2 & 3) was taken. A scribe mark was made on two-of its flat surfaces in the form of an ‘X’ with the help of a razor blade. The scribe was made carefully and was maintained at the same width (approximately) for all samples. The scribe was made such that the bare surface of the steel- sample was exposed through the scribe.

ii. Images of the scribed samples were taken using the optical microscope at magnifications of 1X, 3X, 5X and 10X respectively and the sample weights were recorded.

iii. The experimental set-up for the scribe samples was exactly the same as for the leach-rate study (described in section 4.5.1). The individual sample containers were kept in controlled temperature furnace maintained at 25˚C. Substitute ocean water (300ml for each sample) was prepared as per ASTM D 1141-98 standards with a pH 0f 7.9 - 8.2. The samples were suspended in the sampling bath (which was covered at the top), and dry air-flow in each bath was maintained at 60ml/min with the help of the house air-dessicator and flow-meter connections.

iv. The corrosion study with the scribed samples was performed till seven days, with water aliquot samples being collected every 2nd and 7th day. The collected water aliquots were sent for chemical analysis to calculate the copper concentration. The calculated concentration was used to calculate leach rates and compared to the leach-rate test results (from the leaching study) to verify if the intentional introduction of a cut/ scribe had any influence in accelerating the corrosion and leaching of copper from the paint. This would help take into account a realistic scenario where cuts/ scratches etc. are often likely to be introduced on painted surface in application.

v. Along with the chemical analysis for copper, a physical inspection for corrosion of the test-samples was performed by visually examining them for the extent of rusting/ decaying of the bare and painted steel surface. Optical images were taken at each stage of sample collection to compare and contrast the corrosion phenomenon in progress. The sample weights were also recorded to observe the increase/ decrease in weight due to deposition or loss of the corrosion products.

vi. At the end of the experiment, the copper concentration data coupled with the optical images and weight calculations were used to compare the performance of all the different formulations with regard to corrosion.

The corrosion study interpretations aided in adding weight to the leach-rate study and constructing a comprehensive picture with regard to antifouling performance of all the candidate formulations.

4.8 Characterization Study

The leach-rate and corrosion study of antifouling paints formulations was accomplished with several material characterization tools. The characterization techniques discussed below were used to elucidate on the morphology, mechanical properties, corrosion-resistance and copper leaching ability of the formulated paints and were useful in not only making meaningful interpretations regarding commercial application but also in establishing the basis for preliminary elimination of those formulations which underperformed.

4.8.1 Scanning electron microscopy (SEM) and Energy Dispersive spectroscopy (EDS)

In order to study the topography, composition and distribution of elements across the paint film and to evaluate and compare the extent of corrosion/pitting between different paint formulation both before and after the leaching study scanning electron microscopy coupled with energy dispersive spectroscopy was used Hitachi S-3000N Variable Pressure SEM .[33, 72] It has about 3.0nm resolution at High voltage and 4.0 nm resolution at low voltage. In this study the

SEM-EDS system was used at 20 KV acceleration voltage and 15cm working distance. The samples being thin paint/polymer films had to be sputter coated with thin Ag film before imaging to compensate for the poor electrical conductivity and charging issues of the samples. For every sample after a suitable location of the film was spotted, SEM images at different magnifications were captured and EDS spectrum was taken for elements like (Cu, Ca, Mg, Na, Cl, S and Ag) and an elemental mapping of the same elements was also performed to capture the distribution of these elements throughout the film surface. This procedure was repeated before and after the study to compare the surfaces of different formulations before and after corrosion in the leaching study and correlate it to the influence of additives.

Figure 4.4 Hitachi S-3000N SEM/EDS system used for corrosion study

4.8.2 Nano-Mechanical Studies

The mechanical properties of paint films and the influence of additives on the mechanical properties were ascertained with the help of Nano Indentation tests. These tests were performed using the Hysitron Ubi® Triboindenter a high resolution instrument capable of performing Nano scale indentation, scratch and wear tests along with a host of other Nano-mechanical tests and imaging surfaces using the SPM mode. Nano-Indentation has been established as an important tool for studying the mechanical properties of both bulk-solids as well as well as thin films in the sub-micron scale.[42, 48, 66, 72]

In quasi-static Nano-indentation a normal force is applied to the tip of the indenter and its displacement into the sample is measured. While this displacement is being continuously measured the same tip can be used for imaging the surface via SPM mode. In Nano-Indentation studies the depth of penetration combined with tip-geometry knowledge can be used to indirectly measure mechanical properties like Reduced Elastic Modulus, (Er), Young's Modulus (E) and Hardness (H). For the present study a trapezoidal loading function was used for probing the sample for single indentation measurements both before and after the leaching study to compare the difference in modulus and hardness between samples with differing additives and also to study the degradation of these mechanical properties in due to corrosion in course of the leaching study. In the trapezoidal loading cycle, there is 5-second of loading segment, 2-second of holding segment (at the maximum load) and then 5-second of unloading segment. The reduced modulus (E') is measured as a slope of the load-displacement curve at the unloading segment. The hardness and the Young's modulus can be calculated from the formula as described below. These parameters are calculated using Oliver Pharr's Method as follows:

$$\frac{1}{E'} = \frac{1}{2}\left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}\right)$$

$$E = 0.5\left(\frac{\pi}{A}\right)^{0.5} S$$

$$H = \frac{P_{\max}}{A'}$$

Where E' is the reduced elastic modulus and E1 &□v_1 are the Young's modulus and Poison's ratio for the material and E_2 &□v_2 are that for the tip. H is the hardness, Pmax the pressure and A' is the area.

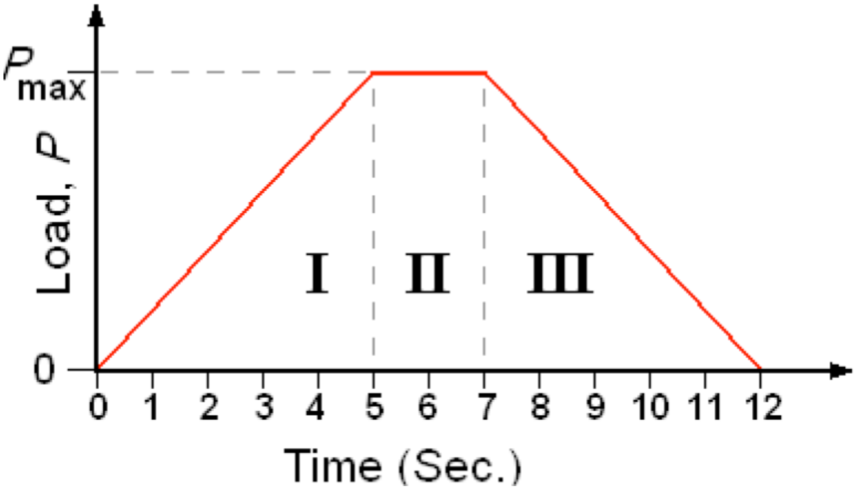


Figure 4.5 Trapezoidal loading cycle for nano-indentation

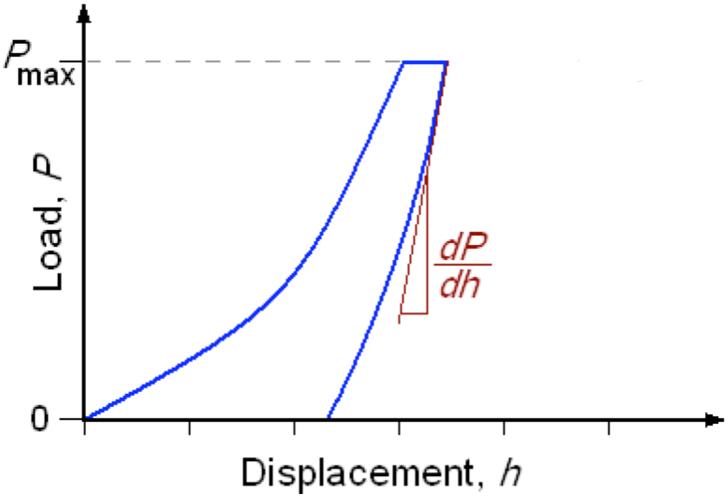


Figure 4.6 Typical load-displacement curve obtained in a nano-indentation

In this study the SPM mode for imaging was not used as the paint film is very soft and can damage and dirty the tip. The tip used was the North Star Cube corner tip with <40nm radius. The Hardness and reduced modulus for each formulation were measured as an average of 36 single indentation tests. The results of the indentation were correlated to the influence of the different additives used on the hardness and modulus of the paint formulation. After the leaching study the samples were corroded to different extents and hence they were probed in the same manner as described above to compare the deterioration of properties and the role of additives in controlling them.

4.8.3 Inductive Couple Plasma-Mass Spectrometry (ICP-MS)

ICP analysis is the abbreviation for inductive coupled plasma analysis. It is a technique where a type of plasma source where electrical current energy is applied to the sample. The electric current energy is produced by electromagnetic induction which is a time-varying effect of the magnetic field. When a varying current is passed, the magnetic field varies leading to varying azimuthal current in rarefied gases leading to breakdown and generation of plasma. Very high plasma temperatures can be reached offering the benefit wherever high density plasma is a requirement and also leaving no element of contamination from the reaction as the electrodes are outside the system. An application of ICP includes mass-spectrometry where it can be used to assay trace concentration (up to 2ppb) of an element in a mixture. ICP-MS has been a popular probe in precisely quantifying the copper concentration when conducting laboratory leaching studies for antifouling systems.[2, 12, 15, 38, 41, 42, 67, 73, 74] In this study ICP-MS has been used to quantify and evaluate copper leaching rates for all leaching study experiments. 10ml sample solution from different time-intervals of the study was sent to Chemical Solutions Ltd. (CSL) for copper analysis by ICP-MS. CSL excels in quantifying as low as ppb concentration of copper in solution with their Perkin-Elmer ELAN 9000 ICP-MS instrument. This technique allows less interferences and faster analysis compared to ICP-OES, Atomic absorption (AA) and graphite furnace atomic absorption (GFAA). To compare and evaluate the accuracy of the results at each time a blank sample of know concentration of cupric nitrate in water was sent for analysis.

4.8.4 Optical Profilometer

Optical Profilometer was used as a characterization tool for this study. The instrument used was Wyko NT9100. This profilometer was used to scan the sample surface and capture a 3 – dimensional image of the sample describing features like surface roughness, depth range (between highest and lowest point of surface) with a color scale and can be used for various applications. For this study, the profilometer was used to image the surface roughness of paint films from different formulations and monitor the progress of corrosion marked by change in surface roughness and formation of pits, porosity etc. The images of samples scanned by the profilometer before, during and after the leaching study help understand the process of corrosion and indirectly relate to the role of the different additives and their concentrations as used in preparing different formulations.

4.8.5 Optical Microscopy

The Nikon optical microscope was used for imaging paint samples for different formulations before and after the leaching study and also for the corrosion study of scribe samples. The images were captured at various resolutions 1X, 3X, 5 X and 10X to study the corrosion pattern of the surface for different samples. These images aid in the understanding of progress of corrosion, the active sites and were eventually correlated to additive performance in terms of controlling the leaching of copper and preventing corrosion of the surface.

4.8.6 Polarization Study

The potentiostat /galvanostat equipment with Corrware software was used to measure OCP and run Potentiodynamic polarization tests on some of the selected formulations of Part I study and formulation 5B (30% Cu_2O + 12.5% Ionomer+ 3.5% viscoplex blend in paint) of Part II study to quantify the corrosion resistance of these formulations and discriminate the influence of additives on the same. Prior to the experiment the samples were taped to keep the exposure area to 1.26cm^2 and a scribe was made on the exposed surface to expose the bare metal. The scribe was made to configure the corrosion protection for scratches and to overcome the barrier protection of the thick coating layers. The samples were equilibrated for 1 hour in 3.5% NaCl salt solution in deionized water to measure the open circuit potential of the system. The counter electrode was graphite and the reference electrode was saturated calomel electrode (SCE). The potential range was selected as -0.25V to + 0.25 V and a scan rate of 1mV/sec was used. After the OCP measurement was complete, potentiodynamic polarization experiment was conducted on each of the the individual sample column set-ups. After all the selected samples were analyzed, they were subject to 24 hours exposure to simulated marine conditions as used for the leach study discussed in section 4.5. As discussed earlier, substitute ocean water was prepared as per ASTM D 1141-98[71] and 300ml; temperature of 25C and air flow at 60ml/min was used for each sample container. After 24 hours of exposure, the samples were air dried and then subject to OCP and potentiodynamic measurements in the same manner and with same conditions as described above. However for the polarization measurements after 24 hours, a new scribed surface was used for measurements and not the previous one to avoid error of prior introduced corrosion effect. The 24 hours of severe exposure to simulated marine conditions was introduced to allow sufficient time for burst release of copper and saltwater penetration into the coating surface to be able to initiate corrosion at active sites. This was to evaluate the corrosion resistance under actual severe conditions and study the additive influence towards protection.

CHAPTER 5

SYNTHESIS OF IONOMER ED-SPAN

5.1 Ionomer

Polymer composed of macromolecules in which a small but significant proportion of the constitutional units have ionic or ionizable groups, or both is termed as an Ionomer. In such compounds, ionic groups are usually present in sufficient amounts (typically less than 10 % of constitutional units) to cause micro-phase separation of ionic domains from the continuous polymer phase. The ionic domains act as physical cross links.[70, 75]

5.1.1 Ionomer for Antifouling Application

The use of an ionomer /ionic polymer or amphiphilllic polymer [75] is new to antifouling application. Polymeric compounds are known to possess hydrophobic properties in general. In case of antifouling paints while hydrophobocity is essential to improve the corrosion resistance and hence durability of the paint; hydrophilicity, leading to paint matrix degradation and or dissolution in water is also desired, for renewed surface generation and in consequence adequate leach rate maintenance purposes.[3, 15, 29, 31, 34, 42] Literature provides sufficient evidence to emphasize on the necessity, of periodic paint matrix degradation to overcome the diffusion barriers developed in due course of time, blocking matrix pores with particulates and retarding the copper/ biocide leach rate from the paint, producing loss in antifouling efficiency.[1, 3, 8, 15, 28, 31, 36, 41, 42, 48, 53] In this regard the use of hydrolysable polymers as a matrix component has been popular for some time. In contrast to the traditional hydrolysable ester groups (which are limited by the extent of esterification & property compromises acceptable in the paint matrix[1-3, 15, 24, 31, 36, 42, 48]), the use of ionomer can be foreseen to be superior in terms of improving control over the extent of matrix degradation by directly controlling polymer loading rate (in paint) and in turn controlling polymer water solubility.

Ionic properties of polymers sometimes help generate conductivity and can act as an additional aid in preventing corrosion.[3, 30, 58, 65, 70, 75] In addition when compared to the hydrolysable ester groups incorporated in the paint polymer backbone; ionomer leave the flexibility of being used as independent additives requiring no changes/compromises to the inherent paint matrix. Thus in case of the ionomer, the paint does not degrade completely with time due to hydrolysis of the decomposable components but gets porous in structure following slow dissolution of additive from the surface. Hence by the use of ionic polymer additives it may be possible to retain the inherent properties of the paint for prolonged periods while achieving steady and desirable biocide release rates.

5.2 Sulfonated Polyaniline for Antifouling Application

Polyaniline was the first conducting polymer whose electronic properties could be reversibly controlled by both protonation and charge-transfer doping. [3, 65, 70]This research explores the potential benefits of sulfonated Polyaniline (conductive) in offering dual benefits of achieving a control over the paint matrix degradation leading to biocide leach-rate control and also improving the corrosion resistance of the paint by charge-transfer via electronic conductivity. Polyaniline (which has several oxidation states) in the emeraldine base oxidation state can be converted from an insulator to a conductor by external protonic doping.[65, 70] Introducing a -SO_3H group on the Polyaniline chain assists in improving the inherent properties of PANI without sacrificing its electronic conductivity. Some of the benefits of sulfonating PANI can be listed as follows:[65, 70]

1. Benzenesulfonic acid is a strong acid; hence Sulfonic acid ring-substituted Polyaniline (SPAN) is capable of self-doping and does not rely on external protonation.

2. Polyaniline has superior stability in air but is resistant to dissolution in water and most organic solvents. The presence of –SO_3H group enhances the electron withdrawing properties of the phenyl ring and improves the environmental stability along with greater solubility. Thus the ED-SPAN can be described as a water-soluble conductive Polyaniline (Ionomer).
3. The self doping capability of ED-SPAN could generate enhanced optical and electrical response to electrochemical potential as compared with the parent Polyaniline due to generation of counter ions from the moieties covalently bound to the polymer.

Thus after reviewing the above properties of externally doped sulfonated polyaniline and keeping in mind the prior hypothesis of employing an ionomer as a material aid for controlling the paint matrix degradation and assisting controlled, steady copper leaching; ED-SPAN was selected as an additive for formulations in this research and was synthesized for the study.

5.3 Synthesis of ED-SPAN

Synthesis of SPAN was performed following the procedure described in.[65, 70] The principle for the synthesis is chemical oxidation of the PANI ring by substitution of an ortho-position phenyl ring proton by the –SO_3Cl group of chlorosulfonic acid which is a strong oxidizing agent. The strong electron withdrawing –OH group of chlorosulfonic acid withdraws the phenyl acidic proton to substitute –SO_2Cl into the ortho-positon of aniline ring along with the elimination of water. The produced compound being a salt of chlorosulfonic acid can thus be further hydrolyzed to produce SPAN. These reactions can be described as follows:

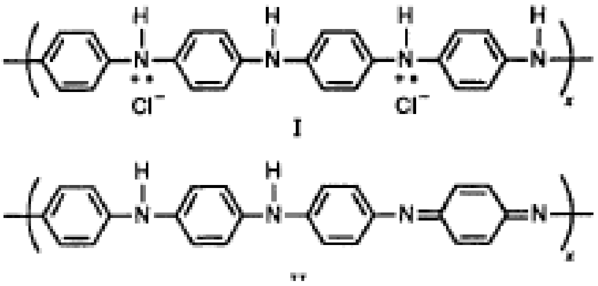
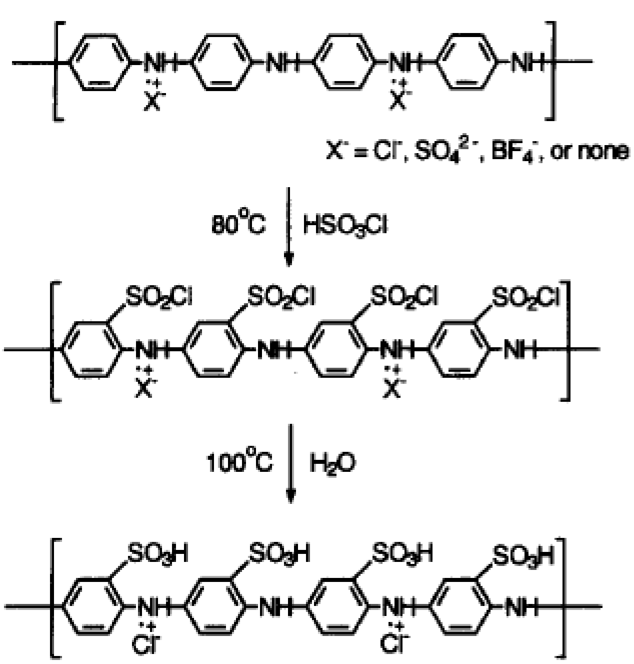


Figure 5.1 Chemical structures of polyaniline



Scheme 1. Synthesis of externally (HCl)-doped sulfonated polyaniline (ED-SPAN).

Figure 5.2 Reaction Scheme for synthesis of externally (HCl) - doped Sulfonated Polyaniline (ED-SPAN)[65, 70]

5.3.1. Experimental

The synthesis of SPAN was accomplished by using the following raw materials:

- Emeraldine hydrochloride powder : alfa aesar
- Chlorosulfonic acid: Cl SO_3H sigma Aldrich (571024)
- 1,2-dichloroethane: $ClCH_2CH_2Cl$ sigma Aldrich (284505)
- Acetone
- Distilled water

Sulfonation of the emeraldine hydrochloride powder was achieved as follows:[65, 70]

- 9.0gm of emeraldine hydrochloride powder was dispersed in about 272 ml 1, 2-dichloroethane solvent in an rbf. The dispersion was heated to 80˚C.

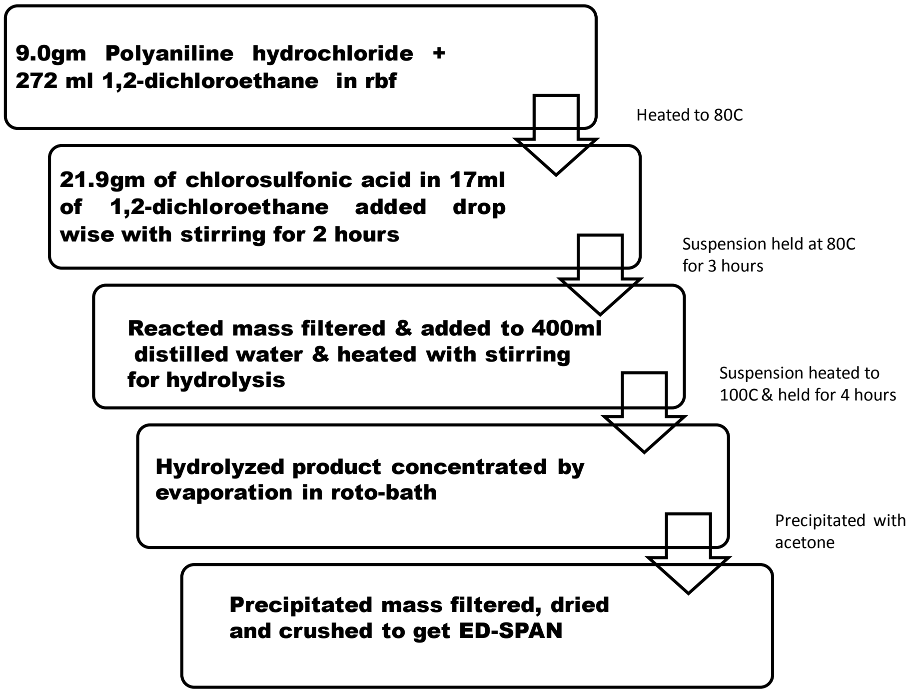


Figure 5.3 Procedure for synthesis of ED-SPAN

- Once the temperature of 80˚C was reached then, 21.9gm of chlorosulfonic acid in 17ml of 1, 2-dichloroethane was added drop wise with continuous stirring. The solvent 1, 2-dichloroethane has a B.P. of 82˚C and so a condenser was used to avoid evaporation loss of solvent. The addition of chlorosulfonic acid had to be performed slowly and carefully due to agglomeration of the sticky mass (upon rapid addition) in the reaction bath preventing homogeneous reaction. The addition was completed in approximately 2 hours with five minutes interval between each addition. The reaction mixture was held at that temperature for 3 hours following complete addition of the chlorosulfonic acid.
- The reacted mass was then separated by filtration and immersed in 400ml of distilled water and heated with a condenser at 100C for four hours to achieve complete

hydrolysis of the chlorosulfonated PANI. The hydrolysis produced a dark green dispersion of fine powder in water.

- The hydrolyzed product was then concentrated to one-third volume by evaporation of water in a roto-bath (with dry ice, under vacuum) and then precipitated with acetone to get ED-SPAN. The precipitated mass was then filtrated with whatman filter paper, dried in a roto-bath and crushed to get fine ED-SPAN powder.

5.3.2. Charactersation of ED-SPAN

After the synthesis of ED-SPAN, it was necessary to analyze the composition of the produced compound and verify that it had the desired composition. This was achieved by performing the following charactersation tests:[65, 70]

- The produced compound was weighed to get an estimate of increase in weight upon oxidative addition of –SO_3H group on Polyaniline and calculate overall synthesis yield.
- The compound (0.0028g dissolved in 20.16g of distilled water by magnetic stirring to achieve 0.01%solution) was analyzed by UV-VIS spectroscopy and compared to the standard spectra for SPAN in the literature.

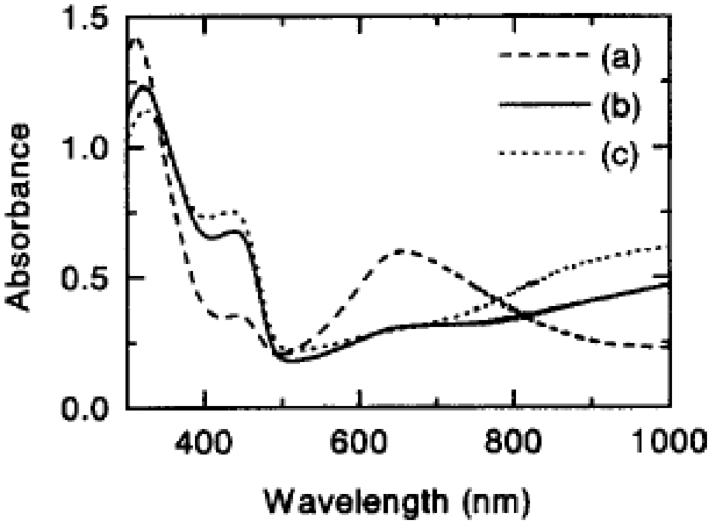


Fig. 1. UV–Vis absorption spectra for ED-SPAN in water with the S/N ratio of (a) 1.3, (b) 0.80, and (c) 0.65.

Figure 5.4 UV-Vis absorption spectra for ED-SPAN in water with S/N ratio of (a) 1.3, (b) 0.80, and (c) 0.65.[65]

The above fig.5.4 compares spectra for ED-SPAN with different S/N ratios. Calculation of the S/N ratios is essential and critical to ascertain the extent of sulfonation achieved in the PANI. This extent of sulfonation controls the ionizability and hence electronic conductivity and water solubility of the ED-SPAN and is in turn directly controlled by the extent of chlorosulfonic acid added. Increasing the chlorosulfonic acid content, increases solubility but reduces conductivity due the electron withdrawing effect –SO_3H group and also its steric hindrance on electronic charge transfer via conjugation.[65, 70] The UV-VIS absorption peaks expected for ED-SPAN are listed as follows;

Table 5.1 Correlations of UV-VIS absorption peaks with different transitions [65]

PEAK	TRANSITION
320nm	PANI for π-π* transition
440nm	440nm – PANI for polaron band transition
650nm	650nm- Undoped quinoid unit.

- The peak intensity around 650 nm increases with S/N ratio (above1.3) implying reduction in polaron bond and increase in undoped quinoid unit. Thus high sulfonation drops conductivity generating an insulating polymer.[65, 70]

Physical properties of ED-SPAN with differing S/N ratios can be viewed and compared from the following table obtained from literature.[65, 70]

Table 5.2 Properties of ED-SPAN with varying S/N ratios [65]

ED-SPAN	$ClSO_3H$ (equiv.)	S/N[a]	Solubility (g/l)	Conductivity[b] (S/cm)
Sample a[c]	2.5	1.30	88	1.66×10^{-5}
Sample b	2.0	0.80	51	5.72×10^{-3}
Sample c	1.5	0.65	22	0.028

[a] From elemental analysis
[b] Four-probe d.c. conductivity at room temperature for a compressed pellet
[c] Sulfonated in 1,1,2,2-tetrachloroethane.

Thus the composition of ED-SPAN is extremely critical for the leaching study and directly controls the paint matrix degradability and also its corrosion resistance.

- The S/N ratio for the prepared ED-SPAN was evaluated by ICP analysis and compared to the above table.

- FTIR of ED-SPAN also generates useful information its composition. The FTIR spectra of the synthesized ED-SPAN were compared to the expected values provided in the literature.

Table 5.3 FTIR peak stretches observed for different bonds in ED-SPAN

PEAKS (cm-1)	GROUP
1172, 1074	Asymmetric and symmetric stretch of O=S═O
703, 615	S-O stretch
615	C-S stretch
818	Out of plane bending of 1,2,4-trisubstuted aromatic ring
2500-3700	Broad peak for ED-SPAN containing water

The FTIR spectra for ED-SPAN were achieved following the standard procedure for solids using KBr pellet.

The results for the characterization of ED-SPAN are summarized below:

UV-VIS Spectroscopy Results: The plot for the UV-VIS spectra for the synthesized ED-SPAN is given below. As compared to the literature the plot shows broad peak in the 340nm and 440nm region indicative of characteristic peak for Polyaniline and polaron band π-π* transition (as discussed in table 5.1).[65, 70]. The peak intensity at 650nm as expected for the undoped quinoid unit with less conjugation; is low indicating that the extent of sulfonation is not very high to cause undoping of the ED-SPAN molecules.[65]

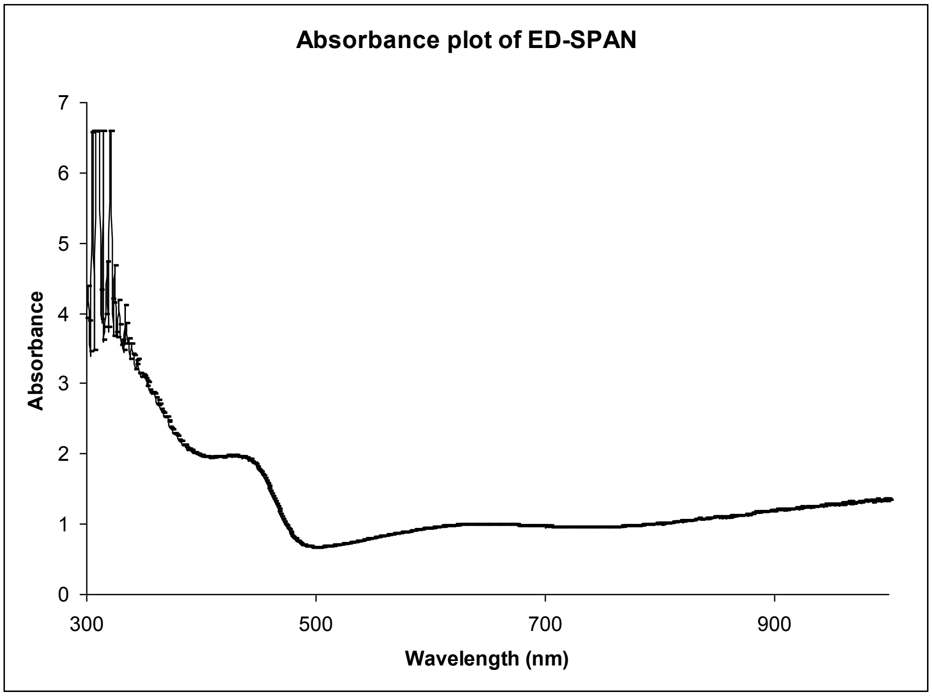


Figure 5.5 UV-Vis absorption spectra for ED-SPAN (synthesized in laboratory)

<u>ICP chemical analysis for S/N ratio:</u> ED-SPAN solution (2% strength) in distilled water was sent for ICP-chemical analysis for sulfur and nitrogen analysis to calculate the extent of sulfonation of the polymer. The S/N ratio was calculated as:

S = 0.1ppm

N = 0.05ppm

S/N ratio = 2

FTIR spectra for ED-SPAN: The FTIR spectra for the synthesized ED-SPAN are given below. The spectra shows the expected peaks for ED-SPAN as discussed in table 5.3

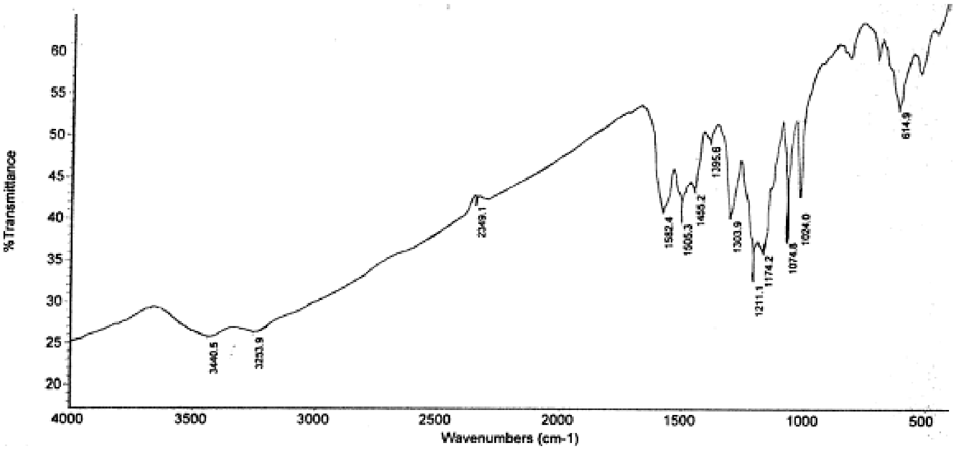


Figure 5.6 FTIR spectra for ED-SPAN synthesized in laboratory

Thus based on the results of the above characterization study the ED-SPAN was considered suitable for further experimentation and use as ionomer for preparing AFP formulations in this study.

CHAPTER 6

RESULTS AND DISCUSSION

The entire work has been divided into two parts. The results of each part have been separately discussed under separate subheadings. The entire study has been divided as follows:

- Part I-Leaching and corrosion study for preliminary elimination of additives
- Part II-Optimization of afp formulation with selected additives

6.1 Leaching and Corrosion Study for Preliminary Elimination of Additives

The first part of this study involved the understanding of the behavior of the additives selected for antifouling formulations and preliminary elimination of those additives which (based on a series of tests as described in Chapter 4,) failed to establish long-term efficiency for antifouling. The elimination/selection process was also governed by formulating issues encountered while formulating the antifouling paints; viz. compatibility with other additives, influence on coating topography, performance in the leach study and accelerated leach-rate study in generating a sustainable leach rate and impact on corrosion-resistance and mechanical properties of the paint system. The additives selected for controlling the leach rate of copper were used to formulate into afp as described in the Table 6.1 below and subject to all the above mentioned experiments for close scrutiny.

Table 6.1 Formulations used in Part I study

Formulation	Composition/ Chemistry	Type	Group
Sample 1 IRCUFIB	42.75 % wt. $Cu2O$ (Interlux Fiberglass Bottomkote)	Commercial Baseline	Group 1
Sample 2 AM42CU	42.75 % wt. $Cu2O$ in Amercoat 238	Internal Baseline	
Sample 3 AM30CU	30.0% wt. Cuprous oxide in Amercoat 238	Control	
Sample 4 AM30CU5DDP	30.0 % wt. Cuprous oxide + 5 % wt. CuDDP in Amercoat 238	Additive	Group 2
Sample 5 AM30CU5VIS	30.0 % wt. Cuprous oxide + 5% wt. Viscoplex in Amercoat 238	Additive	
Sample 6 AM30CU15IO T	30.0% wt. Cuprous oxide +15 % wt. ED-SPAN in Amercoat 238 Top coat	Additive	Group 3
Sample 7 AM30CU15IO B	30.0% wt. Cuprous oxide +15 % wt. ED-SPAN in Amercoat 238 Blend	Additive	
Sample 8 AM30CU5DDPVIS15IO B	30.0% wt. Cuprous oxide + 5 % wt. CuDDP + 5% wt. Viscoplex + 15 % wt. ED-SPAN in Amercoat 238 Top Blend coat	Additive	

6.2 Morphology before leach study

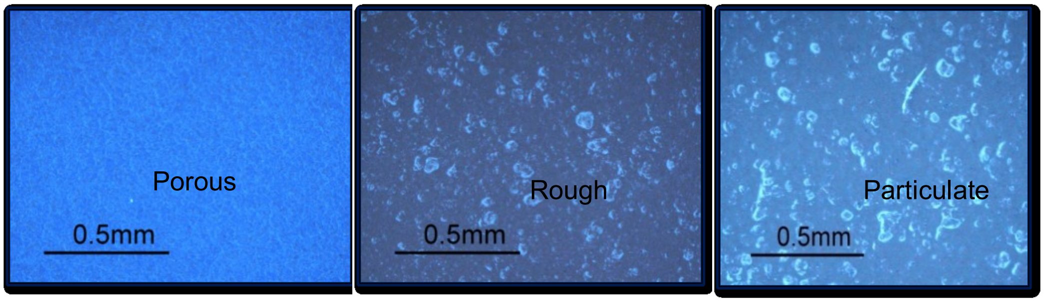
The role of additives in the paint formulation was examined in the context of morphological changes in the structure of the paint. Any changes in microstructure or composition can impact the topography, surface characteristics, roughness, porosity and mechanical properties such as elastic modulus , hardness etc. Changes in these properties can significantly affect the performance of the coating system in water. The outcome from the morphological and structural study will be used to determine the parameters in the optimization study.

6.2.1 Physical Appearance/ texture

The visual observations while sample preparation and thereafter gave some insight to the property changes brought about by the introduction of different additives. The commercial paint (sample 1: IRCUFIB) was very easy to spray and spread and generated a continuous uniform thin film that had a porous appearance and a fine texture. The film scratched easily but did not flake or crack. The control formulations (Sample 2: AM42CU and Sample 3: AM30CU) generated a continuous film but were thicker; less porous and higher in roughness of texture, in particular AM42CU. These films also demonstrated resistance to scratching or flaking.

The additives CuDDP (AM30CU5DDP) and Viscoplex (polyalkyl methacrylate in mineral oil (AM30CU5VIS) demonstrated very different properties in terms of appearance and texture. The paint formulation with 5% CuDDP was relatively difficult to spray and formed a more irregular surface as compared to the control samples. Although not porous, the film appeared rough, flaked easily and possessed a more brittle nature. In contrast the formulation with 5% PAMA (Sample 5) was easy to spray and generated a very smooth hydrophobic film with glossy surface and low porosity. The film was resistant to scratching and flaking.

Optical microscope images before seven day leaching



Sample1 Sample 2 Sample 3

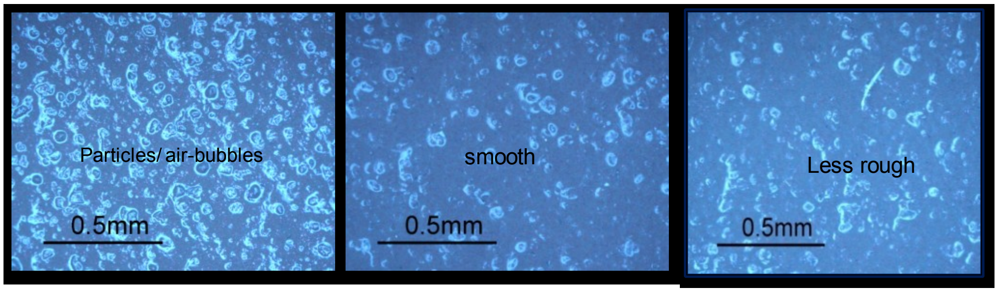
Before test

Sample 1 : Commercial paint
Sample 2 : Paint + 42% Cu_2O
Sample 3 : Paint + 30 % Cu_2O

Figure 6.1 Optical Images of control formulations before leaching

The formulations with Ionomer as an additive were coated in two different ways to ascertain the performance from both approaches. The details of the coating procedure are described in Chapter 4 sectio**n 4.4** The Ionomer which comprised of low specific gravity ED-SPAN was difficult to spray due to it particulate nature. Due to high particulate loading with Ionomer and Cu2O, AM30CU15IO B had poor spreading and demonstrated cracking of the paint film **(Fig.6.3).** The paint matrix in this case seemed insufficient to bind the particulates and failed to generate a continuous film. The paint film for AM30CU15IO T showed no cracking was rough with little particle agglomerates on the surface. Both these paint films were soft and had no tendency of flaking or brittleness.

Optical microscope images before seven day leaching



Sample 4 Sample 5 Sample 3

Before test

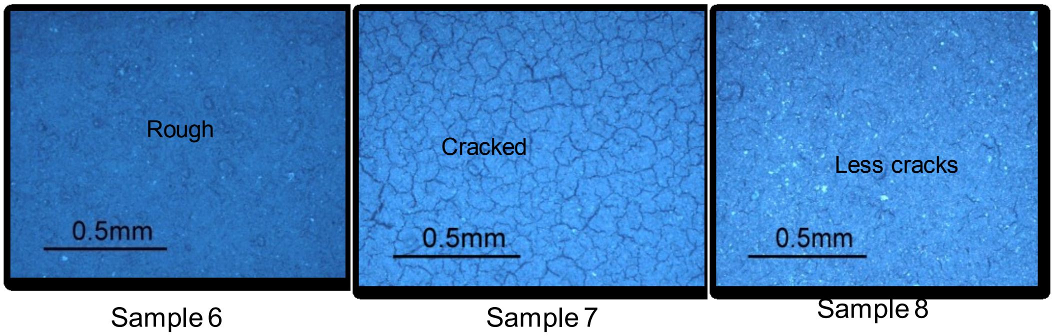
Sample 4 : Paint + 30% Cu_2O + CuDDP
Sample 5 : Paint + 30% Cu_2O + Vis
Sample 3 : Paint + 30 % Cu_2O

Figure 6.2 Optical Images of additive formulations before leaching

The film for Sample AM30CU5DDPVIS15IO B which combined all additives (Table 6.1) in a blend comprised of only 40% of the base paint matrix. The paint film showed fewer cracks and was more uniform. The texture of the film was rough, but no brittleness was evident.

The optical microscopic images of the 8 samples (Fig.1, 2 3) are in agreement with the visual observations. The scratch properties and brittleness was inspected for all eight formulations while scribing them for corrosion study as discussed in section 4.7.

Optical microscope images before seven day leaching



Before test

Sample 6 : Paint + 30% Cu_2O+Ionomer (T)
Sample 7 : Paint + 30% Cu_2O+Ionomer (B)
Sample 8 : Paint + 30 % Cu_2O +Ionomer + CuDDP +VIS

Figure 6.3 Optical Images of ionomer/additive formulations before leaching

6.2.2 Topography of sample Formulations

The visual observations while sample preparation and after gave some insight to the property changes brought about by the introduction of different additives.

Sample 1 (IRCUFIB): The commercial paint sample contains 43% Cu as one of its active ingredients. The paint film appeared continuous but porous before corrosion (as seen from the SEM and optical profilometer images below).

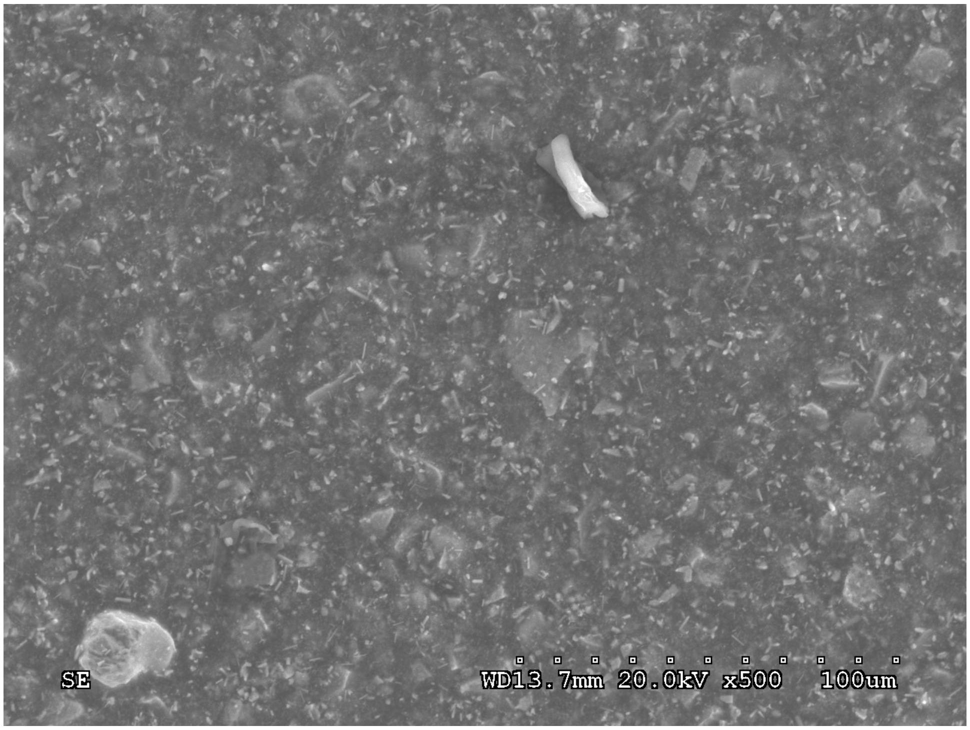
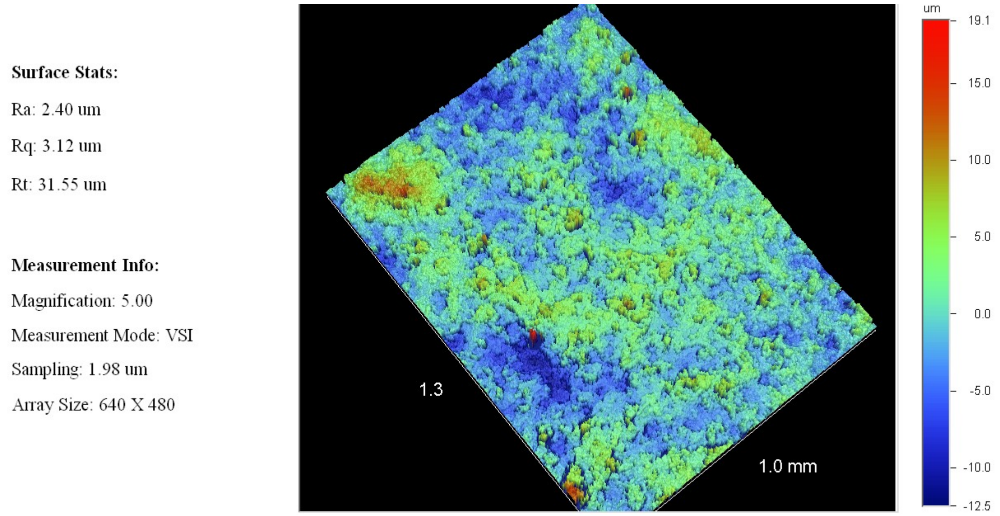


Figure 6.4 SEM Image of topography commercial formulation before leaching

The surface roughness was 2.4 um. The SEM image depicts a uniform & dense packing of materials of different composition as seen by the contrast in shades of different parts of the surface. The brighter particles (needle shaped) could be of copper (high molecular weight compared to other ingredients). This is also confirmed by the EDS-Maps for distribution of different elements (Cu, Mg, Na, and Ca) across the surface. Thus as expected the EDS-maps reveal a very dense and uniform distribution of copper throughout the surface while concentrations of Ca, Mg and Na are fairly low.


Surface Stats:

Ra: 2.40 um

Rq: 3.12 um

Rt: 31.55 um

Measurement Info:

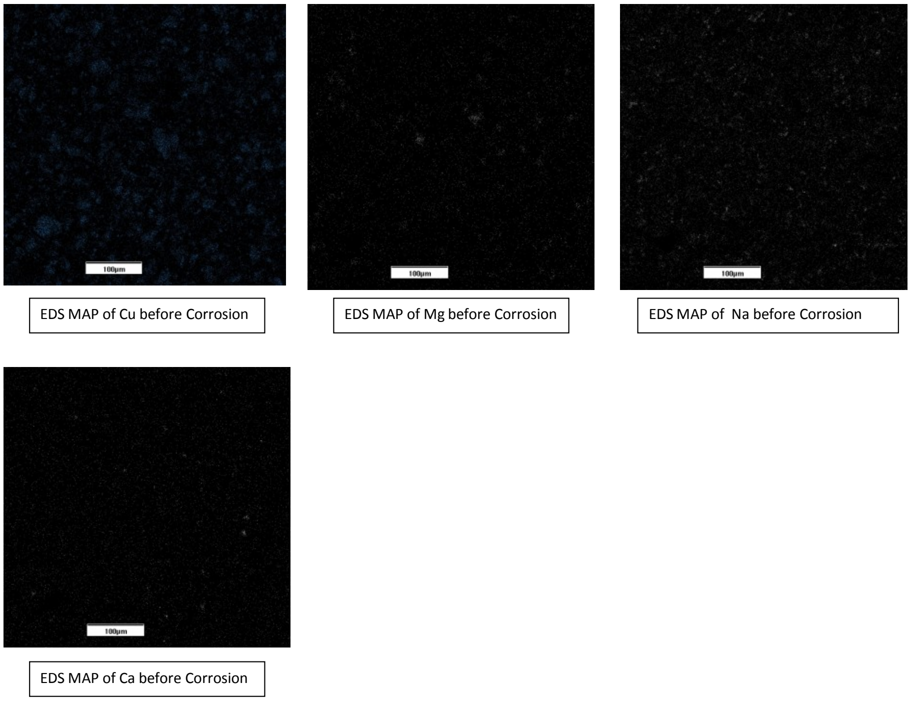
Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.5 Optical profilometer image of topography of sample 1 before leaching



EDS MAP of Cu before Corrosion

EDS MAP of Mg before Corrosion

EDS MAP of Na before Corrosion

EDS MAP of Ca before Corrosion

Figure 6.6 EDS maps of sample 1 before leaching

Sample2/ Control (AM42CU): The control sample formulation with 43% Cu_2O comparable to the commercial sample (surface roughness 1.8um from optical profilometer) with dense distribution of particulate matter all over the surface. From the EDS-maps the particles contributing to the rough topography appear to be that of Cu_2O as seen by its distribution. The surface appears free from voids, pores, cracks or and the salt concentration is almost negligible

Sample 3/ Control (AM30CU): The control paint sample contains 30% Cu as one of its active ingredients. The SEM image and the optical profilometer image show the surface to be rough and uneven as seen by the presence of undulations throughout the surface.

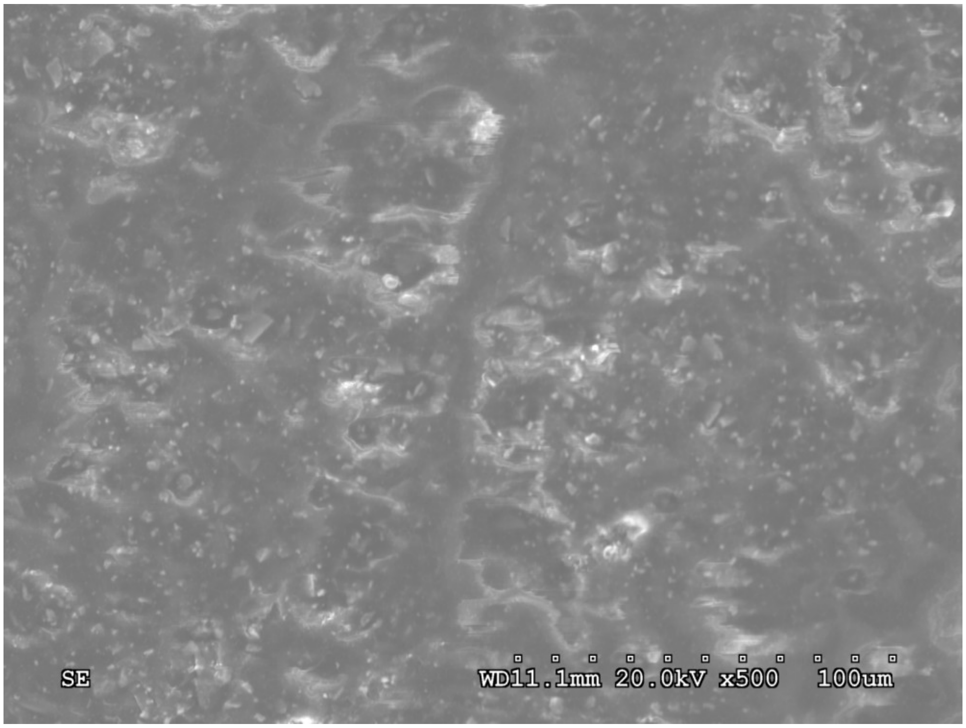
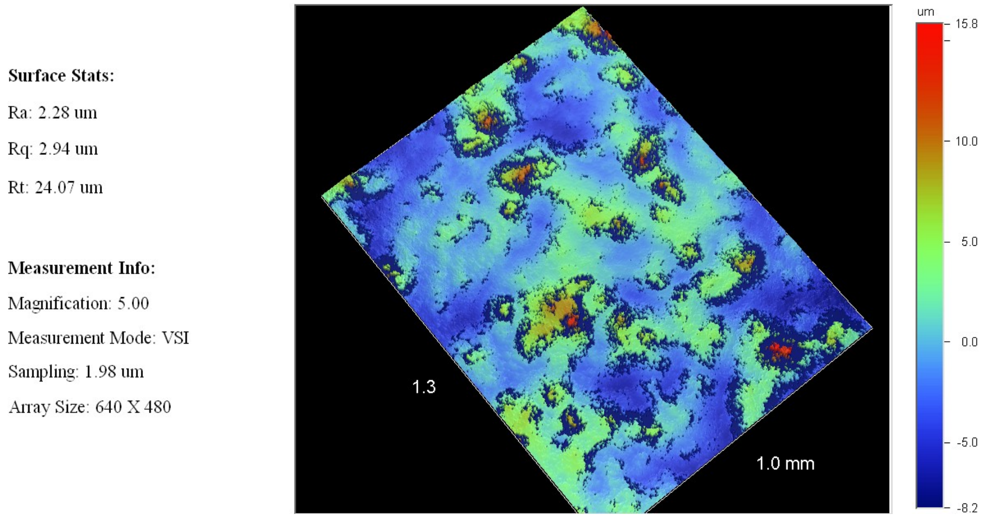


Figure 6.7 SEM Image of topography Sample 3 before leaching



Surface Stats:

Ra: 2.28 um

Rq: 2.94 um

Rt: 24.07 um

Measurement Info:

Magnification: 5.00

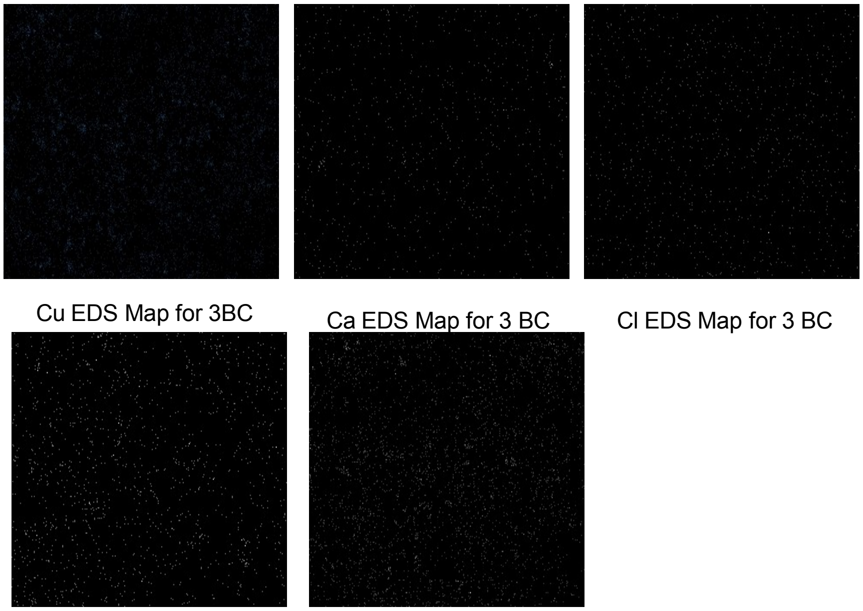
Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.8 optical profilometer image of topography of sample 3 before leaching

The surface roughness is about 2.28 um as seen from the profilometer 3D profile. The surface shows no evidence of salt deposits (SEM Image) and the low concentration distribution of Na, Ca, Mg and Cl on the surface.



Cu EDS Map for 3BC

Ca EDS Map for 3 BC

Cl EDS Map for 3 BC

Mg EDS Map for 3 BC

Na EDS Map for 3 BC

Figure 6.9 EDS maps of sample 3 before leaching

Sample 4 (5% CuDDP): The sample with CuDDP had a rough topography full of voids (SEM Image in leaching study 6.4)due to inconsistent spraying and air entrapment (due to particles blocking spray nozzle). The surface roughness was found to be 3.93 with the profilometer.

Sample 5 (5% Viscoplex) [AM30CU5VIS]: As discussed earlier, this sample appeared to be most smooth and low on roughness with visual observations. The surface roughness was 3.68um and the SEM image exhibited a less uneven topography. The surface was free from voids, pores and cracks.

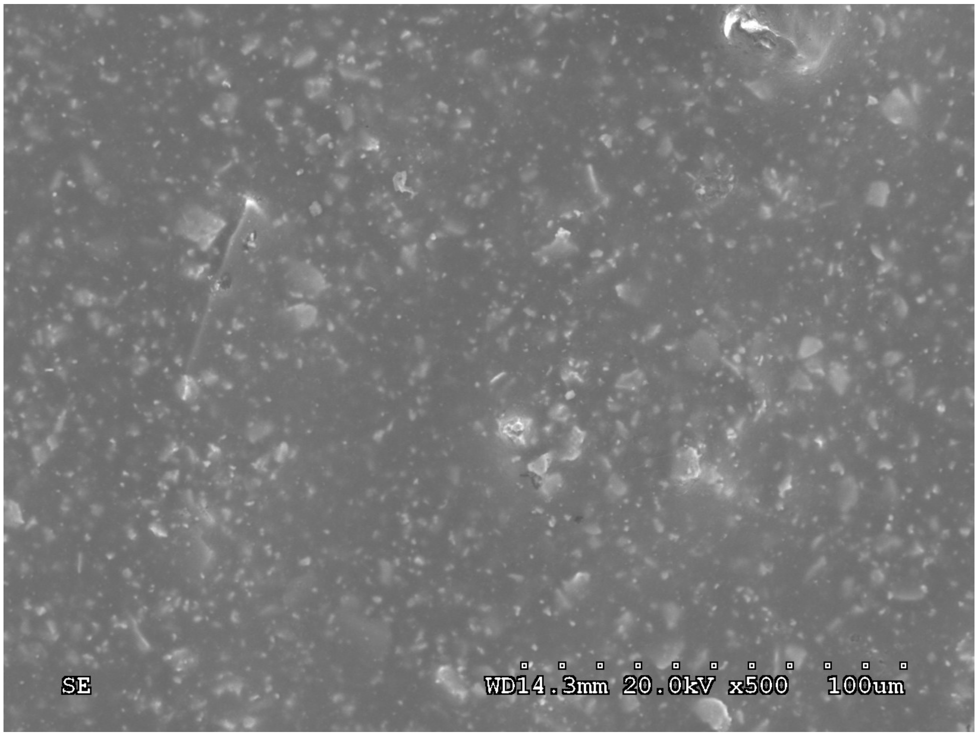
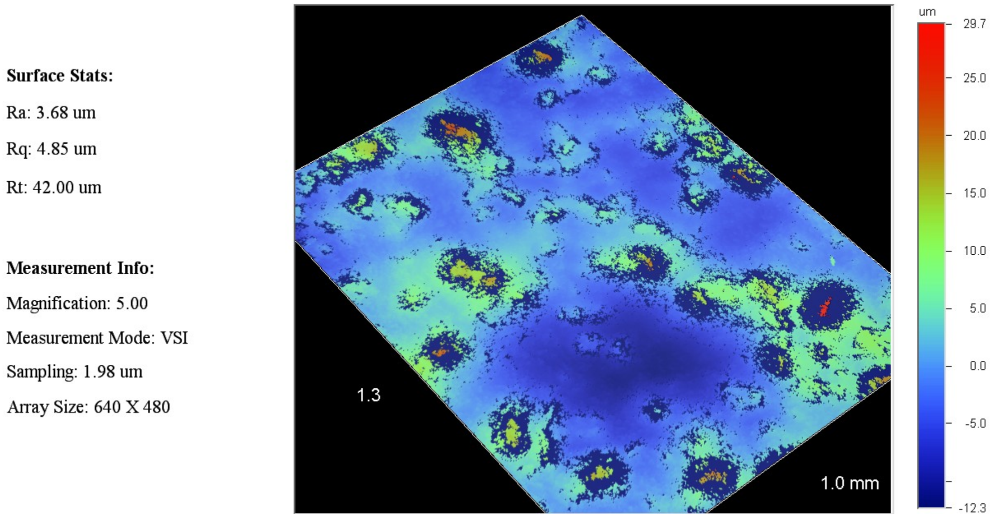


Figure 6.10 SEM Image of topography Sample 5 before leaching

The EDS maps depict a uniform distribution and dense packing of Cu throughout the surface while the elemental concentrations of Ca, Na, Mg and Cl were almost negligible, which is as expected before corrosion.



Surface Stats:

Ra: 3.68 um

Rq: 4.85 um

Rt: 42.00 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.11 Optical profilometer image of topography of sample 5 before leaching

Sample 6 (15% Ionomer in Top Coat) [AM30CU15IO T]: This sample demonstrated a rough surface due to the amorphous Ionomer particles which saturated the paint.

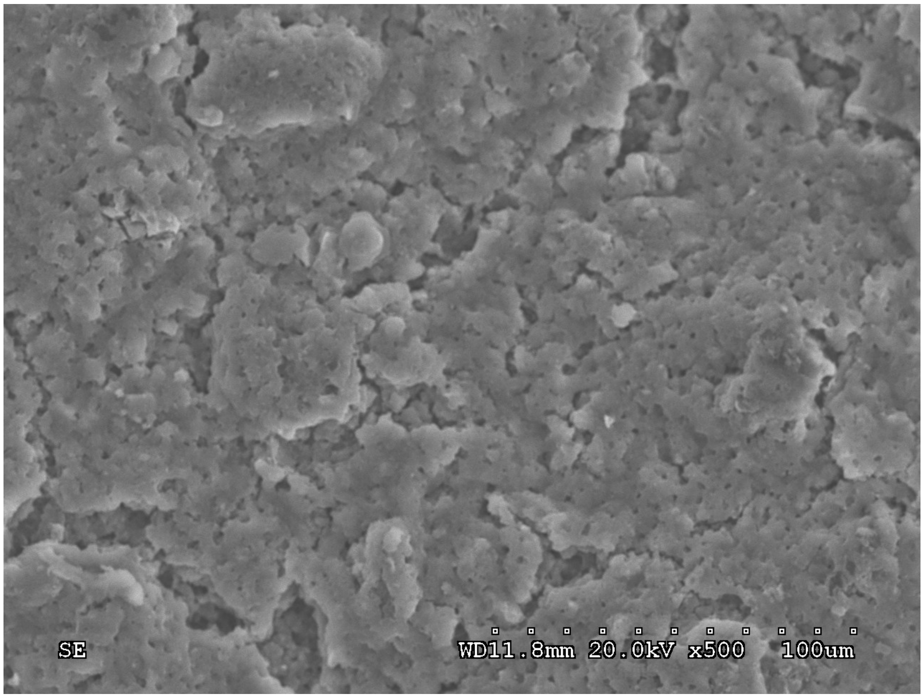
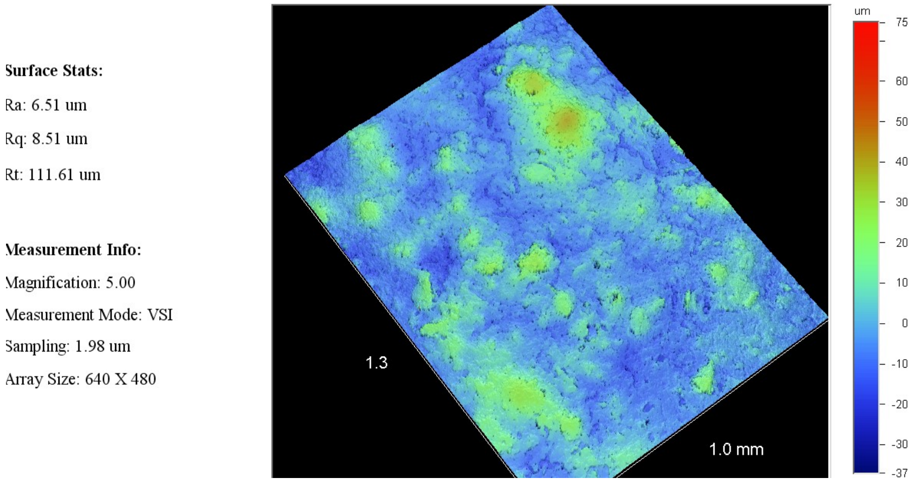


Figure 6.12 SEM Image of topography Sample 6 before leaching

The surface comprised of small pin holes (Profilometer Image below) and few hair line cracks on some parts. As known from the chemistry, the EDS maps showed a negligible concentration of Cu (which is present in the underlying layer and not on top-most one) or any salt on the surface. The sulfur concentration across the surface is fairly uniform indicating uniform ionomer distribution.

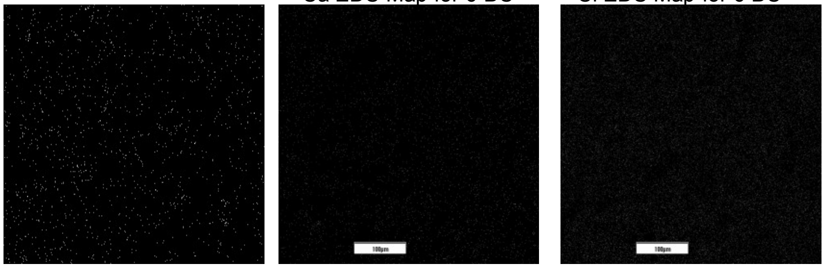


Surface Stats:
Ra: 6.51 um
Rq: 8.51 um
Rt: 111.61 um

Measurement Info:
Magnification: 5.00
Measurement Mode: VSI
Sampling: 1.98 um
Array Size: 640 X 480

Figure 6.13 Optical profilometer image of topography of sample 6 before leaching

Cu EDS Map for 6 BC
Ca EDS Map for 6 BC
Cl EDS Map for 6 BC



Mg EDS Map for 6 BC
Na EDS Map for 6 BC
S EDS Map for 6 BC

Figure 6.14 EDS maps of sample 6 before leaching

Sample 7 (15% Ionomer as blend) [AM30CU15IO B]: As discussed in physical observations, this sample showed a very rough and cracked surface with a dense distribution of copper and sulfur (from Ionomer) all over the surface showing a homogeneous composition. The cracked surface topography appeared as if it would exhibit poor corrosion behavior and uncontrolled leaching performance.

Sample 8 (all additives in a blend) [AM30CU5DDPVIS15IO B]: This sample with all additives in a blend had a rough topography with some cracks.

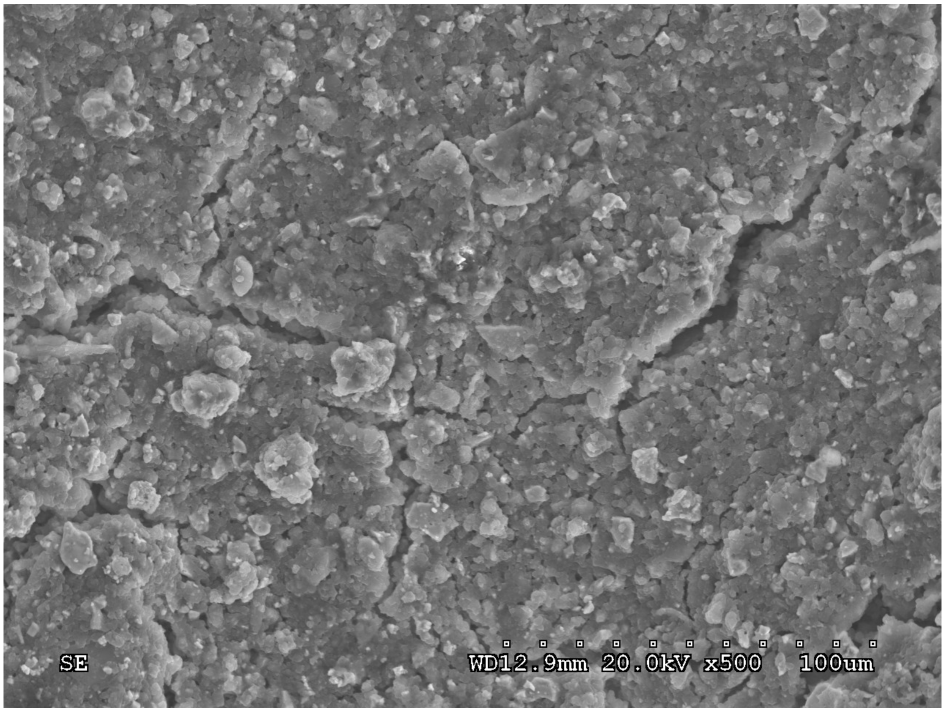
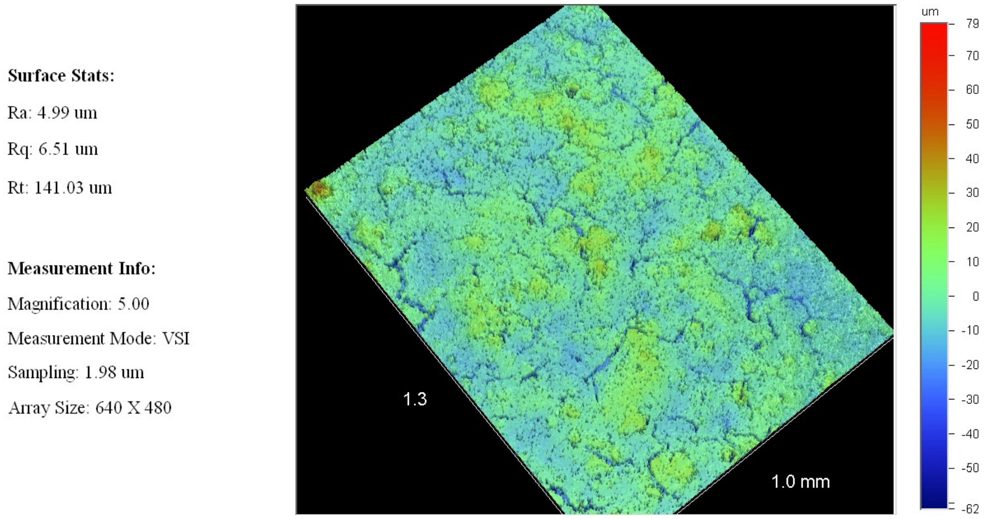


Figure 6.15 SEM Image of topography Sample 8 before leaching

The small particles on top of the continuous matrix likely to be of copper oxide (as seen from the EDS Map of Cu below). The surface roughness is 4.99um which is higher than the control sample but lower than that Sample 6 (with only Ionomer top coat) or Sample 7 (Ionomer and copper oxide blend), although the concentration of binder (paint matrix for this sample is much lower. This could be due to Viscoplex which seemed to coat and bind all pigments and reduce the roughness contributed by them.


Surface Stats:

Ra: 4.99 um

Rq: 6.51 um

Rt: 141.03 um

Measurement Info:

Magnification: 5.00

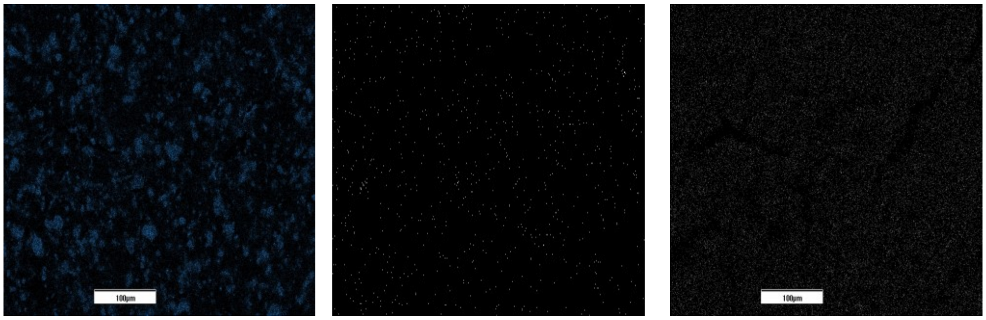
Measurement Mode: VSI

Sampling: 1.98 um

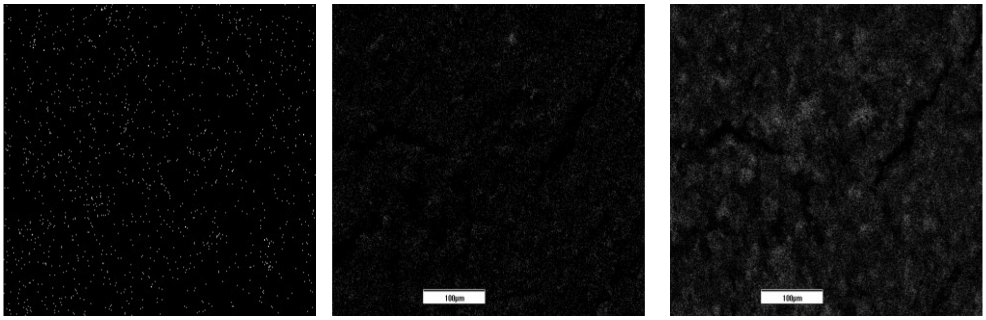
Array Size: 640 X 480

Figure 6.16 Optical profilometer image of topography of sample 8 before leaching

Sodium and chlorine is also uniformly distributed across the surface along with sulfur indication uniform distribution of Ionomer on the surface. Ca and Mg concentration is almost negligible confirming that the chloride concentration is not from their salts. The chloride salts could be from Ca and/or magnesium or from Na. In this case the Ionomer already would have some sodium chloride salt content owing to the ionic sulfonic acid group. If the cation were replaced by Ca or Mg to form $CaCl_2$ or $MgCl_2$ that would take place from sea water (which contains these ions) and could be indicative of some corrosion.



Cu EDS Map for 8 BC Ca EDS Map for 8 BC Cl EDS Map for 8 BC



Mg EDS Map for 8 BC Na EDS Map for 8 BC S EDS Map for 8 BC

Figure 6.17 EDS maps of sample 8 before leaching

6.2.3 Mechanical properties of formulations

One sample for each of the eight formulations was subject to single indentation tests as discussed in section 4.8.2. The indentation test results for all 36 indents were averaged to calculate the reduced elastic modulus. The average reduced elastic modulus for each formulation has been plotted against the sample no. in fig. 6.18. The reduced modulus values include error bars based on standard deviation.

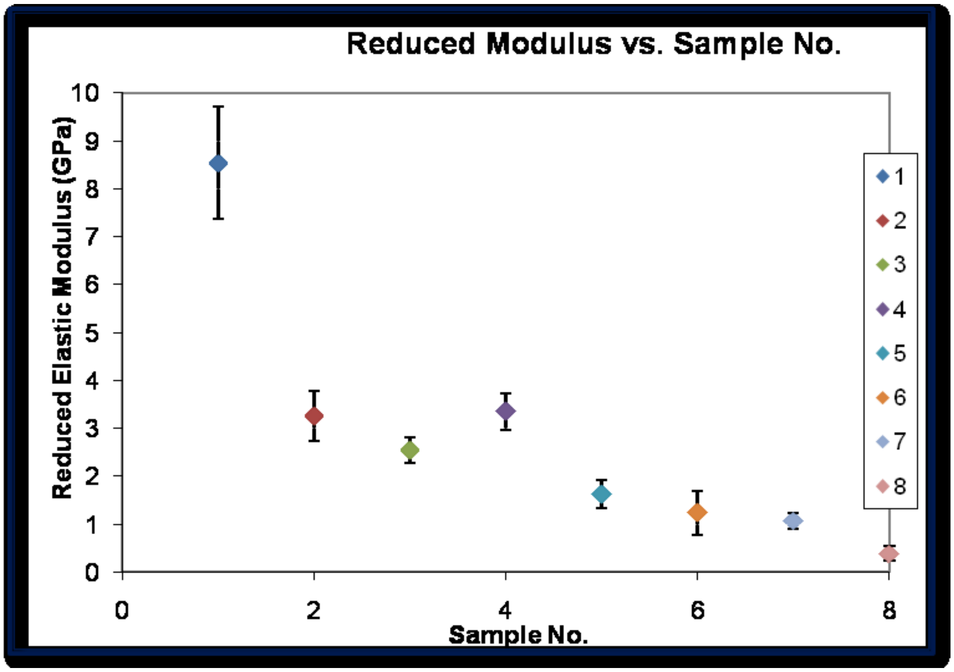


Figure 6.18 Reduced modulus of Part I study formulations before leaching

The variation in the reduced modulus of different samples can directly be assigned to the difference in additives per formulation, since all other parameters were kept constant. The commercial paint has the highest reduced modulus ~ 8.5 GPa. The reduced modulus of the control sample with 42% Cu_2O is about 3.5 GPa. The copper levels in the commercial and control samples being the same, the difference in reduced modulus is due to the difference in matrix and other ingredients of the paint recipe. The control sample with 30% Cu_2O is marginally lower than the control with 42% Cu_2O at ~ 2.5GPa. The difference between the two controls being only in the copper (I) oxide concentration, it may appear that higher copper level acts as a filler for the paint matrix thus raising its reduced modulus. The Er values for sample 4 containing 5% CuDDP with 30% Cu_2O is higher than the control with 30% Cu_2O depicting the influence of CuDDP in directly raising the E_r value. This can be attributed to the bulky CuDDP molecules which occupy the intermolecular spaces between the polymer chains and hinder the stress-relieving capability of the polymer chains by reducing the hydrodynamic volume.[62-64] Sample 5 containing PAMA, appears to have a lower reduced modulus compared to the control samples < 2GPa, perhaps an effect of the high molecular weight and viscosity of the material. A 5% concentration of Viscoplex (PAMA) significantly lowered the E_r values. Sample 6 with Ionomer in the top coat and Cu_2O in the underlying coat had an even lower value of E_r ~1 GPa and similar was the case with Sample 7 which had a blend of Cu_2O and Ionomer. The amorphous nature of ED-SPAN polymer chains filling the paint matrix at 15% concentration in addition to 30% Cu_2O lowered the Er values significantly. Finally in case of sample 8 which contains all additives at a total concentration of 55% with only 45% epoxy paint matrix altered the E_r value of the matrix to drop it from 2.5 GPa to <1GPa.

The range of variation of hardness of the commercial sample from the control and additive samples was much smaller than the reduced modulus (0.225-0.025 GPa). The trend for variation of hardness was as calculated from the averaged results of 36 single indentation tests was similar to that observed for reduced modulus as seen in fig.6.5; commercial sample having the highest hardness and the sample with all additives (sample8) being the lowest.

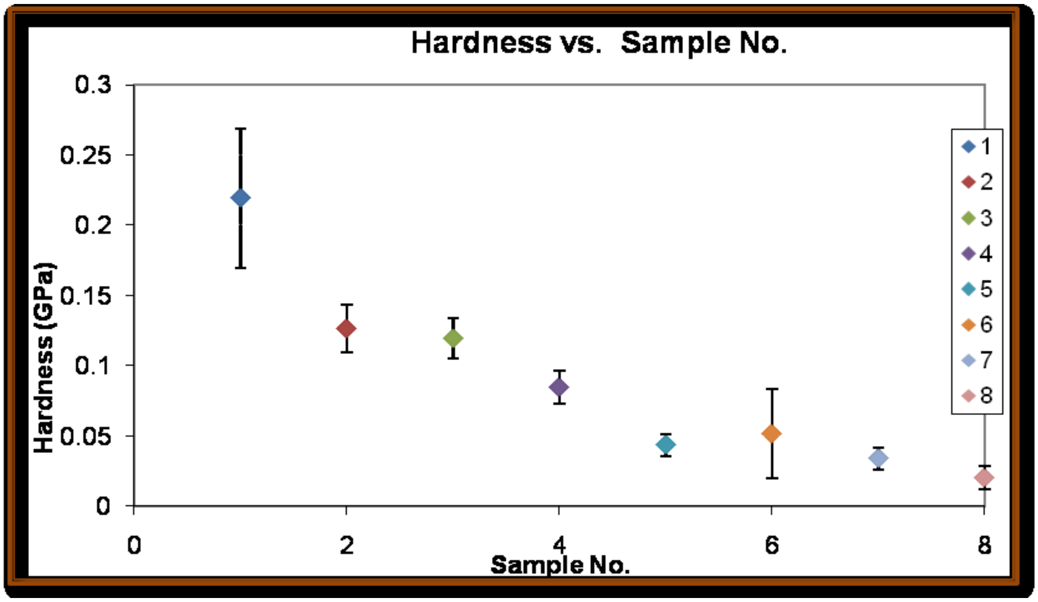


Figure 6.19 Hardness of Part I study formulations before leaching

6.3 Accelerated Leach Rate Test

The accelerated leaching test was performed using sodium glycinate salt solution in a highly alkaline pH (10.2) to accelerate the leaching of copper and dissolution of paint matrix. The test procedure has been described in chapter 4 section 4.6. After three days of ageing in sodium glycinate solution, 10ml of each sample was sent for ICP chemical analysis of copper in order to calculate the leach rate. A plot of the copper leach rate in mg/cm^2/3days from all 8 formulations vs. the sample no. can be seen below: Fig.6.20 The leach rate varies from 3.5mg/cm^2 – 0.07mg/cm^2. As discussed in the test procedure[67], the purpose of this tests is to be able to predict those formulations which will be able to leach sufficient copper to prevent fouling for at least 6-12 months by overcoming all diffusion barriers through matrix dissolution in water. As discussed earlier, 4.6. only those formulations leaching >1.3mg/cm^2 Cu in three days of the test would be able to survive the actual conditions with a sustainable leach rate for at least 6 months. Those less than 1.3mg may or may not last that long and would tend to foul instead.

From the plot it can be seen that the commercial paint shows a very high leach rate of about 3.5mg/cm2 in 3 days while all other formulations except sample 6 show a very low leach rate <1 mg/cm^2. The leach rate of the formulation 6 with 15% Ionomer as a top coat on an underlying coat containing paint with 30% Cu_2O is 1.2mg/cm^2 which is very close to the rate required for surviving 6-12 months in the marine environment. Thus based on the accelerated leaching test results it appears that the Ionomer formulation has a very good chance of surviving the actual marine conditions with an adequate copper leach rate and would be a good candidate for the optimization study.

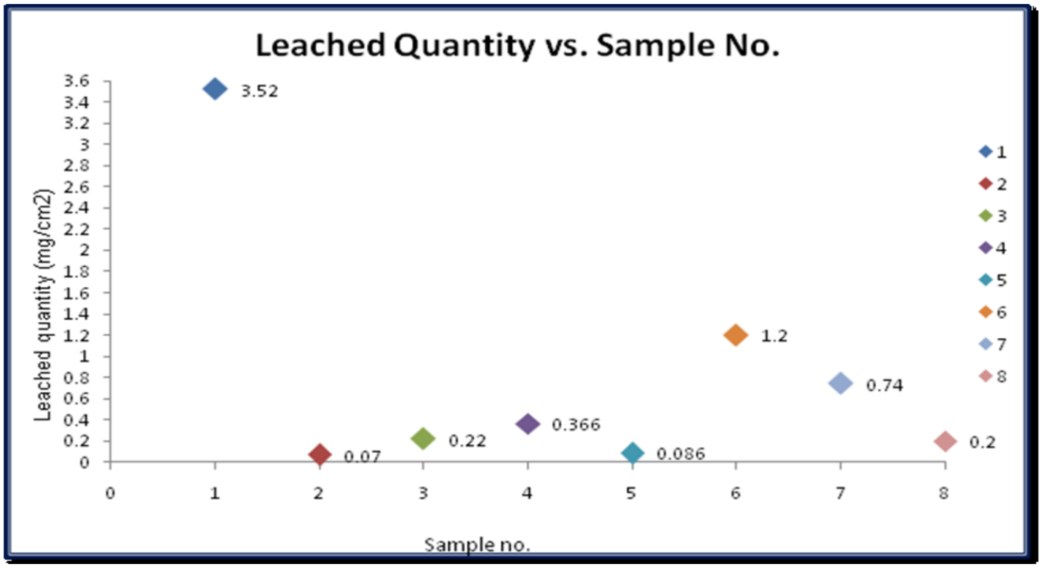


Figure 6.20 Plots of leach rate results from accelerated leaching test

Leached amount must be > 1.3mg/cm2 in 3 days

An important thing to note here that although the accelerated leaching test gives some idea for preliminary elimination of formulations which can and cannot survive the actual environment, yet it should not be completely used as a deciding factor and should instead be substantiated with regular leach-rate study data. The reason for this can be understood from the fact that this test relies on dissolving the paint matrix in a highly alkaline medium pH 10.2 and forming a copper complex with sodium glycinate. In this study however, all formulations are not comprised of equal proportions of the paint matrix; the commercial paint has 58% base paint and ingredients while the experiment formulations contain 45-70% base paint as there binder. Also it can be seen from the results that the Ionomer formulation (Sample 6) which has about 85% paint matrix on its top coat has generated a high leach rate while the control sample 2 with 58% paint has generated the lowest leach rate of 0.07mg. Also the formulation with Viscoplex which has 65% paint in its matrix has a very low leach rate of 0.08mg/cm2 clearly depicting the binding action of PAMA in reducing copper release. In case of sample 8 which has only 45% paint matrix, the leach rate should have been the lowest but is still 0.2mg/cm2 due to the presence of the Ionomer, which is water soluble and which assists matrix degradation, enhancing copper release and leach rate renewal.

Thus based on the accelerated leaching study it can be suggested that the Ionomer exhibits characteristics of assisting leach rate renewal and would be a suitable candidate for further trials. The Viscoplex also shows the ability of binding or controlling copper release and could help with controlling burst release; thus being a suitable candidate for the optimization study. The CuDDP sample shows neither strong binding characteristics nor good degradation characteristics. However, it should be realized that the accelerated test is not the most accurate measure for preliminary elimination and its results must be carefully analyzed before making any interpretations.

6.4 Copper Leach rate and Corrosion Study

The copper leaching and corrosion study was conducted as per procedure described in Chapter 4 Section 4.5. This study was performed to get a comprehensive knowledge of the behavior of different additives in controlling the leach rate of copper at various stages of immersion. Most of the AFP's developed so far have been unable to provide sufficient control on the burst release of copper resulting in excessive loss of copper in the early stages of immersion setting up diffusion barriers and causing loss of antifouling efficiency. From the leach study conducted with the 8 formulations it was observes that the burst release of copper occurs in the first 24 hours of immersion in water and thereafter the leach-rate drops to attain a steady state value. To estimate the leach-rate of copper at various stages, 10 ml water samples were collected on the 1st, 4th, 7th day of the study and the samples were sent for ICP analysis (section 4.5). The ICP copper analysis results for the leach- study have been combined in the table below 6.2

Table 6.2 Leach rates of copper for formulations in PART I study

Formulation	Leach rate ($ug/cm^2/day$) Day 1	Leach rate ($ug/cm^2/day$) Day 1-4	Leach rate ($ug/cm^2/day$) Day 4-7
Sample 1 Commercial (43% Cu)	31	10.3	9.6
Sample 2 Paint + 43% Cu_2O	49.6	18.1	1.0
Sample 3 Paint + 30% Cu_2O	31.0	2.1	3.0
Sample 4 Paint + 30% Cu_2O +5% CuDDP	18.2	6.4	1.7
Sample 5 Paint + 30% Cu_2O +5% Viscoplex	19.8	8.4	1.3
Sample 6 Paint + 30% Cu_2O +15% Ionomer (top coat)	9	3	3
Sample 7 Paint + 30% Cu_2O +15% Ionomer (blend)	238	53	50
Sample 8 Paint + 30% Cu_2O +15% Ionomer (top coat) +5% Viscoplex +5% CuDDP	108	1.0	18

A trend for copper leach-rate variation can be better understood from the plot of the leach-rates of different formulations Fig.6.21

From the leach rate data, the following can be interpreted:

- The commercial paint showed a very high leach rate. The porous spongy nature of the paint film as observed from the microscope images (6.1) and the knowledge that it comprises of hydrolysable binders like rosin; affirm the fact that there is high burst release of copper due to hydrolysis of the matrix (Ref. of rosin) and eventually the leach rate drops due to build up of diffusion barriers.

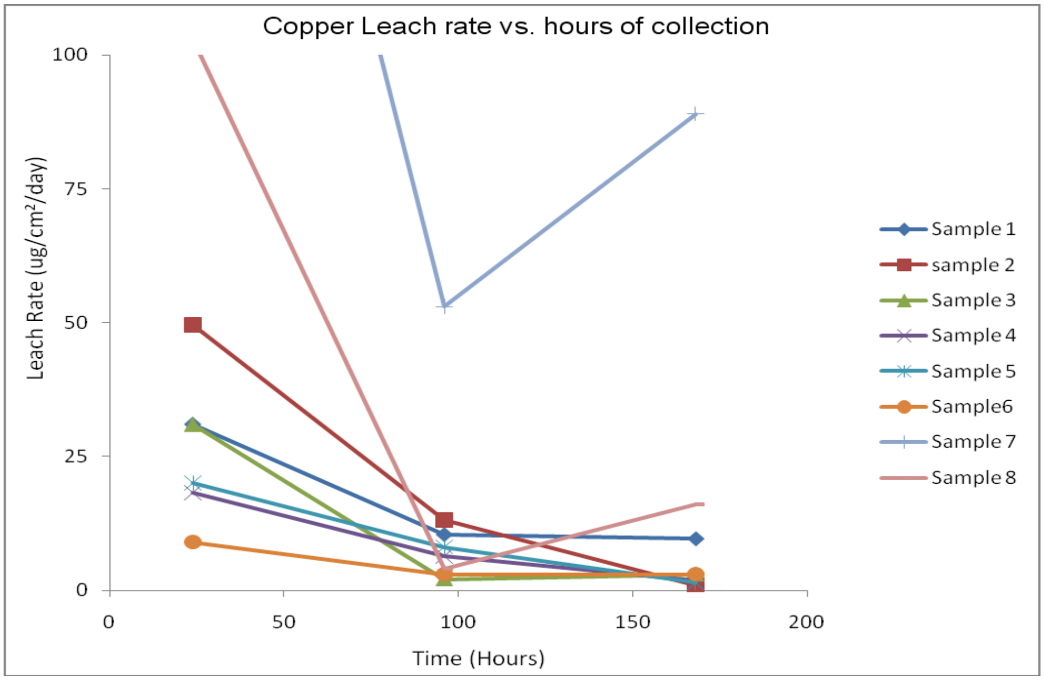


Figure 6.21 Plots of leach rate results from seven day leaching test

The steady state leach rate of 10ug/cm2/day is lower than the antifouling requirement of 15ug/cm2/day.

- The control sample with 42% Cu comparable to the commercial paint showed an even higher burst release of 50ug/cm2/day but the leach rate dropped significantly by the 4th and 7th day of the experiment. The higher concentration of Cu_2O in this formulation account for the higher burst release and the lack of hydrolysable binders which can help matrix degradation and leach rate sustainence explain the drastic drop in copper leach rate eventually. This is further supported by the weight/thickness plots discussed later which depict weight and thickness increase with time due to swelling and pore blockage instead of decreasing due to copper loss.
- The control sample with 30% Cu_2O (Sample3) produced a burst release comparable to the commercial sample inspite of the lower copper concentration due to lack of binding elements in the matrix. The set-up of diffusion barriers once again caused leach rate

drop eventually. Due to lack of hydrolysing components like rosin the drop in leach rate was higher than the commercial sample(31ug- 3 ug).

- The leach rate trend for Sample 4 with 5% CuDDP in addition to 30% Cu_2O follows a similar pattern with the difference that it has a much lower burst release rate, which drops down even further through day 4 and day7. This trend for CuDDP finds explanation from the fact that it is a bulky molecule dispersed through the paint matrix, restricting the rapid release of copper from the paint. The drop in the leach rate eventually is again due to insufficient degradation of paint matrix and diffusion barriers for reasons described above. Thus, although this formulation shows some control on burst release, it doesn’t aid leach rate renewal at all. The corrosion-resistance for this sample was also observed to be poor and will be discussed subsequently in section 6.5.
- The burst release rate of Sample 5 containing 5% PAMA (Viscoplex) showed a significant drop when compared to the control sample although; the two contain the same proportion of copper. This clearly indicates the binding tendency of the high viscosity PAMA. The high viscosity of PAMA would likely be binding the particulate matters of the formulation; in this case Cu_2O and reducing the unrestrained release upon immersion. The binding effect of PAMA however continues so that the leach rate drops even further through the 4th & 7th day of experiment due to diffusion barriers. Unlike Sample 4, this formulation showed no visible evidence of corrosion and appears a suitable candidate as a binder for burst release control
- The formulation with 15% Ionomer in the top-coat and 30% Cu_2O in the underlying coat produced a low burst release rate of copper which dropped even more in due course of the test. Thus at a first glance even though it seems from the initial data that the ionomer two-coat system fails to give an adequate leach rate for antifouling; a closer examination reveals, that the top-coat of sample 6 contains 85% of insoluble epoxy

paint matrix which doesn't allow water to penetrate within and dissolve copper oxide from the underlying layer. Only those parts of the matrix which contain the ionomer, dissolves in water on immersion and allows copper to be leached. From this perspective it appears that with only 15% ionomer concentration the formulation still gave a good release rate. This data is in agreement with the hypothesis which expects ionomer to dictate controlled release of copper. The ionomer can be a suitable candidate for optimization study since there are several alternatives of reducing the matrix content or increasing the ionomer concentration to cause more matrix breakdown and raise the leach rate to the desired value.

- The formulation with a blend of ionomer and Cu_2O had a poor surface coverage due to improper spreading and cracking of the paint film. This was due to a high amount of loading (45%) with powdered material and insufficient matrix to bind the additives. Since the paint film was cracked a high leach rate was expected. Keeping with the expectation the burst release rate of sample 7 turned out to be 238ug/cm2/day which dropped down to 50ug at the end of the study. The blend didn't work well and the lack of a binder which could coat the particles and bind them to the matrix to produce a continuous film was realized.
- The last formulation combined the effects of all additives. It included CuDDP and PAMA which as seen for sample 4&5 reduced the burst release and it also had ionomer which as seen with sample 6&7 enhanced release by matrix dissolution, The burst release for this sample was still very high 108ug/cm2/day but then the release rate dropped significantly on the 4th day and balanced at 18ug/cm2/day on the 7th day. The mechanism occurring in this leach process can be explained as follows: the formulation comprises of very little paint matrix to bind all the additives, thus generating uncontrolled burst release also seen in case of control sample2. In spite of the low matrix content, the binding effects of PAMA and CuDDP help reduce the burst release

to some extent so that it is less than what was seen for sample7. Thus once again the binding action of PAMA and CUDDP were clearly established. The high release set-up heavy diffusion barriers dropping the leaching process to negligible. But after the 4th day the leaching renews to a rate of 18ug/cm2/day. This could be due to a wetting period for the ionomer; which finally starts dissolving after the 4th day of immersion in water and sustains the copper release at the desired value of 18ug/cm2/day. These results also lead to the belief that the ionomer and PAMA would be suitable additives for optimization study where one possesses the ability to restrict copper release and other possesses the ability to renew it.

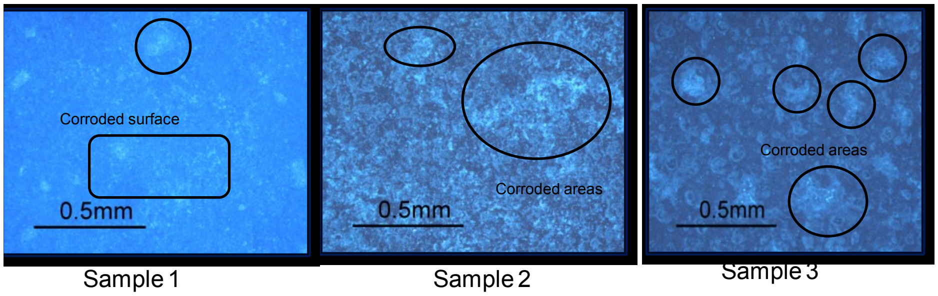
6.5 Morphology after leach study

6.5.1 Physical Appearance/ texture

The visual observations after the leaching experiment tell a great deal about the nature and influence of the additive on the overall performance of the paint. The commercial paint (sample 1: IRCUFIB) was significantly corroded, although there was no evidence of rusting or cracking/peeling, there was white scaling on the surface and an increase in the porosity and roughness of the texture. The control formulations (Sample 2: AM42CU and Sample 3: AM30CU). Of these two controls the sample with higher percentage of copper oxide seemed to have extensively corroded with some rusting on the corners and a visible erosion and roughness of parts. This can be seen from the optical images (below) taken after corrosion. The control with 30% Cu_2O did not corrode as much and had a relatively smoother texture with fewer erosion/pitting sites compared to sample2.

The additives CuDDP (Sample 4) and PAMA (Sample 5) again demonstrated very different properties in terms of appearance and texture after the leaching study. Sample 4 with 5% CuDDP showed heavy corrosion and rusting. A part of its film had disintegrated due to excessive brittleness. The surface showed larger irregularities and pits. In contrast the formulation with 5% PAMA (Sample 5) was on the lower side of corrosion and pitting. The surface appeared as intact and smooth as it was before corrosion. Optical microscope images reveal small corroded sites but there was no cracking, peeling or rusting of sample as seen from images below.

Optical microscope images after seven day leaching



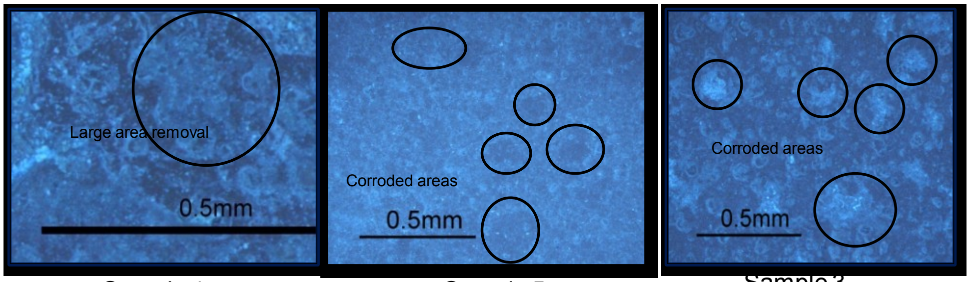
Sample 1 Sample 2 Sample 3

After test:

Sample 1 : Commercial paint
Sample 2 : Paint + 42% Cu_2O
Sample 3 : Paint + 30 % Cu_2O

Figure 6.22 Optical Images of control samples after leaching

Optical microscope images after seven day leaching



Sample 4 Sample 5 Sample 3

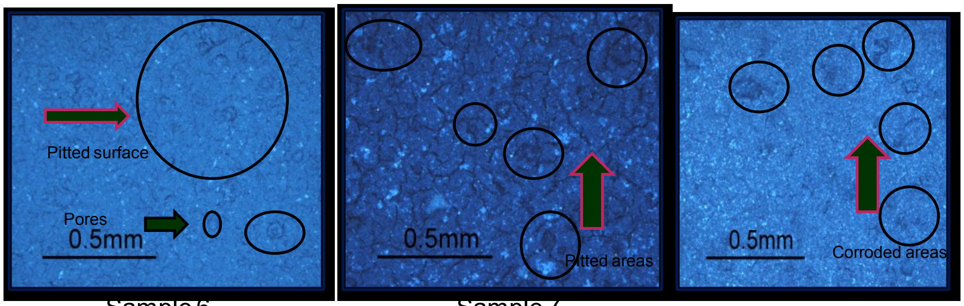
After test

Sample 4 : Paint + 30% Cu_2O + CuDDP
Sample 5 : Paint + 30% Cu_2O + Vis
Sample 3 : Paint + 30 % Cu_2O

Figure 6.23 Optical Images of additive formulations after leaching

The formulations with Ionomer as an additive showed different behavior. As discussed earlier Sample 7 which had a cracked surface to start with was most corroded among the three but with no rusting, blistering or peeling of paint film. Sample 6 with Ionomer as top coat showed very little evidence of corrosion. There was no rusting, cracking etc. and optical images reveal micro pores on the surface (likely by ionomer dissolution in water) which could have served as the source for copper release. Sample 8 with all additives in a blend also maintained integrity after leaching and showed larger micro pores on the surfaces in its optical images. A smaller concentration of the paint matrix would have been the reason for extensive disintegration of surface and higher porosity. This sample also demonstrated no rusting or brittleness after leaching.

Optical microscope images after seven day leaching



Sample 6 Sample 7 Sample 8

After test

Sample 6 : Paint + 30% Cu_2O+Ionomer (T)
Sample 7 : Paint + 30% Cu_2O+Ionomer (B)
Sample 8 : Paint + 30 % Cu_2O +Ionomer + CuDDP +VIS

Figure 6.24 Optical Images of Ionomer/additive formulations after leaching

6.5.2 Topography of sample Formulations after leaching

The visual observations after the leaching study gave some insight to the property changes brought about by the introduction of different additives.

<u>Sample 1 [IRCUFIB]:</u> The paint film for the commercial sample after leaching for seven days appeared continuous but corroded (as seen from the SEM and optical profilometer images below). The surface roughness was lowered slightly 1.96 um due to ironing out of the irregular surface geometries after erosion in water. The SEM image reveals the presence of salt deposits on the surface.

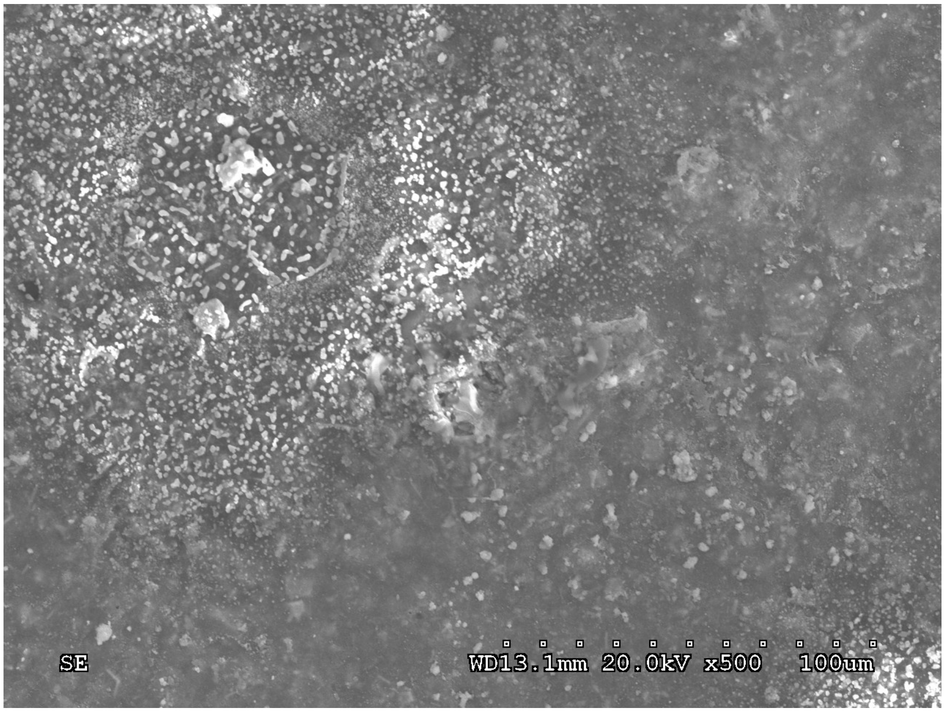
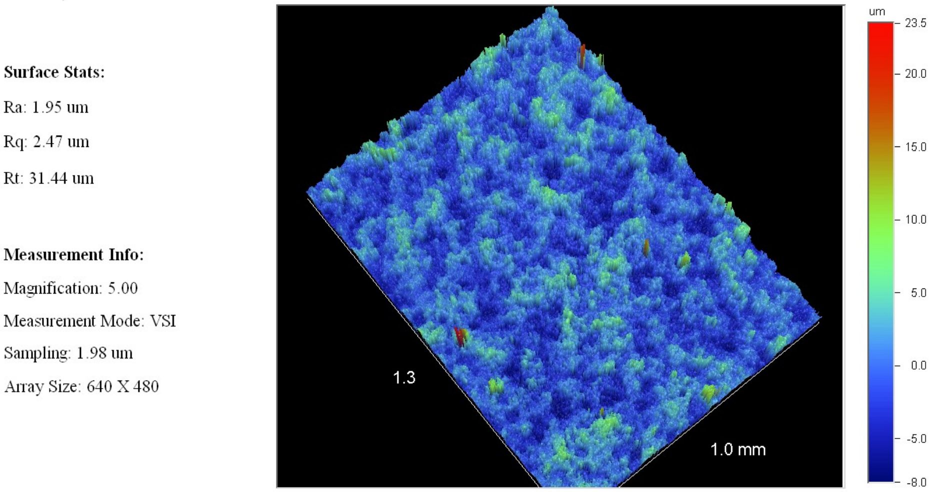


Figure 6.25 SEM Image of topography of Sample 1 after leaching


Surface Stats:

Ra: 1.95 um

Rq: 2.47 um

Rt: 31.44 um

Measurement Info:

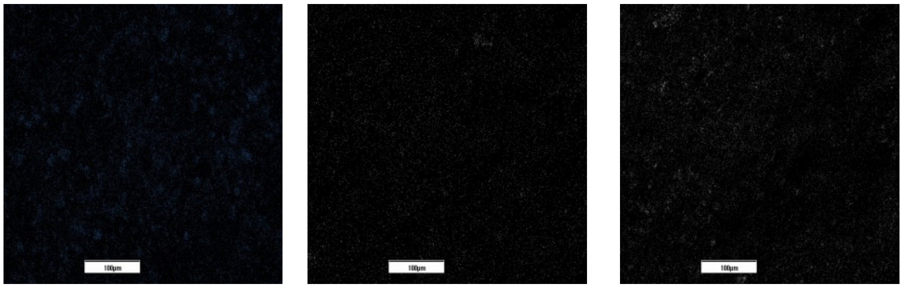
Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

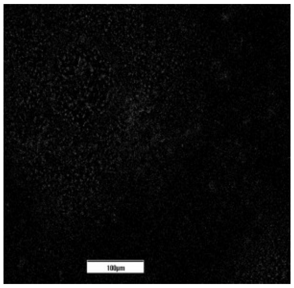
Figure 6.26 Optical profilometer image of topography of Sample 1 after leaching



EDS MAP of Cu after Corrosion

EDS MAP of Mg after Corrosion

EDS MAP of Na after Corrosion



EDS MAP of Cl after Corrosion

Figure 6.27 EDS maps of Sample 1 after leaching

The EDS map for Cu reveals a drop in the concentration of Cu across the surface (decrease in the density of packing) especially decrease in the size and number of agglomerates of copper on the surface. Both the SEM and profilometer images reveal the presence of small pits/depressions on the surface likely created during erosion/removal of agglomerates due to dynamic force of water in the leaching bath. Also the concentration of salt deposits in the vicinity of the depressions/pits explains preferential corrosion at those sites.

<u>Sample 2 (Control Sample) [AM42Cu]:</u> The control sample with a higher concentration of copper oxide showed greater roughness and underwent more corrosion and leaching as seen from the results above. The surface had large erosion sites with excessive salt deposits.

<u>Sample 3 (Control Sample) [AM30CU]:</u> The control sample with 30% wt. of copper oxide showed lower roughness and underwent less corrosion and leaching as seen from the results in the previous sections. The surface had relatively smaller erosion sites with salt deposits (as

seen in the SEM images and EDS maps). The surface roughness after corrosion increased from 2.28 to 4.43um.

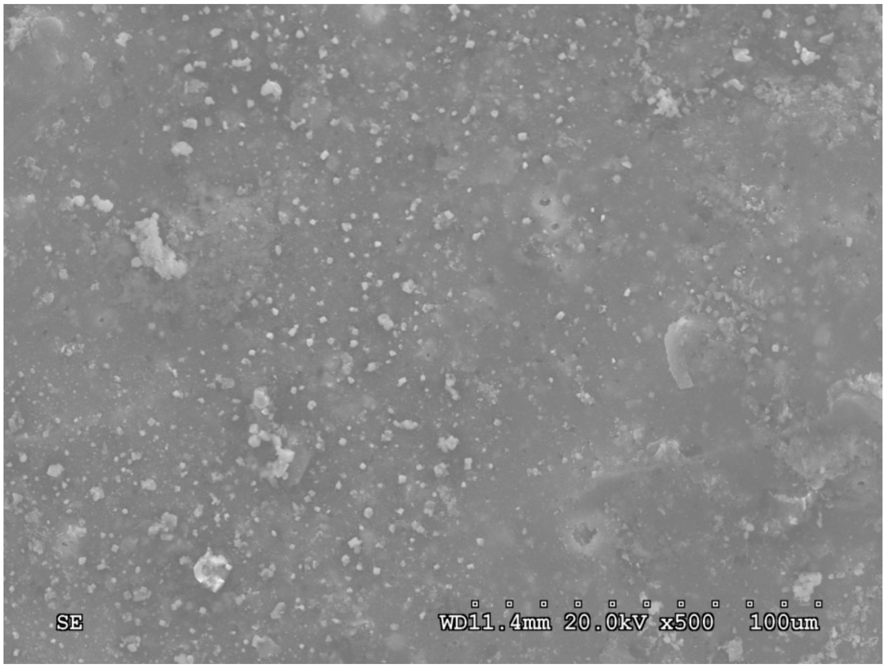
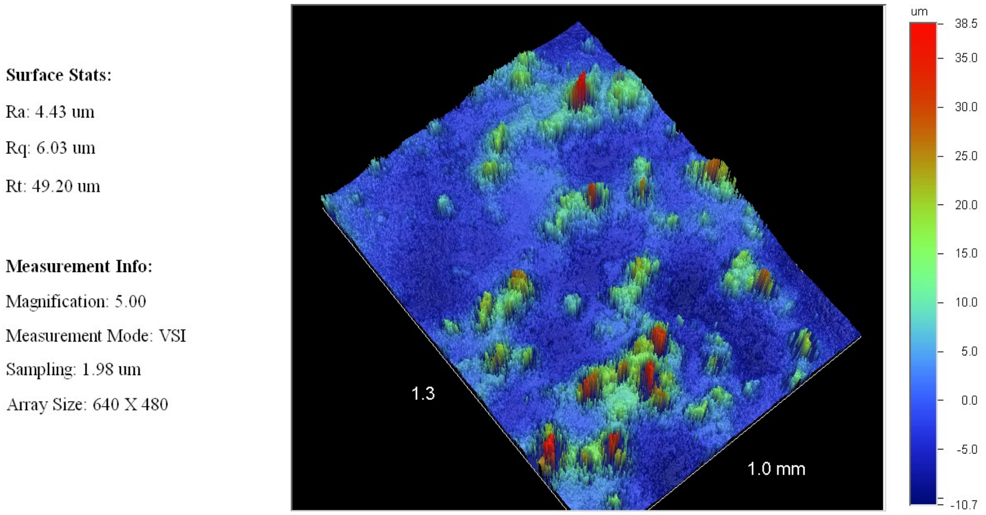


Figure 6.28 SEM Image of topography of Sample 3 after leaching



Surface Stats:

Ra: 4.43 um

Rq: 6.03 um

Rt: 49.20 um

Measurement Info:

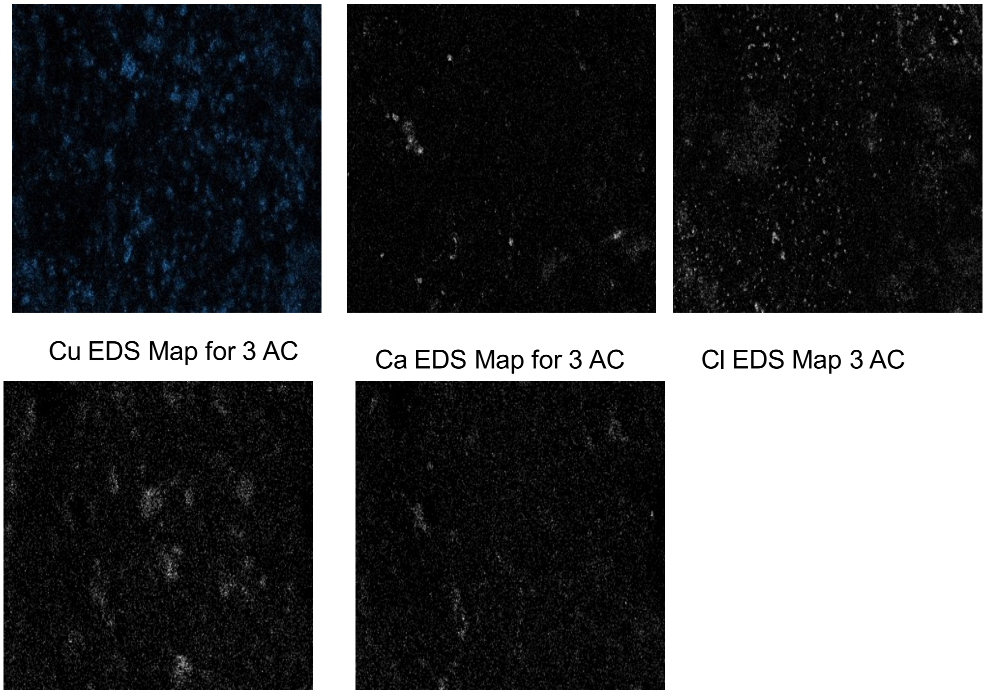
Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.29 Optical profilometer image of topography of Sample 3 after leaching



Cu EDS Map for 3 AC

Ca EDS Map for 3 AC

Cl EDS Map 3 AC

Mg EDS Map 3 AC

Na EDS Map 3 AC

Figure 6.30 EDS maps of Sample 3 after leaching

A comparison of the EDS maps before and after corrosion, it appears that the concentration of Cl, Na, Mg and Ca increased after corrosion and especially seems to be concentrated at certain active sites where localized corrosion may have initiated.

Sample 4 (5 % CuDDP): This sample underwent excessive corrosion as discussed in the earlier sections of physical observations and leaching results. The surface roughness after corrosion almost doubled from 3.98 to 6.78um. The salt and rust deposits and corroded areas were visible to the naked eye.

Sample 5 (5 %Viscoplex): The topography for this sample remained smooth even after corrosion with fewer small sized eroded/corroded sited with some salt deposits.

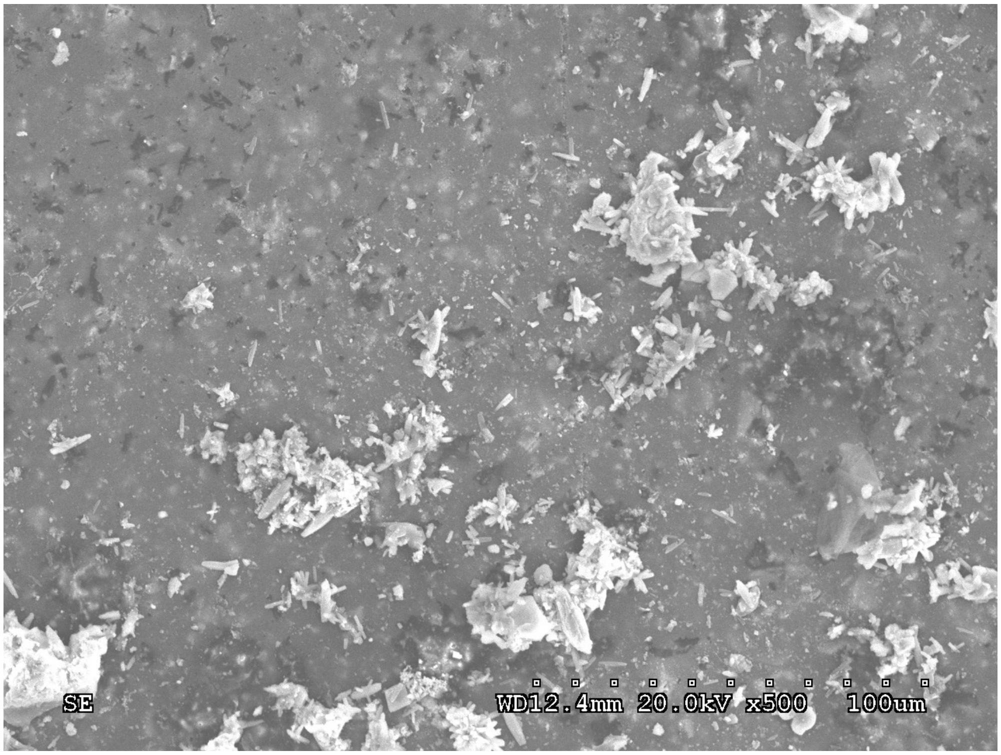


Figure 6.31 SEM Image of topography of Sample 5 after leaching

Surface Stats:

Ra: 3.07 um

Rq: 4.01 um

Rt: 31.80 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

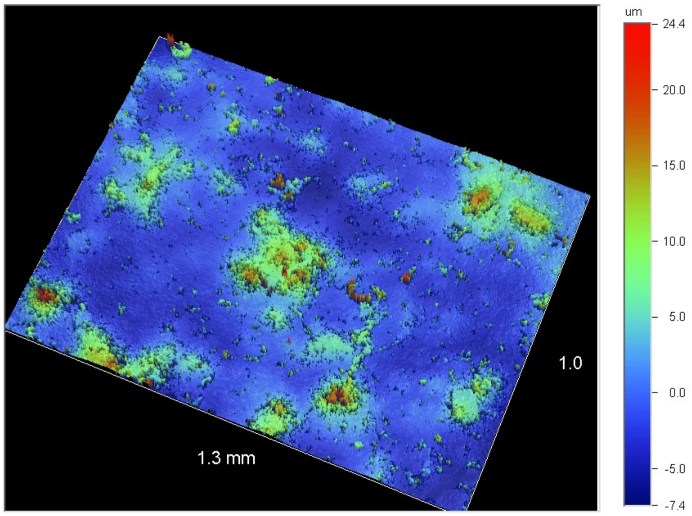
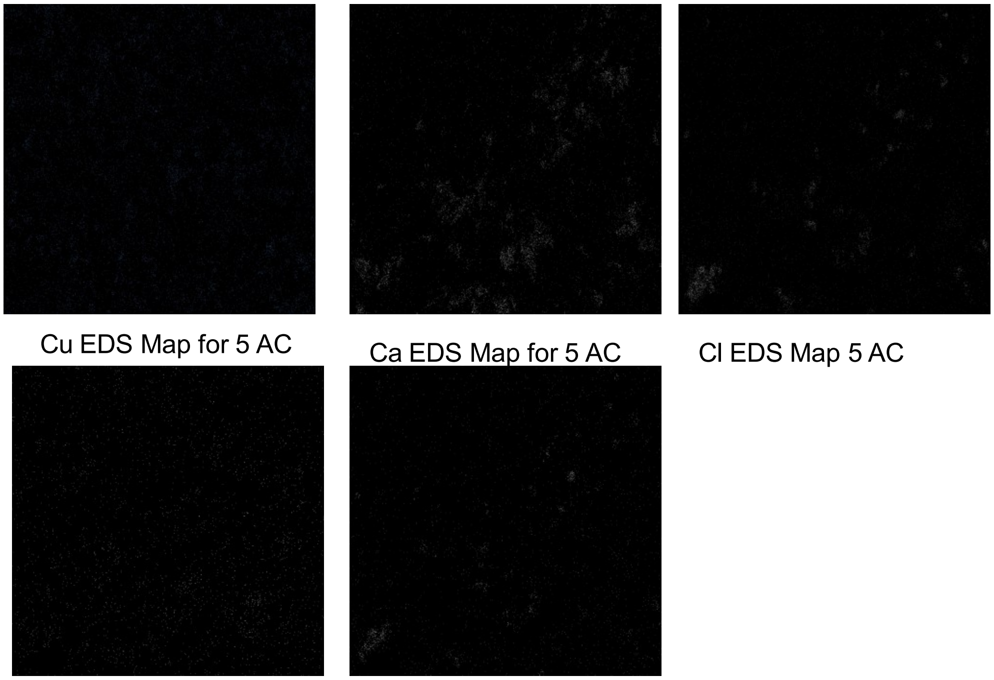


Figure 6.32 Optical profilometer image of topography of Sample 5 after leaching



Cu EDS Map for 5 AC

Ca EDS Map for 5 AC

Cl EDS Map 5 AC

Mg EDS Map 5 AC

Na EDS Map 5 AC

Figure 6.33 EDS maps of Sample 5 after leaching

The surface roughness decreased after corrosion due to ironing out of irregular sites /particles from the surface.

Sample 6 (15 % ED-SPAN in topcoat): the Ionomer sample after corrosion demonstrated higher level of porosity of the surface with small salt deposits at some cracks and pores. The increase in porosity is by virtue of the ionomer solubility in water. These pores as seen from the leach study results supported the release of copper from the underlying layer. The salt deposits could be due to ion exchange with the $–SO_3H$ group of the Ionomer or due to localized corrosion.

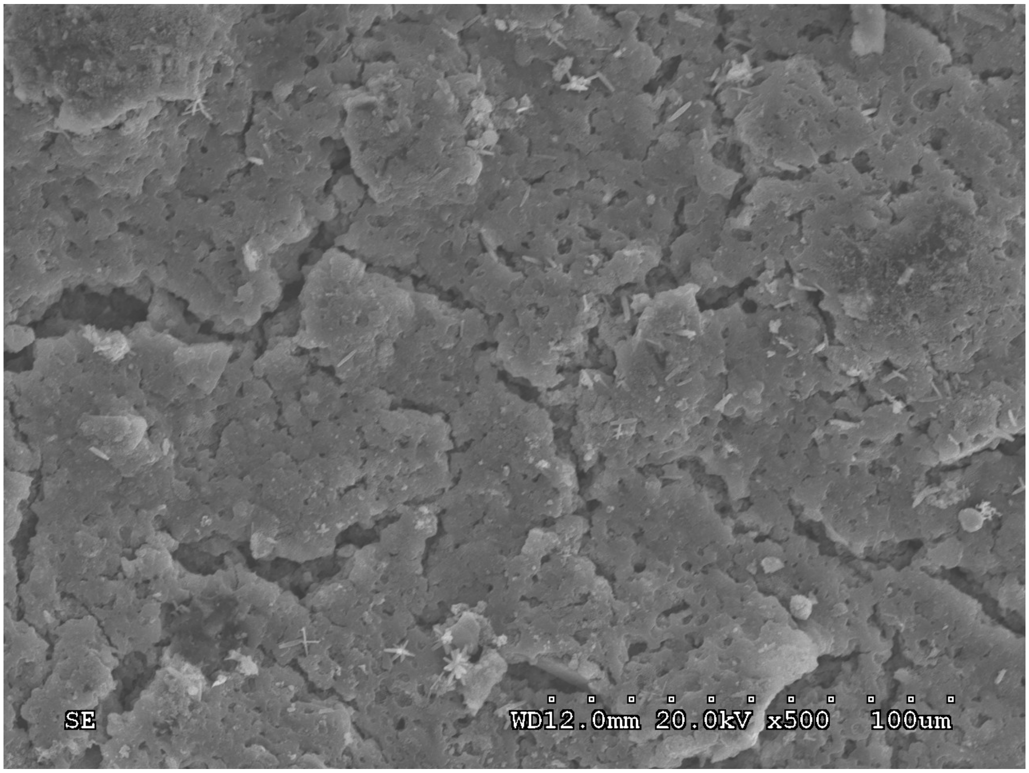
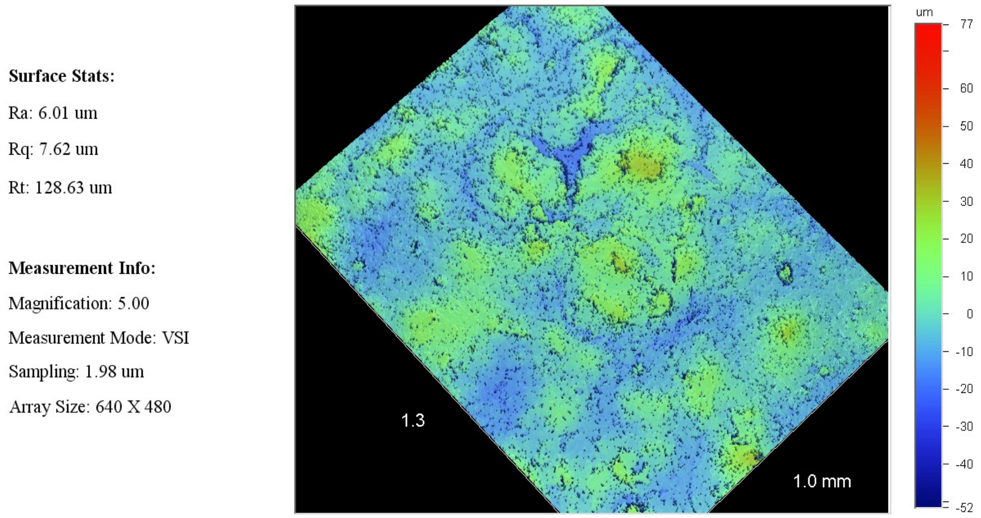


Figure 6.34 SEM Image of topography of Sample 6 after leaching

The surface roughness reduces after corrosion 6.01um again due to dissolution of ionomer agglomerates and due to the erosive effect of water.



Surface Stats:

Ra: 6.01 um

Rq: 7.62 um

Rt: 128.63 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.35 Optical profilometer image of topography of Sample 6 after leaching

Sample 7 (15 % ED-SPAN in blend): This sample demonstrated a poor performance in terms of corrosion. Due to the presence of large cracks on the surface the sample failed to maintain a smooth topography and low roughness after corrosion due to uncontrolled copper release and excessive corrosion and salt deposits contributing to increased roughness at all cracked active sites.

Sample 8 (All additives in a blend): The topography of sample 8 after the leaching study changed in terms of developing tremendous number of pores across the surface leading to increase in surface roughness from 4.99 to 7.45 um.

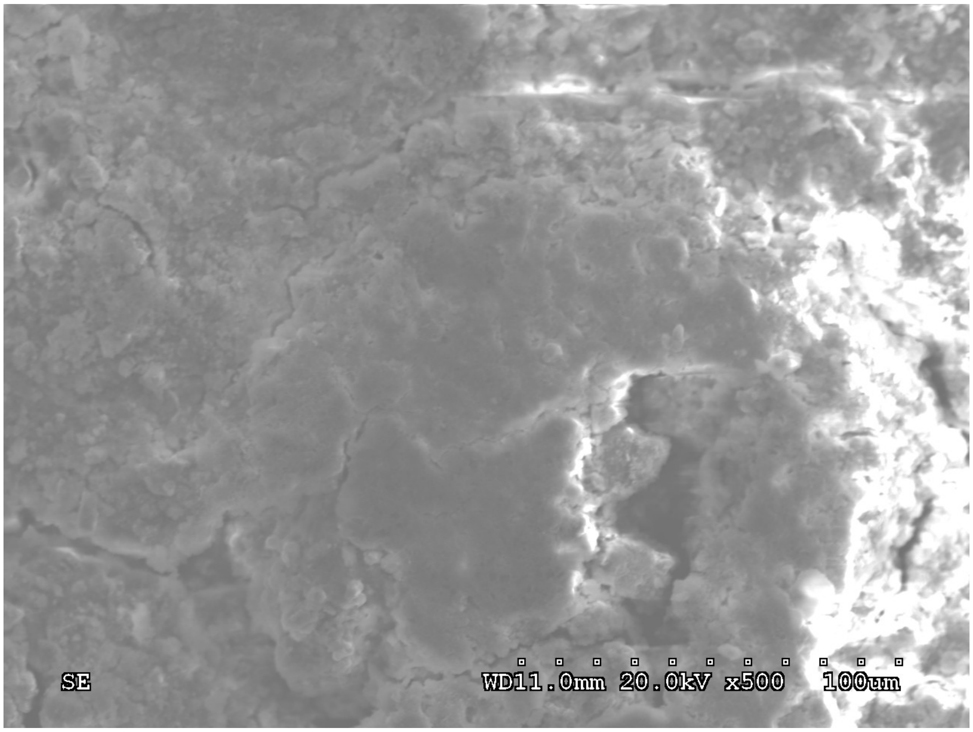


Figure 6.36 SEM Image of topography of Sample 8 after leaching

Surface Stats:

Ra: 7.45 um

Rq: 8.84 um

Rt: 97.92 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

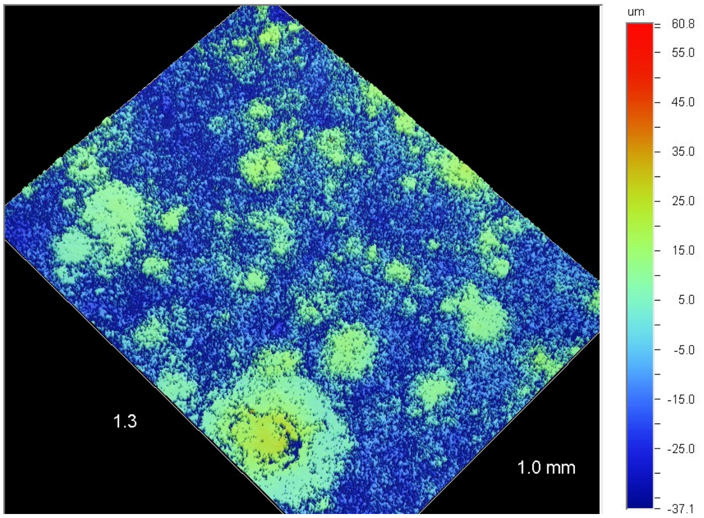
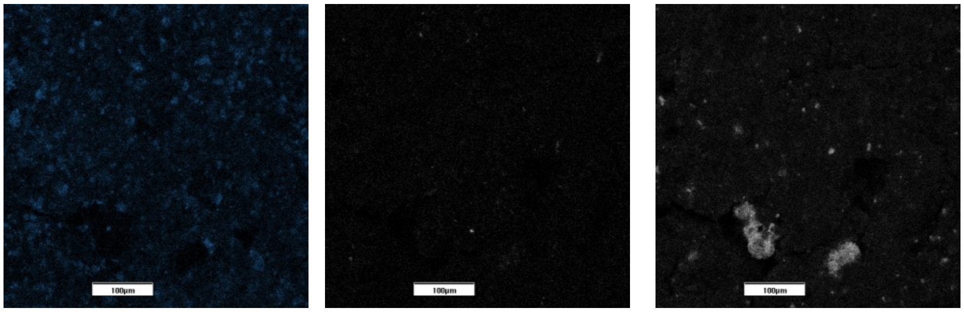
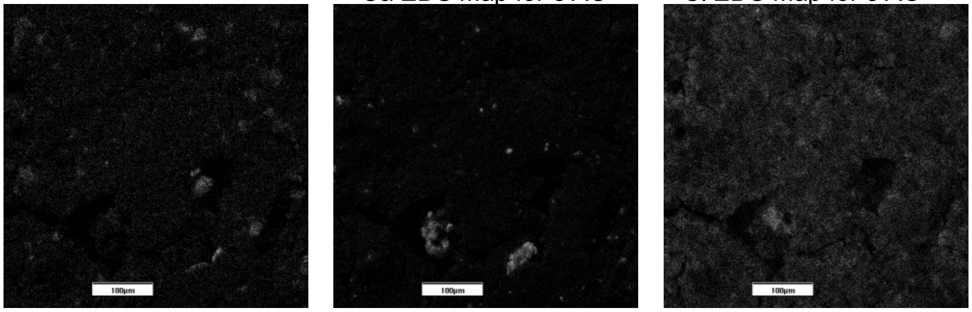


Figure 6.37 Optical profilometer image of topography of Sample 8 after leaching



Cu EDS Map for 8 AC
Ca EDS Map for 8 AC
Cl EDS Map for 8 AC



Mg EDS Map for 8 AC
Na EDS Map for 8 AC
S EDS Map for 8 AC

Figure 6.38 EDS maps of Sample 8 after leaching

The sample possessed a low concentration of matrix (45%) and in addition 15% ED-SPAN which was water soluble and aided matrix decomposition. Thus the ionomer dissolution accompanied by copper release generated high porosity in the surface after leaching for seven days. Also the EDS maps after corrosion reflect a higher concentration of Na, Mg and Cl after corrosion and a reduction in concentration of Cu and S at some holes/pits revealing excessive leaching in some parts where matrix may have decomposed. The higher concentration of Na, Cl Na and Mg at the pitted sites reveal their participation in localized corrosion.

6.5.3 Mechanical properties of formulations

Single Indentation tests (procedure in 4.8) were performed on all the leaching study samples after drying for at least 72 hours to remove all moisture. The indentation test results for all 36 indents were averaged to calculate the reduced elastic modulus. The average reduced elastic modulus for each formulation has been plotted against the sample no. in fig. 6.40The reduced modulus values include error bars based on standard deviation.

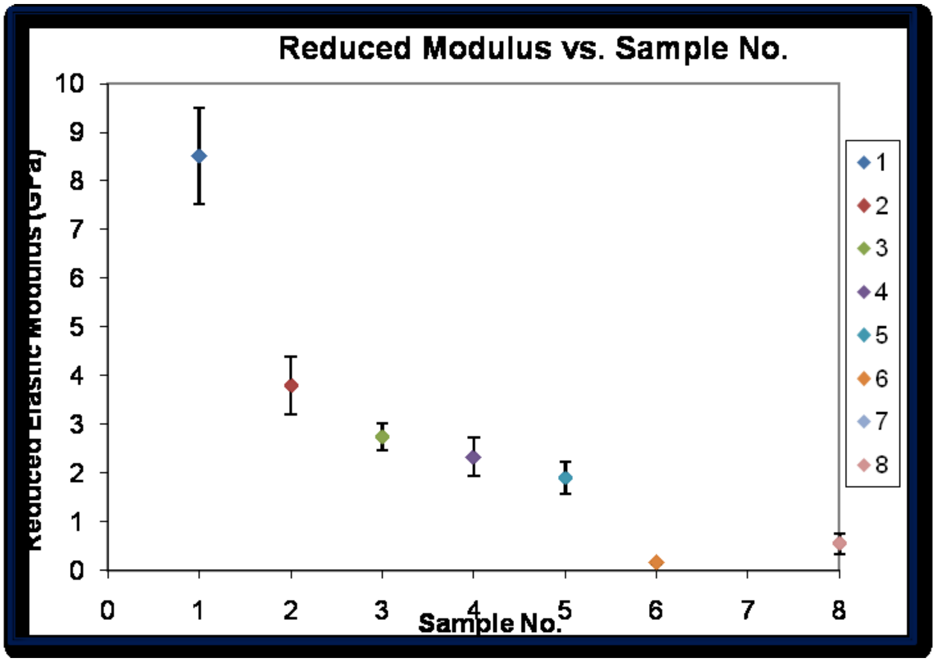


Figure 6.39 Reduced modulus for Part I study formulations after leaching

The trend followed after leaching for seven days in an active salt environment with erosion /corrosion and other degradation mechanisms in action still follows the pattern as before the leaching study. Sample 4 with CuDDP as the additive seems to have dropped in modulus after leaching probably due to extensive corrosion of the surface as was seen from the optical images in the previous section. As regards the Ionomer, the dissolution of the same in water (owing to its solubility) may have caused the matrix to degrade and generate further drop in the modulus value. The surface roughness for sample 7 after leaching had increased significantly so that indentation study could not be performed on that sample. In general for most samples the reduced elastic modulus did not change after leaching/corrosion indicating that the additive did not change the paint properties after corrosion or did not cause change of modulus and hence elastic properties after corrosion.

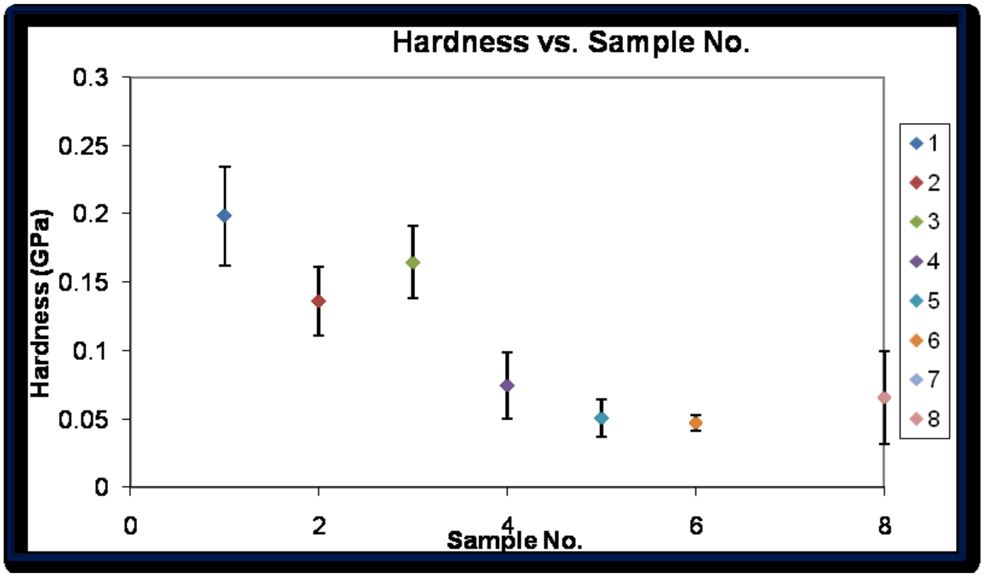


Figure 6.40 Hardness for Part I study formulations after leaching

The trend for hardness values after corrosion/leaching was again similar to that before the experiment. The hardness for sample 4 reduced a little after corrosion probably due to severe wear/erosion and degradation of the surface. The hardness of the Ionomer samples 6 & 8 also increase slightly after the leaching study. A probable reason for this could have been the loss of some ionomer by dissolution (as seen from porous surface images) as a result of water immersion. The ionomer as discussed earlier appears to be reducing the matrix hardness because of the higher flexibility of ED-SPAN molecules with longer C-S and pendant $–SO_3H$ group which hinders close packing and symmetry[62-64]. Ionomer dissolution increased the matrix content to raise the hardness.

6.5.4 Weight and Thickness Measurements

Weight and thickness measurements were performed after each coat in sample preparation to ensure that the consistency of each coat was as desired. Measurements of the sample weight and thickness were also performed at each stage of the leaching study after sampling. The samples were completely dried and then their weights recorded before immersion in water bath for next sampling. A plot of the weight and thickness of the different formulation samples in course of the leaching study can be seen below.

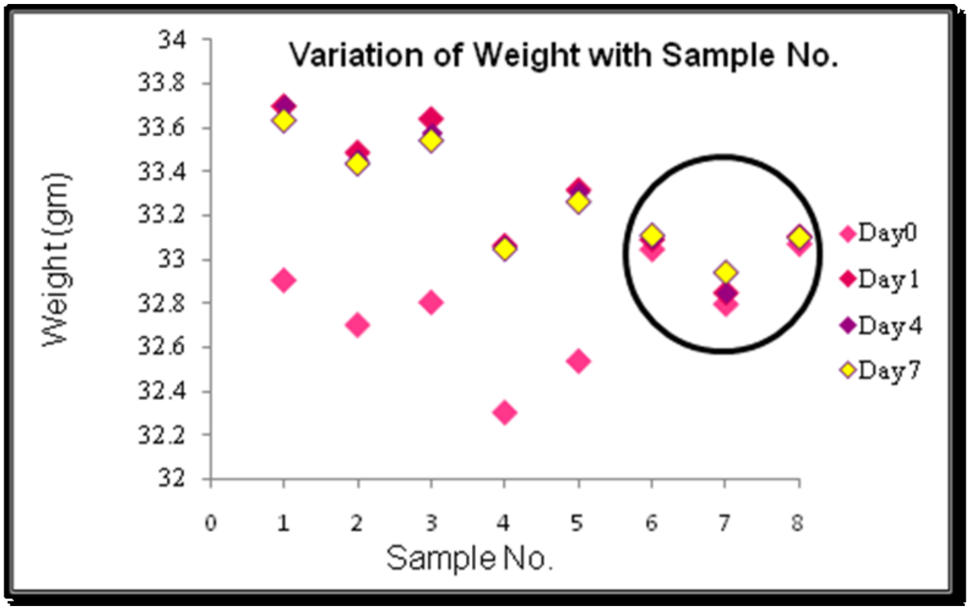


Figure 6.41 Plot of weight vs. Sample No. for Part I Study formulations

From the weight plot above it can be seen that weights of samples 1-5 increases after the first day of leaching significantly. This is due to swelling of the paint due to swelling tendency of the polymer in water (non-solvent). Also the diffusion of water through the pores on the surfaces causes some water entrapment in the paint film so that the weight of the sample is higher than its initial weight. Also corrosion at the active sites and salt deposits (as seen from SEM –EDS images) could be responsible for the weight gain. Thus even though there is ample leaching of copper, the weight of the samples increases instead of decreasing.[3, 15, 48] After the first day the diffusion barriers build-up so that leach-rate of copper from paints drops. At this stage the loss/gain in sample weight seems to have stabilized where the swelling is compensated by the loss in weight due to leaching so that the net weight of the samples does not change much (as seen by the overlapping weight points on the 4th and 7th day of leaching).

The variation in weight in due course of the leaching study for the samples containing ionomer (sample 6-8) is different from the first five samples. The weight change for all ionomer samples is very low all throughout the study irrespective of whether the ionomer is present as a top coat or a blend in the formulation. These samples (6-8) do not show swelling due to water retention or swelling. This is due to the high water solubility of the ionomer and due to the presence of smaller concentration of insoluble paint matrix (sample 8). Thus on immersion in water the swelling and water retention is counterbalanced by the dissolution of ionomer in water and in turn copper leaching and paint matrix degradation. Thus constancy in weight is an indication of the fact that the ionomer dissolution would be helpful in overcoming diffusion barriers, preventing corrosion and replenishing the copper leaching rate.

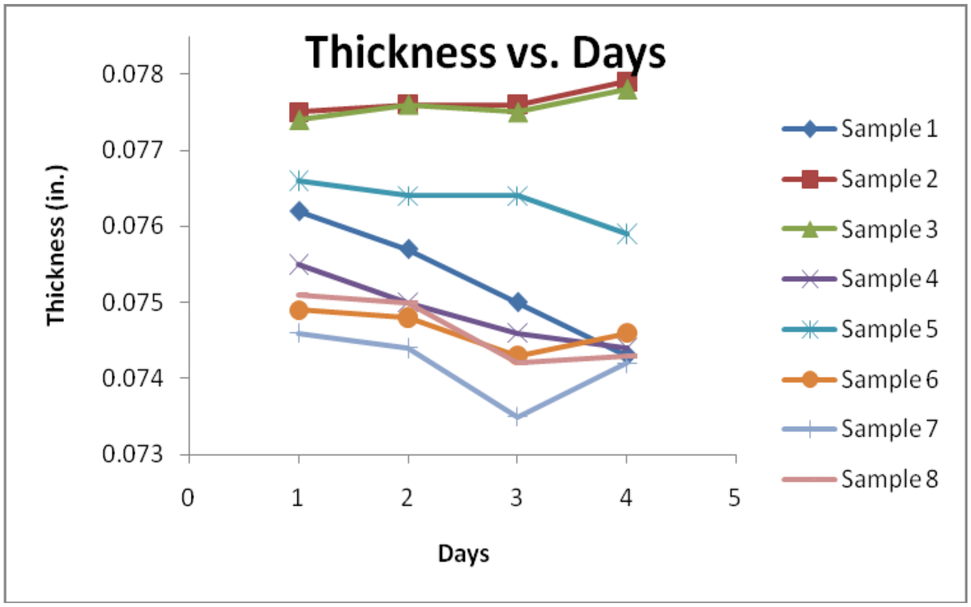


Figure 6.42 Plot of thickness vs. Sample No. for Part I Study formulations

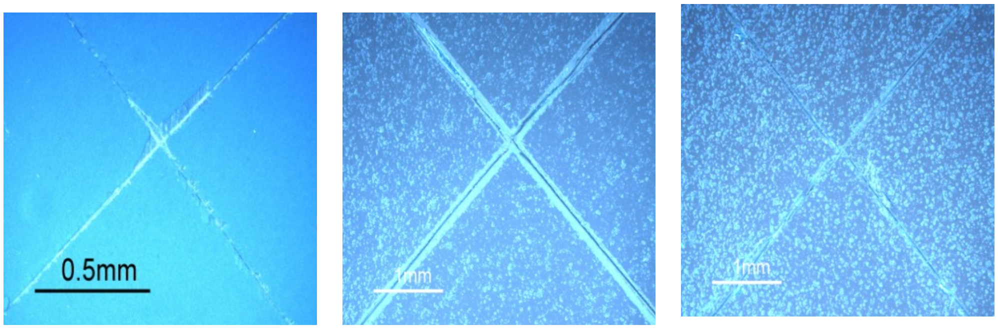
The trend for thickness variation of the samples in course of the leaching study shows very different behaviors as well. The commercial paint (sample 1) shows a steep decrease in thickness while the control samples (2 &3) show an increasing trend of thickness which is agreement to the observations in the weight plots. For the commercial paint sample the results contradict the weight results. The increase in weight with a decrease in thickness can only be explained by excessive water absorption by the paint and or deposit of corrosion products in active sites. This trend is also followed by sample 4 with CuDDP additive which again was observed to have undergone significant corrosion.

Once again all three samples with Ionomer additive (Sample 6-8) follow a different trend where the thickness decreases after an initial rise (1st day of leaching) and finally stabilizes to almost constant value. This trend could be due to a threshold period required for the ionomer –paint matrix to soften and dissolve and release copper, so that initial wetting period involves water absorption and rise in weight, immediately followed by a rapid loss in weight due to ionomer dissolution and copper release. The stabilization in thickness again agreement to the observations with the weight variation pattern due to a balance between diffusion barriers/corrosion products and ionomer-copper dissolution in water.

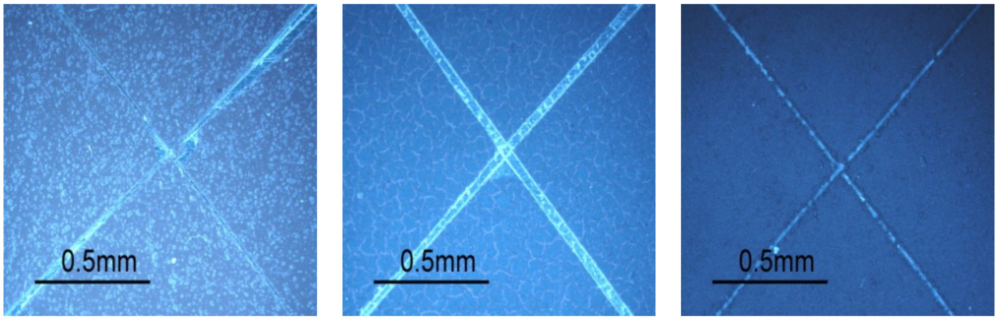
6.6 Corrosion study of scribed samples

The copper leaching and corrosion study was conducted as per procedure described in Chapter 4 Section 4.5. The scribe test was conducted on all coatings to evaluate the corrosion resistance of the coatings and the influence of different additives in controlling it. This test is used to simulate conditions where scratch or discontinuity is introduced into the system and the ability of the system to heal or resist further corrosion is examined.

The optical images of the scribed samples before the leaching study can be compared from the figure above. The surface features of the different formulations can be distinguished as discussed in section 6.2. It is clear that none of the samples show any traces of corrosion or rust or salt deposition and pitting on it. These images when compared to the images taken after the seven day leaching study on these samples; highlight the corrosion vulnerability of the samples.



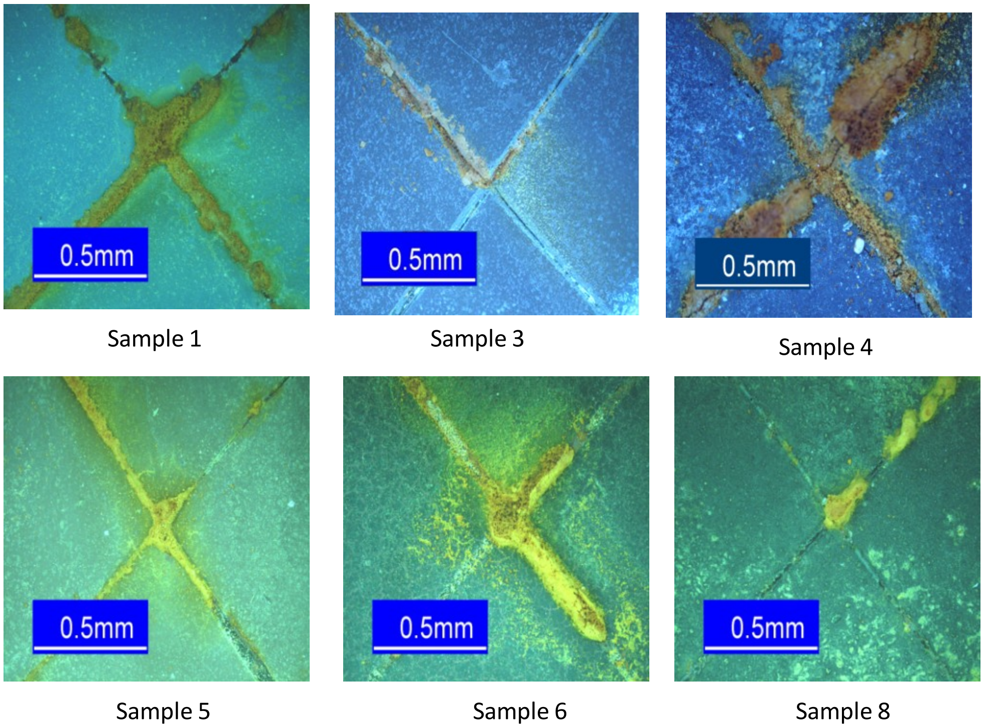
Sample 1 Sample 3 Sample 4



Sample 5 Sample 6 Sample 8

Figure 6.43 Optical Images of Part I study formulations before scribe corrosion study

From the sample images after the scribed sample leaching study some observations common to all samples include rusting of the scribed region where the bare metal is exposed to the harsh sea-water conditions and in addition salt deposition and pitting of the coated surface. The extent of rusting and corrosion of the different samples is related to the influence of the additives used in the recipe. The amount of corrosion and coating damage is maximum for the sample 4 with 5%CuDDP and 30% Cu_2O as additives. The inhomogeneity of the formulation due to poor blending generated different phases which showed poor resistance to corrosion. These results are similar to the findings in the leach study and the morphological study discussed in section 6.4. The samples with Viscoplex and Ionomer as the additive showed incomplete coverage of the scribed area indicating some protection against corrosion.



Sample 1 Sample 3 Sample 4

Sample 5 Sample 6 Sample 8

Figure 6.44 Optical Images of Part I study formulations after scribe corrosion study

The commercial sample doesn't have extensive corrosion and salt deposition on the coating surface but it has no protection of the scribed region which got heavily corroded.

Table: 6.3 Leach Rates for scribe samples of Part I study

SAMPLE	Leach rate (Day 0-2) ug/cm^2/day	Leach Rate (Day 3-7) ug/cm^2/day
Sample 1 (IRCUFIB)	14.1	10.6
Sample 2 (AM42CU)	35.8	5.8
Sample 3 (AM30CU)	17.4	1.1
Sample 4 (AM30CU5DDP)	14.3	12.7
Sample 5 (AM30CU5VIS)	8.5	2.5
Sample 6 (AM30CU15IO T)	6.3	2.5
Sample 8 (AM30CU5DDP5VIS15IO B)	37.8	23.7

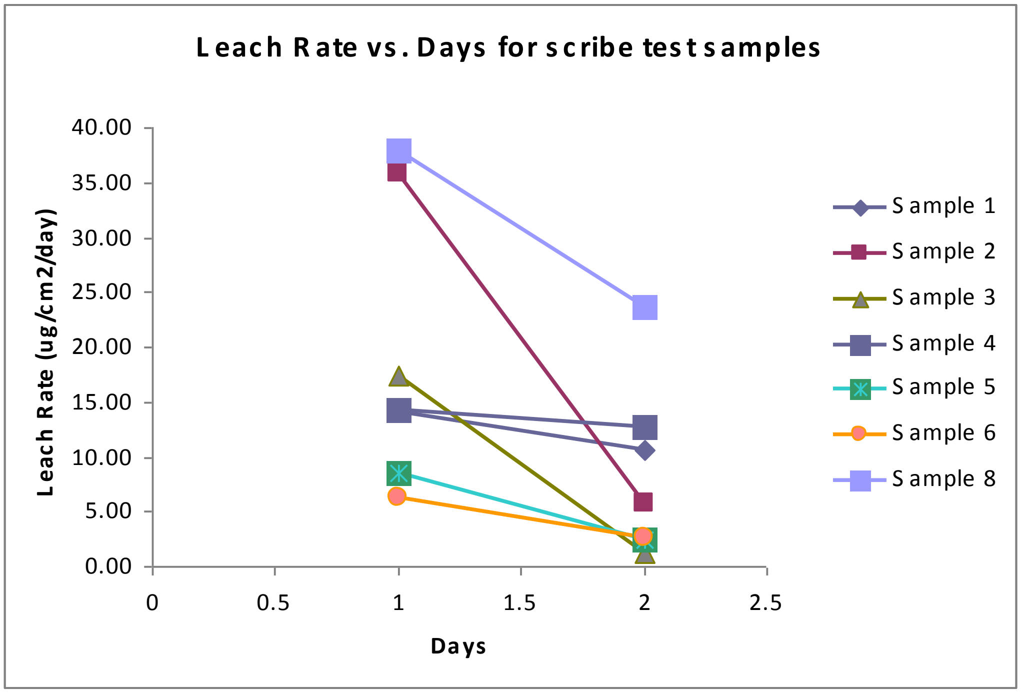


Figure 6.45 Leach Rate Plots for Part I study formulations scribe corrosion study

The leaching rate data for the scribed samples were similar to the leach-rate calculated on un-scribed samples. This is encouraging as it denotes that in the event of a scratch the leach rate of copper does not overshoot and raise environmental concerns. However the leach rate of sample 4 with CuDDP was much higher confirming that in the event of scratching the coating loses corrosion resistance and instead leads to an excessive release of copper which can be concerning.

Part II Optimization Study

6.7 Optimization of leach rate of antifouling paint formulation with selected additives

The second part of this study involved the use of the selected additives i.e. Viscoplex and ionomer ED-SPAN to develop a formulation which produces the desired leach rate (15 ug/cm^2/day) for antifouling and possesses the ability to maintain it at that value throughout the service life of the paint. To explore the feasibility of the additives in generating a suitable formulation for antifouling a DOE involving different combinations of the additives was designed. This matrix was designed based on the results obtained in Part-I of the study from the individual and combined use of the additives. As discussed earlier in Chapter 4 (section 4.2) two different approaches were adopted for the optimization study; first where all additives (Cu_2O, Viscoplex and ED-SPAN were blended together in paint) and second where Cu_2O was applied as a separate undercoat and ED-SPAN-Viscoplex combination in paint applied as a final top most coat. Apart from the leach rates, all other parameters like corrosion under normal and aggravated conditions (scribe study), change of modulus or hardness and weight/thickness studies were included to discriminate the best combination of these additives. The different combinations of Viscoplex and ED-SPAN as used in this study are described below.

Table 6.4 Formulations for the blend series of Part II study

	Composition/ Chemistry	Group
Sample 1B	30.0% wt. Cuprous oxide +15 % wt. ED-SPAN+ 5% wt. Viscoplex blended in base paint	Group 1 Blend Series
Sample 2B	30.0% wt. Cuprous oxide +15 % wt. ED-SPAN+2% wt. Viscoplex blended in base paint	

Table 6.4 - *Continued*

Sample 3B	30.0% wt. Cuprous oxide +10 % wt. ED-SPAN+ 5% wt. Viscoplex blended in base paint	
Sample 4B	30.0% wt. Cuprous oxide +10 % wt. ED-SPAN+ 2% wt. Viscoplex blended in base paint	
Sample 5B	30.0% wt. Cuprous oxide +12.5 % wt. ED-SPAN+ 3. 5% wt. Viscoplex blended in base paint	

Table 6.5 Formulations for the top-coat series of Part II study

Formulation	Composition/ Chemistry	Group
Sample 1T	15 % wt. ED-SPAN+ 5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cuprous oxide in base paint as undercoat	Group 2 Top Coat Series
Sample 2T	15 % wt. ED-SPAN+ 2% wt. Viscoplex in base paint as Top coat 30.0% wt. Cuprous oxide in base paint as undercoat	
Sample 3T	10 % wt. ED-SPAN+ 5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cuprous oxide in base paint as undercoat	

Table 6.5 - *Continued*

Sample 4T	10 % wt. ED-SPAN+ 2% wt. Viscoplex in base paint as Top coat 30.0% wt. Cuprous oxide in base paint as undercoat	
Sample 5T	12.5 % wt. ED-SPAN+ 3.5% wt. Viscoplex in base paint as Top coat 30.0% wt. Cuprous oxide in base paint as undercoat	

6.8 Morphology before leach study

The study of morphological features like topography, homogeneous composition, modulus, hardness, active sites etc. have been found (from Part-I of study) to be particularly important in evaluating the corrosion behavior of additives and their effectiveness in deterring or promoting corrosion when exposed to a harsh environment. Thus the study of these properties while trying to optimize a suitable composition for antifouling would be useful in determining the concentrations of additives. The following features were observed for formulations listed in Table above.

6.8.1 Topography, Physical Appearance/ texture before leaching

The physical appearance and topography of all samples of the blend series and the top coat series were very similar owing to very little variations in the composition. The blend series samples were a slightly higher in roughness than the top-coat series. This can be understood from the fact that the blend series of samples contain a large number of additives and very small proportion of binder or paint matrix (50-58%) compared to the top-coat samples where the binder content is much higher (80-88%).

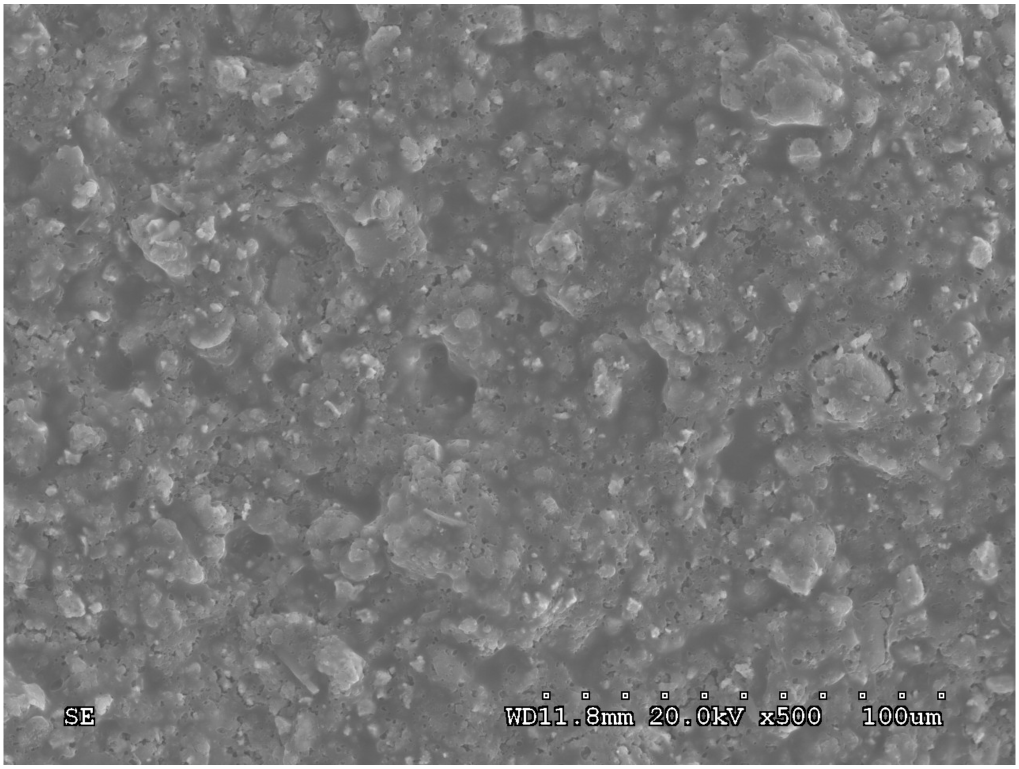
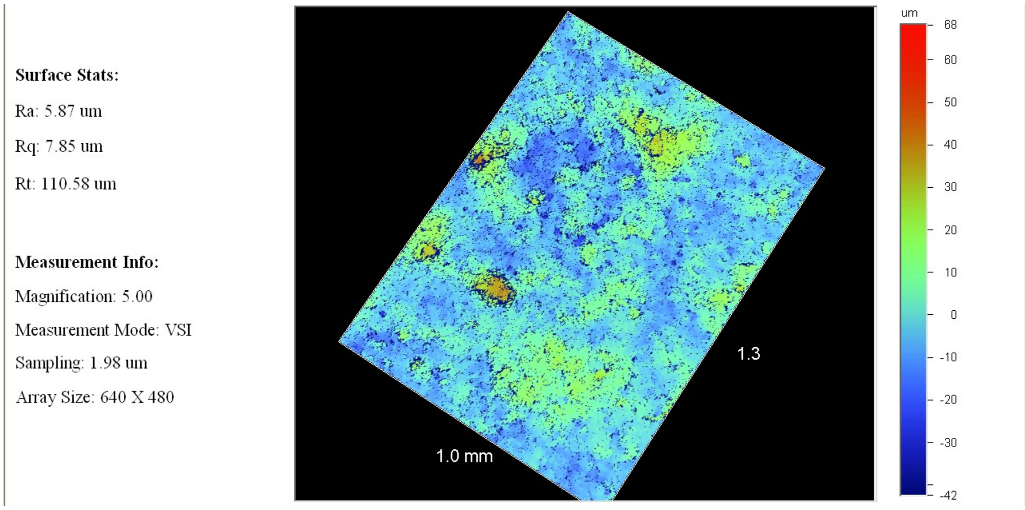


Figure 6.46 SEM Image of topography of Sample1B before leaching



Surface Stats:

Ra: 5.87 um

Rq: 7.85 um

Rt: 110.58 um

Measurement Info:

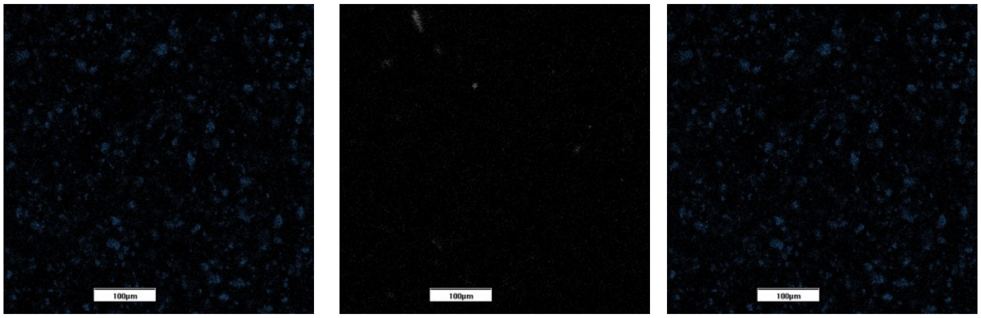
Magnification: 5.00

Measurement Mode: VSI

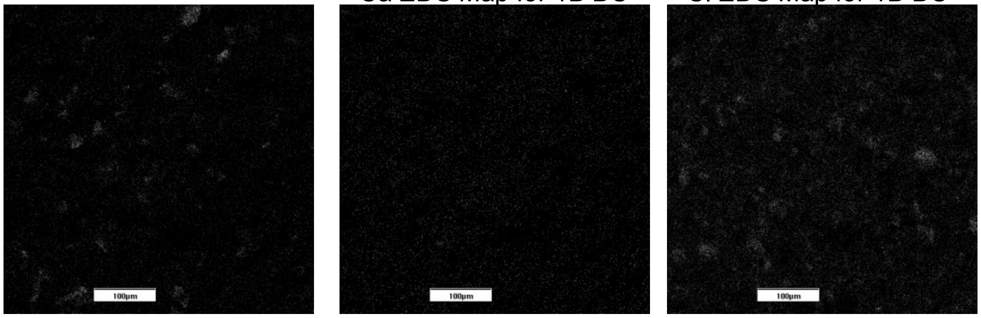
Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.47 Optical profilometer image of topography of Sample 1B before leaching



Cu EDS Map for 1B BC Ca EDS Map for 1B BC Cl EDS Map for 1B BC



Mg EDS Map for 1B BC Na EDS Map for 1B BC S EDS Map for 1B BC

Figure 6.48 EDS maps of Sample 1 B before leaching

Also samples which contain a higher proportion of Viscoplex (1B, 3B, 5B and 1T, 3T and 5T with almost 5% Viscoplex) had a smoother surface due to better binding of the particles by Viscoplex (as seen from the profilometer images). In contrast the samples with lower Viscoplex had a higher roughness due to lack of sufficient binder for the particulate matters as for example sample 2B with higher content of ionomer and ,lower concentration of Viscoplex had the highest surface roughness (7.07um).

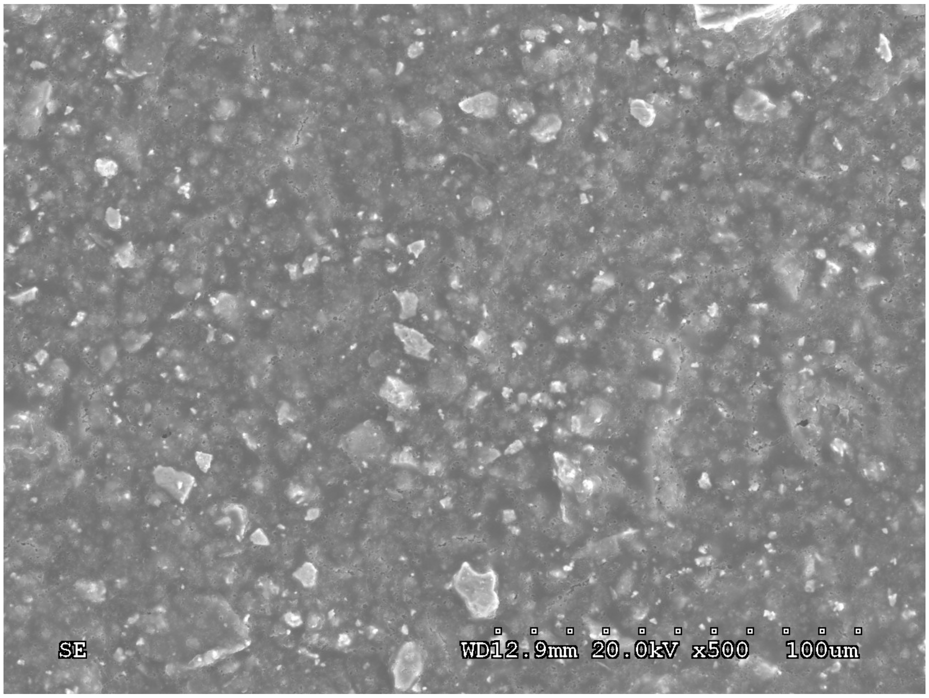
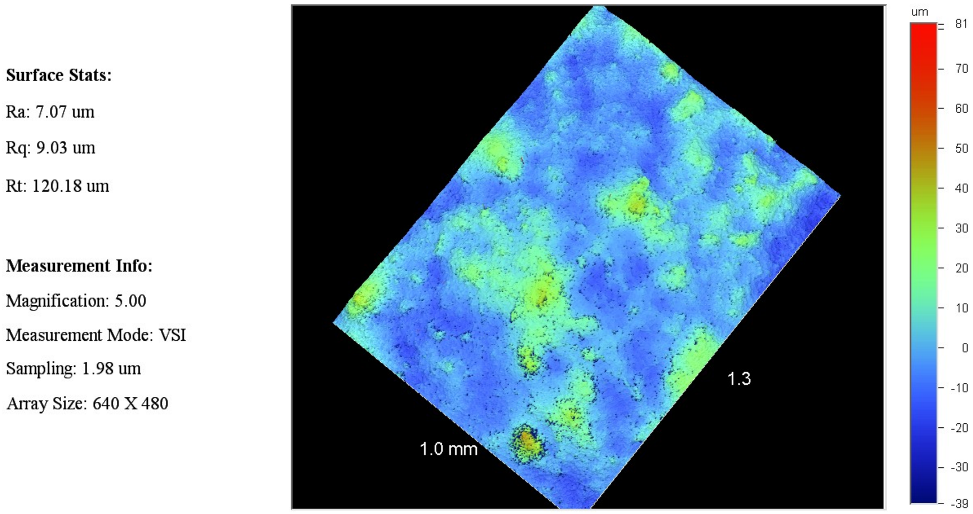


Figure 6.49 SEM Image of topography of Sample 2B before leaching


Surface Stats:

Ra: 7.07 um

Rq: 9.03 um

Rt: 120.18 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.50 Optical profilometer image of topography of Sample 2B before leaching

The topography of this sample appears to be very irregular which projecting particles of separate phases as seen from the SEM images.

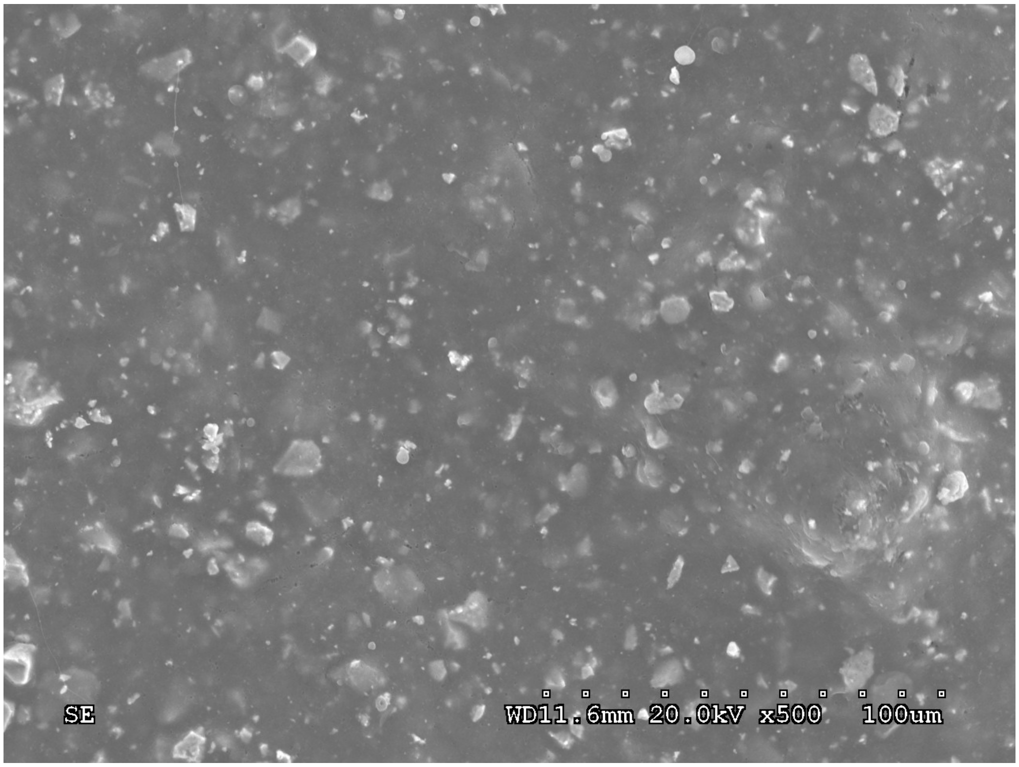
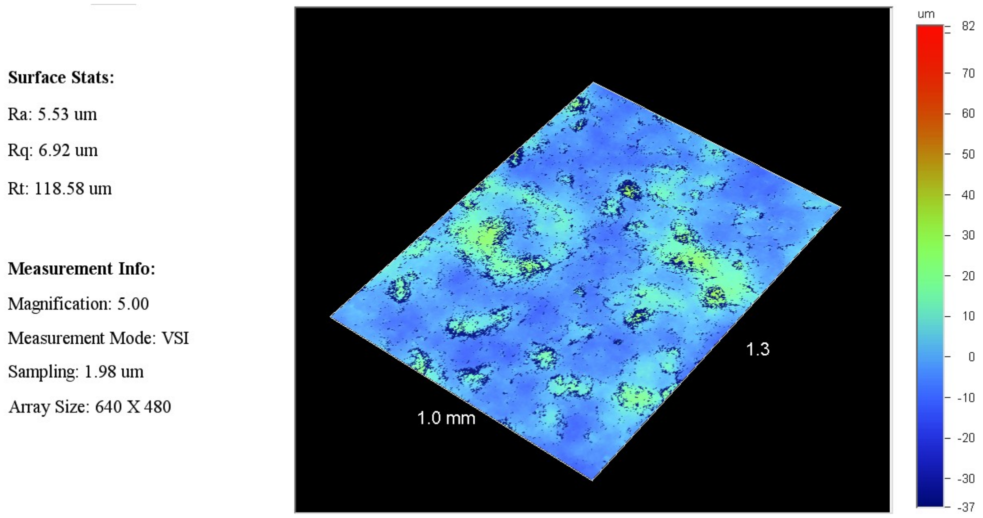


Figure 6.51 SEM Image of topography of Sample 3B before leaching

The EDS-Maps depict uniform distribution of copper and sulphur throughout the surface indicating uniform distribution of ionomer and copper oxide across the surface. The concentration of Mg, Ca appears to be low before the leaching study indicating absence of salt deposits on the surface.



Surface Stats:

Ra: 5.53 um

Rq: 6.92 um

Rt: 118.58 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.52 Optical profilometer image of topography of Sample 3B before leaching

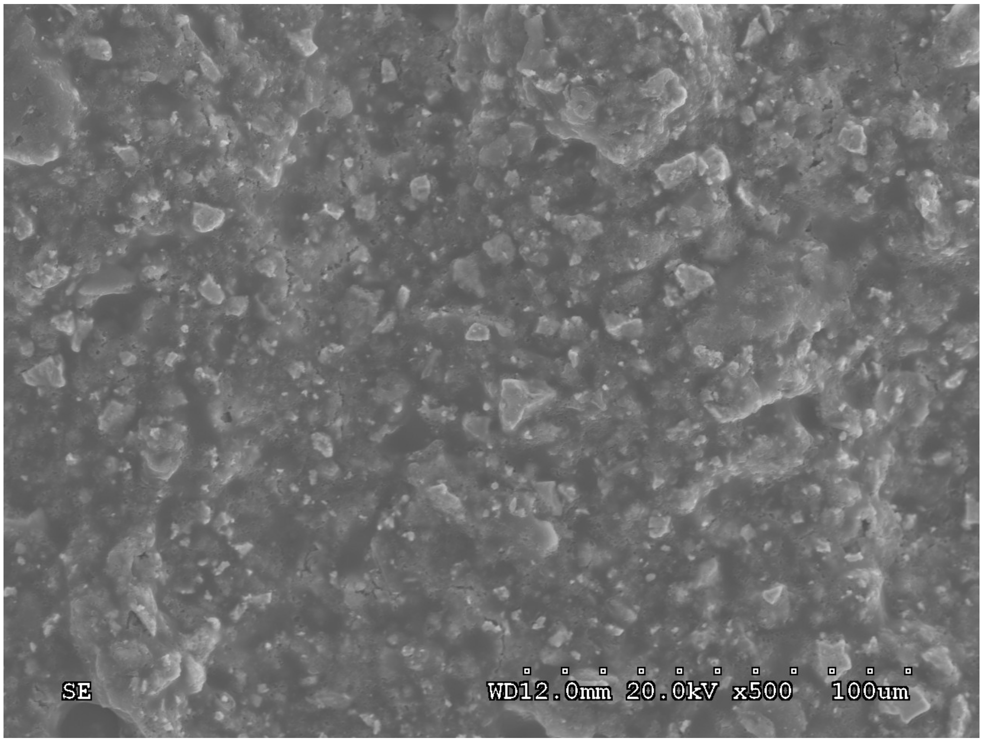
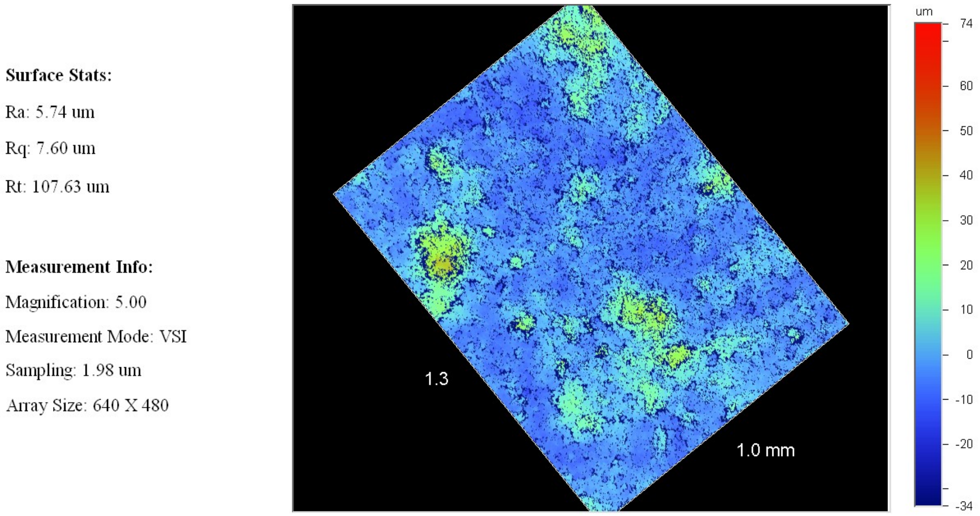


Figure 6.53 SEM Image of topography of Sample 5B before leaching



Surface Stats:

Ra: 5.74 um

Rq: 7.60 um

Rt: 107.63 um

Measurement Info:

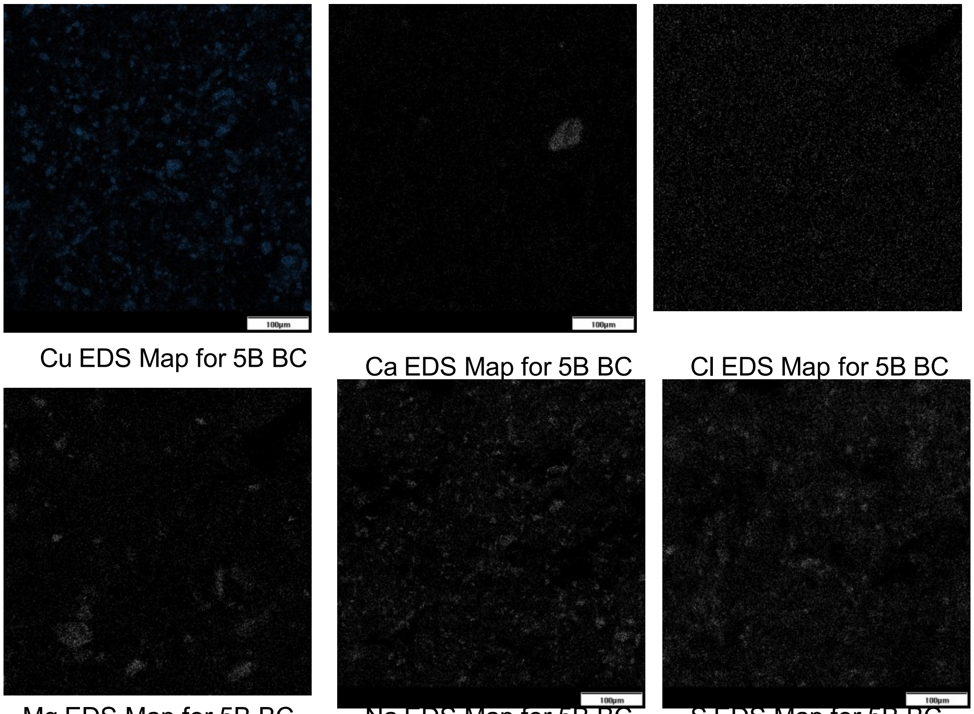
Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.54 Optical profilometer image of topography of Sample 5B before leaching



Cu EDS Map for 5B BC

Ca EDS Map for 5B BC

Cl EDS Map for 5B BC

Mg EDS Map for 5B BC

Na EDS Map for 5B BC

S EDS Map for 5B BC

Figure 6.55 EDS maps of Sample 5 B before leaching

The presence of Na and Cl is owing to the ionomer which contains a sodium salt of Sulfonic acid. In general all samples exhibit a certain level of porosity, roughness and irregularity owing to the amorphous natured ionomer which in some cases is compensated by the smooth binding effect of Viscoplex. None of the samples have any pits or cracks or any active corrosion sites.

6.8.2 Mechanical properties of formulations

To evaluate the mechanical properties like reduced elastic modulus and hardness and associate the influence of ionomer ED-SPAN and Viscoplex on these properties, Nano-indentations were performed on all the blend and top-coat series samples. The observation can be summarized as follows:

<u>Blend Series:</u> In case of the blend series three different parameters influenced the reduced modulus and hardness of the coating; concentration of ED-SPAN, Viscoplex and paint matrix.

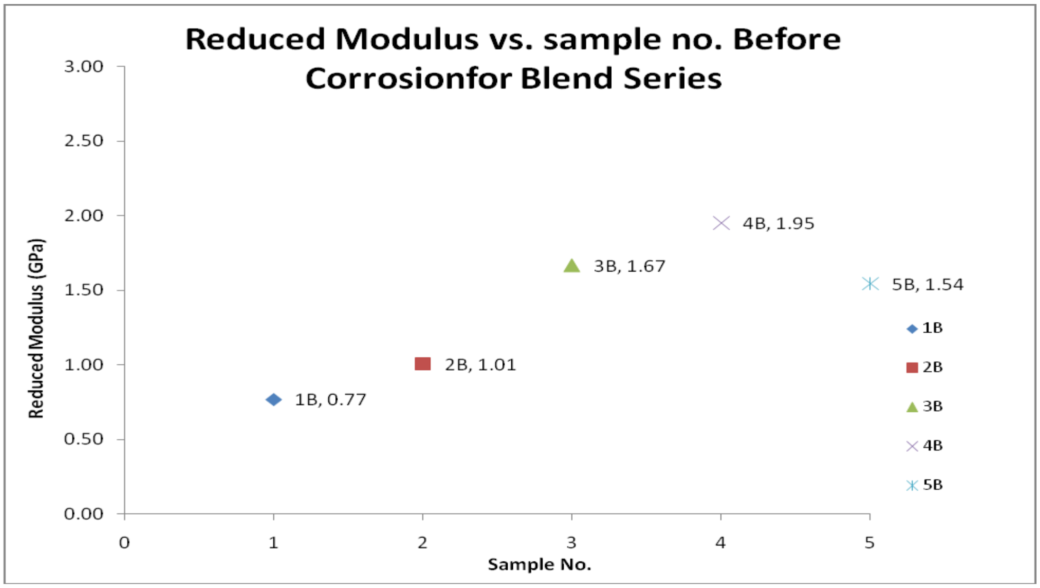


Figure 6.56 Reduced modulus of blend series for Part II study formulations before leaching

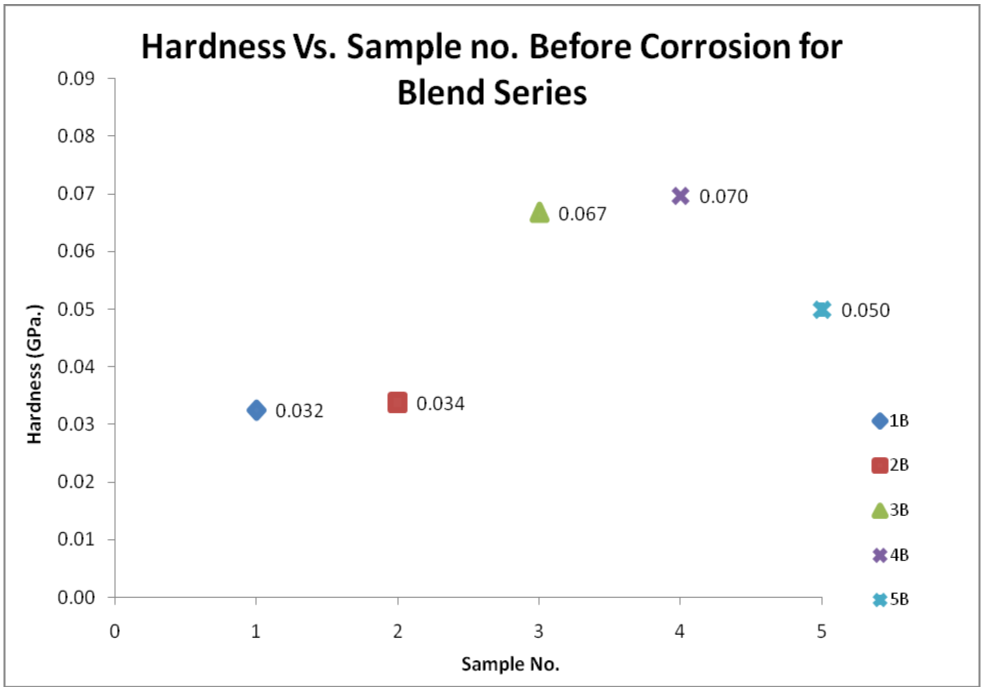


Figure 6.57 Plot of hardness of Blend Series for Part II study formulations before leaching

The sample 1B which had the lowest concentration of paint and highest amount of ionomer and Viscoplex had the lowest reduced modulus while sample 4B with the highest matrix concentration and lowest amount of ionomer and Viscoplex had the highest reduced modulus. In general it can be seen that;

- Higher concentration of ionomer ED-SPAN reduces the modulus. E.g. Sample 1B , 2B (higher ionomer) < 3B,4B,5B (lower ionomer)
- Higher concentration of Viscoplex reduces the modulus Er. E.g. Sample 1B < 2B & 3B< 4B where 1B and 3 B have 5% Viscoplex and 2B and 4B have 2% Viscoplex
- Higher concentration of paint matrix increases the modulus. E.g. sample 4B with 58% base paint has the highest Er value and 1B with only 50% paint has the lowest. For the rest of the samples too the same trend applies.
- Sample 5 B which had intermediate proportions of all additives gave a medium value of modulus.

These observations are found to be in agreement with the trend seen in Part-I study with individual additives. The decrease in modulus with increasing proportions of ionomer and Viscoplex is likely due to their amorphous nature and viscoelastic behavior. The hindered structure of Sulfonated Polyaniline with pendant –SO_3H group and long –C-S single bond length incorporated extra flexibility to the molecules preventing the close-packing of chains and crystalline nature. Similarly the flexibility from the ester groups (C-O) in Viscoplex, the compound has a higher flexibility. This coupled with the high molecular weight and viscoelastic nature contributes to decreasing the modulus value when blended in epoxy base paint. The epoxy paint being cross-linked in nature after curing has a lower flexibility and higher modulus.

As regards the hardness it can be seen from the plot of hardness vs. sample that it is comparable to trend observed with reduced modulus. Again sample 4B with highest concentration of paint and, lowest concentration of ionomer and Viscoplex had the highest hardness while sample 1B with the lowest matrix content and higher proportions of additives had lowest hardness.

Top-Coat Series: In case of the top-coat series, the concentration of the additives was the same with the difference that there was no copper oxide in the top coat. The absence of copper oxide produced some differences in the results. The nano indentation results of the top coat series lead to the following observations:

- For the top coat series the hardness and reduced modulus values were affected by concentration of ionomer, Viscoplex and base paint matrix.
- Due to a higher concentration of base-paint in all top-coat formulations compared to the blend series formulations, the modulus and hardness before the leach study for this series was higher than the blend series.
- The trend for hardness and reduced modulus was the same.

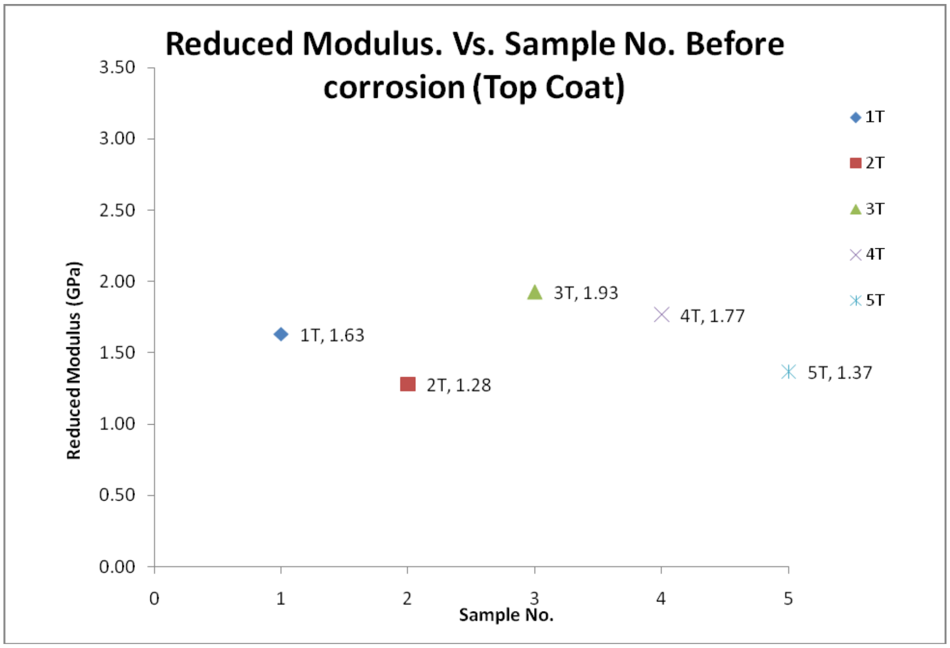


Figure 6.58 Reduced modulus of top coat series for Part II study formulations before leaching

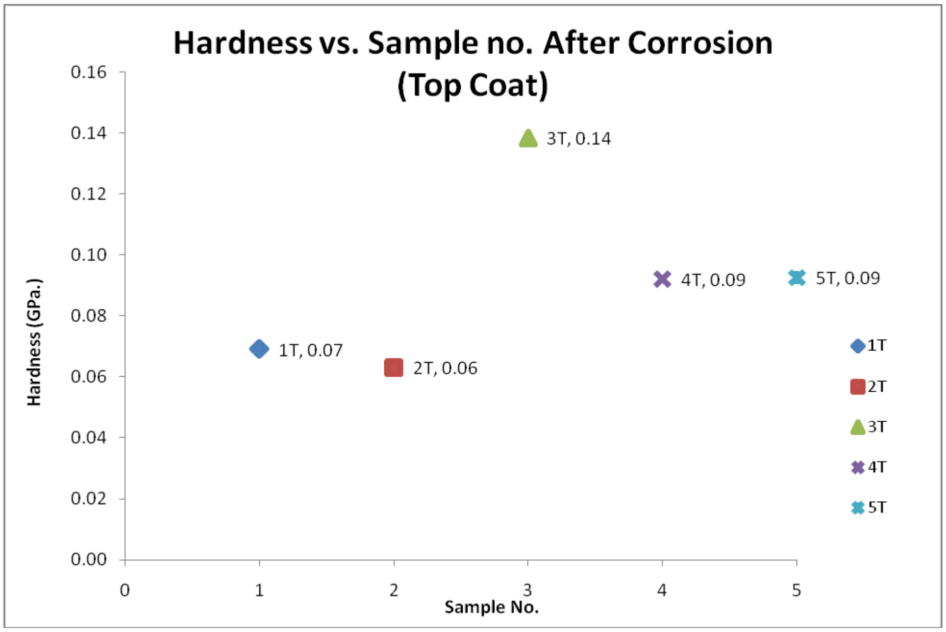


Figure 6.59 Hardness of top coat series for Part II study formulations before leaching

- Viscoplex in the absence of cuprous oxide seemed to be having a positive influence on the modulus and hardness values. Sample 1T (5% Viscoplex)> 2T (2% Viscoplex), 3T (5% Viscoplex)> 4T (2% Viscoplex) in reduced modulus and hardness. From Part-I study and blend series data it has been established that Viscoplex in the presence of cuprous oxide reduces the modulus and hardness of the coating. However in the absence of cuprous oxide the behavior is different and is not clearly understood at this stage.

6.9 Copper Leach rate and Corrosion Study

The results of the leach rate studies have been summarized below:

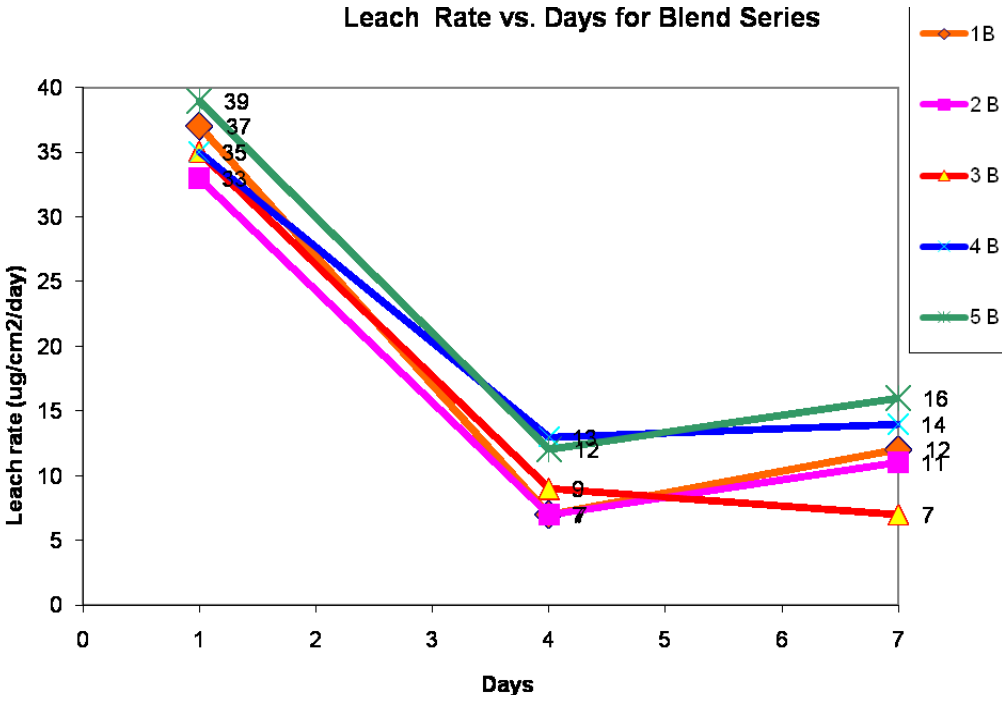


Figure 6.60 Plot of leach rates for the blend series of part II study

Table 6.6 Leach rates of the blend series for Part II study

	Matrix Content	DAY 1 ug/cm^2/day	DAY 4 ug/cm^2/day	DAY 7 ug/cm^2/day
1B (15% IO+30% Cu_2O+ 5% VIS)	50%	37	7	12
2B (15% IO+30% Cu_2O+ 2% VIS)	53%	33	7	11
3B (10% IO+30% Cu_2O+ 5% VIS)	55%	35	9	7
4B (10% IO+30% Cu_2O+ 2% VIS)	58%	35	13	14
5B (12.5% IO+30% Cu_2O+ 3.5% VIS)	54%	39	12	16

All samples displayed a common trend of a high burst release rate between 30-40 ug/cm^2/day, followed by a drop in release rate from the second to the fourth day of release at 7-12 ug/cm^2/day and then a rise in release rate in the range of 7-16 ug/cm^2/day from the fourth to the 7th day of the experiment. This trend is similar to what was observed for all Ionomer formulations (Sample 6-8) in Part I study. Thus unlike the commercial sample or the individual additive formulations trend, these formulations exhibit a capability of reviving the leach-rate by overcoming diffusion barriers , degrading paint matrix and renewing newer surface for continued release. For some formulations the drop in the release rate on Day4 of sampling is 12-13 ug/cm^2/day which after considering a 10-15% error margin of ICP analysis (Chemical Solution data10-15% difference, rather lower from actual value) can be considered close to the desired rate of 15ug/cm^2/day and sufficient to inhibit fouling.

Some of the factors that influence the leach rate of copper from paints need consideration while analyzing the leach results. These are;

- Variation in concentration of Ionomer: higher concentration facilitates higher release
- Variation In concentration of Viscoplex : higher concentration drops release rate
- Variation in concentration of Matrix : higher concentration drops release rate

In the leach study a combination of all these three factors worked into producing the leach rate as obtained in the table above.

Sample 1 B (15% IO+30% Cu_2O+ 5% VIS): The composition of this sample is similar to that of Sample 8 of Part I study with the exception that it doesn't have any CuDDP (5% in latter). Compared to the results of Sample 8, the burst release of Sample 1B was much lower at a value of 37 ug/cm2/day. In spite of having a high burst release the leach rate drops as low as 7 and then revives to 12 ug which may still be insufficient in deterring fouling. The paint matrix content of this formulation was the lowest in the DOE, so it should have contributed to higher release. The Ionomer concentration also being high should increase the release rate of copper. However the Viscoplex concentration of 5% is too high so that it reduces the release rate from the burst release to the 4th day until the Ionomer would dissolve again to expose new surface with higher release of copper. Although a good control over burst release the sample loses its releasing efficiency in the interim period to Ionomer dissolution and runs the risk of getting fouled during this period.

Sample 2 B (15% IO+30% Cu_2O+ 2% VIS): The paint matrix content (53%) of this formulation was the higher than 1B in the DOE, so it should have contributed to lower release. The Ionomer concentration still being 15% should increase the release rate of copper. In this case the Viscoplex concentration is dropped to 2% so that it should result in an enhancement of the release rate as compared to 1B. However the leach rate results for the two formulations are comparable denoting balance between the increase of matrix content and reduction in Viscoplex content.

Sample 3 B (10% IO+30% Cu_2O+ 5% VIS): This formulation has a high concentration of matrix (55%), a high concentration of Viscoplex (5%) and a low concentration of the Ionomer (10%) all of which would contribute to a reduction in the release rate of copper. This is found to be in agreement with the actual leach study results. The leach rate starts at 35 and drops to 9 ug/cm2/day.

Sample 4 B (10% IO+30% Cu_2O+ 2% VIS): This formulation has the highest concentration of matrix (58%) and a low concentration of the Ionomer (10%) all of which would contribute to a reduction in the release rate of copper but it has a low concentration of Viscoplex which should reduce the binding action on the release rate. As a net result of the balance of these three different driving forces, the ultimate leach rate of copper was found to be better than sample 3B, at 35-14 ug/cm2/day range. This shows that the binding action of Viscoplex is much severe when working with a lower concentration of Ionomer so that it overrules the binding effect of the paint matrix itself. Although the leach rate on the 4th and 7th day is a little below the desired value of 15ug, yet this samples possesses a good chance of working in the actual conditions

Sample 5 B (12.5% IO+30% Cu_2O+ 3.5% VIS): This formulation has all additives in proportions in between 1B and 4B formulations. The leach results indicate that the concentration of the paint matrix, Viscoplex and Ionomer content balance out to give a good performance with copper release. The burst release was a little high but the leach rate after dropping still remained around 15ug level indicating a good and continuous control on fouling without periods of low leaching which allow fouling to occur. In this respect the formulation was superior to the commercial paint whose leaching efficiency was found to drop significantly after the 1st day of immersion in spite of having such a large concentration of copper oxide (43%). The present paint manufacturers load a higher concentration of copper oxide in paint to achieve a longer service life for antifouling paint, but if the leach rate drops below 15ug/cm2/day as found for the commercial paint, the purpose of such a high loading is defeated since once a surface gets fouled, there is not much that can be done to protect or retrieve it.

Top Coat Series:

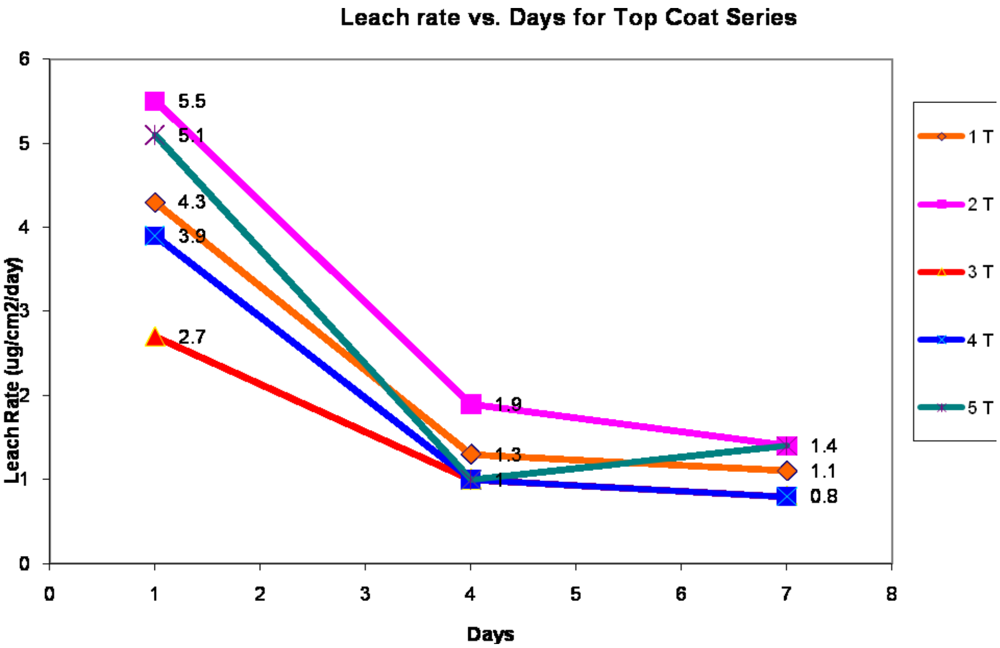


Figure 6.61 Plot of leach rates for the top-coat series of part II study

Table 6.7 Leach rates of the top-coat series for Part II study

SAMPLE	Matrix Content of top coat	DAY 1 ug/cm^2/day	DAY 4 ug/cm^2/day	DAY 7 ug/cm^2/day
1T (15% IO+5% VIS)	80%	37	7	12
2T (15% IO+2% VIS)	83%	33	7	11
3T (10% IO+5% VIS)	85%	35	9	7
4T (10% IO+2% VIS)	88%	35	13	14
5T (12.5% IO+3.5% VIS)	84%	39	12	16

The leach study results for the Top Coat series follows the same trend as for the Blend series. The difference lies in the quantity of copper leached. The leach rate for all top coat samples was found very low compared to the desired range of 15ug/cm2/day. The reason for such low release comes from the high matrix content (80-88%) for all top coat formulations. As seen from the blend series results; higher matrix content reduces water diffusion into the coating restricting release. Not only do all the top coat formulations contain a high amount of base paint in the top coat but also they contain up to 5% Viscoplex which acts as a strong binder and reduces the release rate further. The Ionomer supports release by self-dissolution in water. Thus depending on the content for base paint, Ionomer and Viscoplex; sample 3T which had a very high content of base paint, highest amount of viscoplex and low amount of Ionomer gave the lowest leach rate while samples 1T, 2T and 5T which had a lower paint content and higher proportions of Ionomer gave relatively higher leach rates. In this case too, samples with lower concentration of viscoplex (2T, 4T and 5T) performed better in terms of leaching.

As discussed in chapter 4, one of the limiting factors to increasing the Ionomer concentration in the top coat series of samples was difficulty in sample preparation. But based on the leach rates calculations it is clear that Ionomer ED-SPAN and viscoplex combination in the top coat of paint is capable of controlling the leach rate and restricting high burst release. If on a large scale production, higher loading of Ionomer in paint would be possible, then the targeted rate of 15ug/cm^2/day of copper release could be achieved with the top coat formulations and additive optimization.

6.10 Morphology after leach study

6.10.1 Topography and Physical Appearance/ texture after leaching

The surface features of most formulations remained the same after the leaching experiment. Changes such as small pitting, increase in porosity, salt deposits on the surface were seen for all samples. Unlike the control samples of the Part I series or the commercial sample which displayed a rough porous surface with some traces of rusting after corrosion during the leach study, none of the samples of the blend series or the top coat series showed any such behavior.

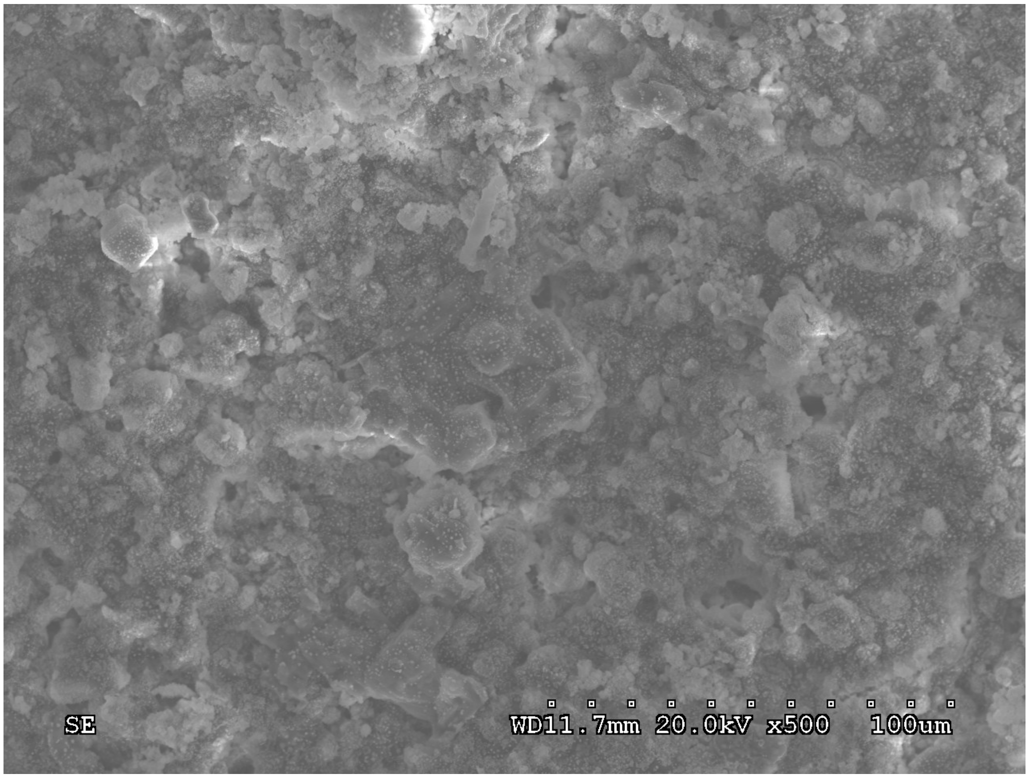
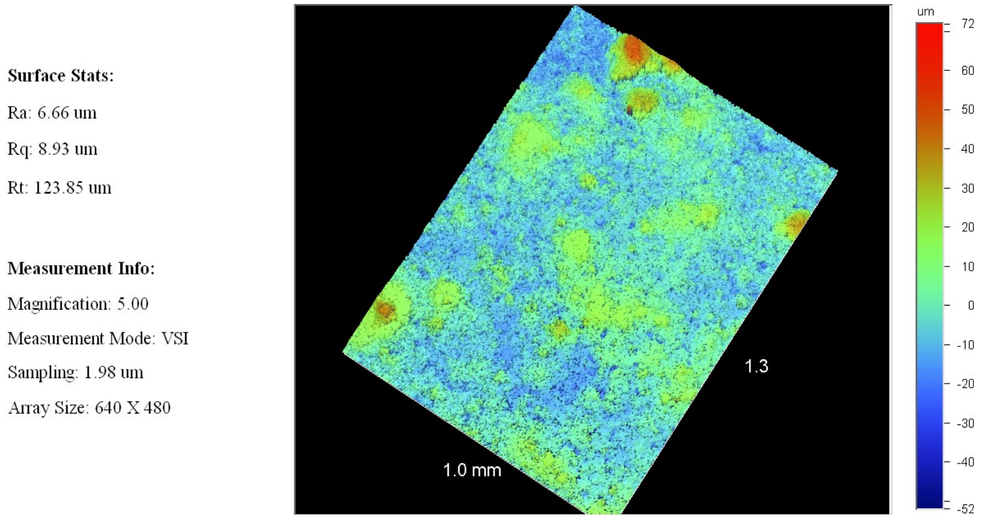


Figure 6.62 SEM Image of topography of Sample 1B after leaching



Surface Stats:

Ra: 6.66 um

Rq: 8.93 um

Rt: 123.85 um

Measurement Info:

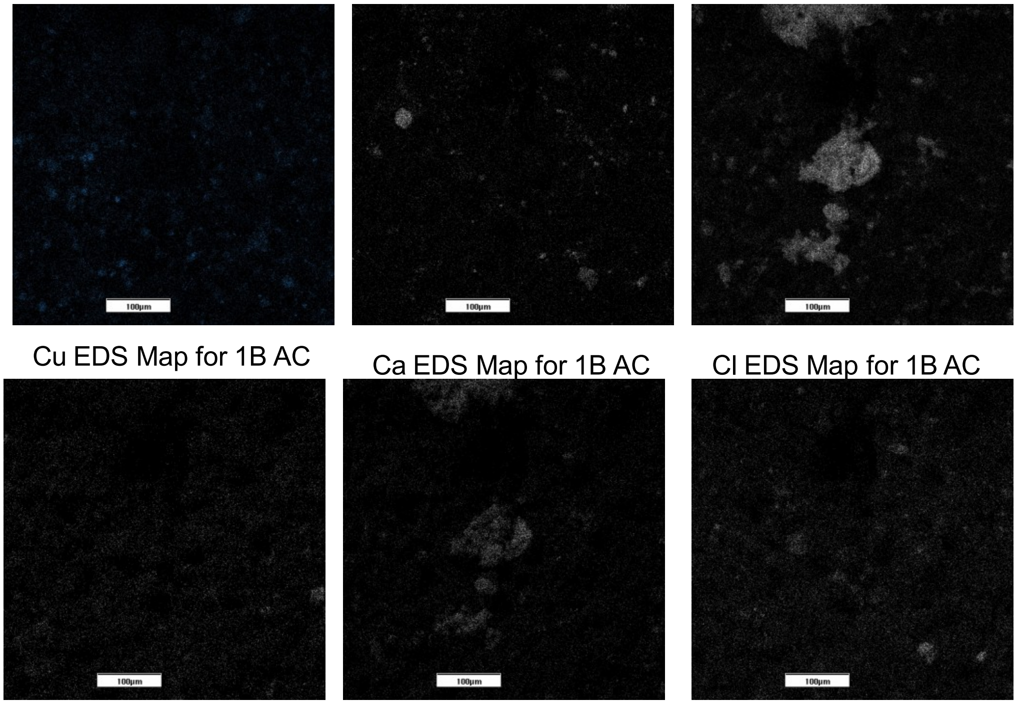
Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

Figure 6.63 Optical profilometer image of topography of Sample 1B after leaching



Cu EDS Map for 1B AC

Ca EDS Map for 1B AC

Cl EDS Map for 1B AC

Mg EDS Map for 1B AC

Na EDS Map for 1B AC

S EDS Map for 1B AC

Figure 6.64 EDS maps of Sample 1 B after leaching

The general trend was that the samples developed a higher porosity but had no cracks or rusting even on the corners. The profilometer images indicate that the roughness had reduced after the leaching for some samples while it had increased for some others. This can be understood from the fact that the dynamic forces of water and air bubbled through the water bath during the seven days of leaching which caused erosion of the projecting particles on the surface. Dissolution of ionomer and release of cuprous oxide from the surface contributed to decrease reduction in surface roughness. Formulation with only 10% ionomer underwent a higher corrosion and increase in surface roughness as for sample 3B and 3T.

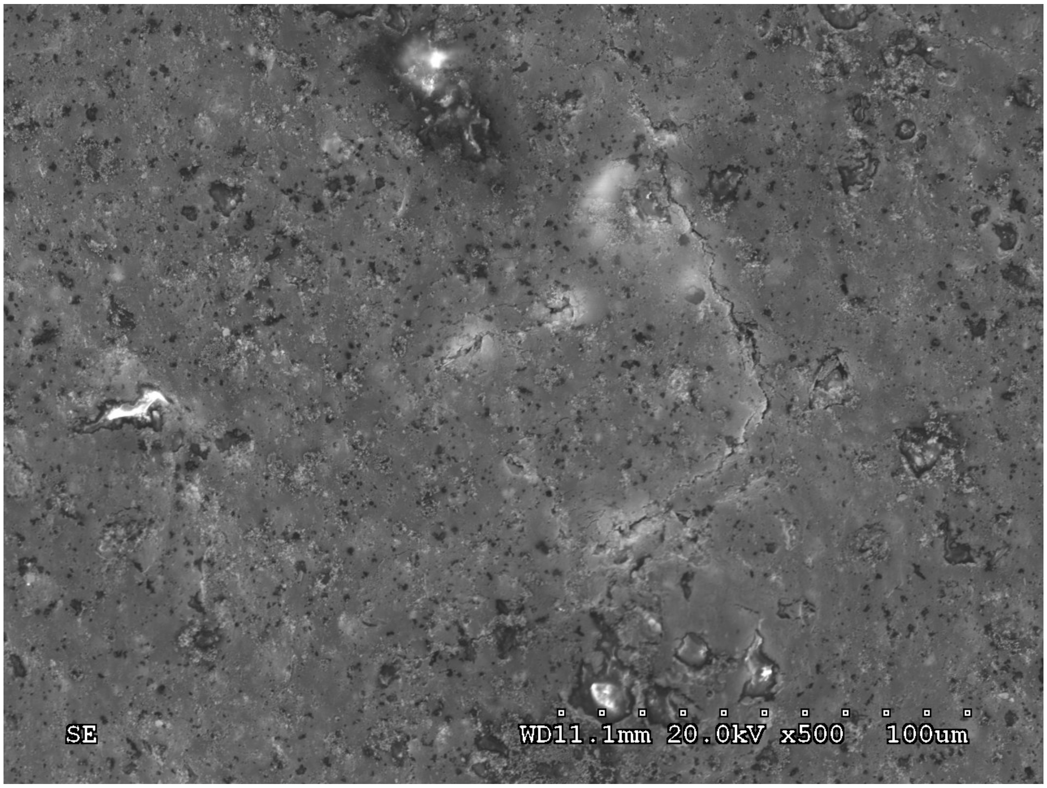


Figure 6.65 SEM Image of topography of Sample 3B after leaching

Surface Stats:

Ra: 5.96 um

Rq: 7.08 um

Rt: 45.72 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

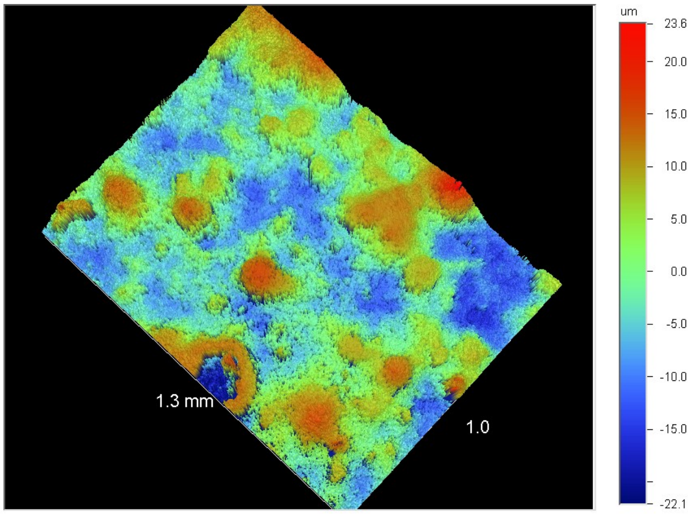
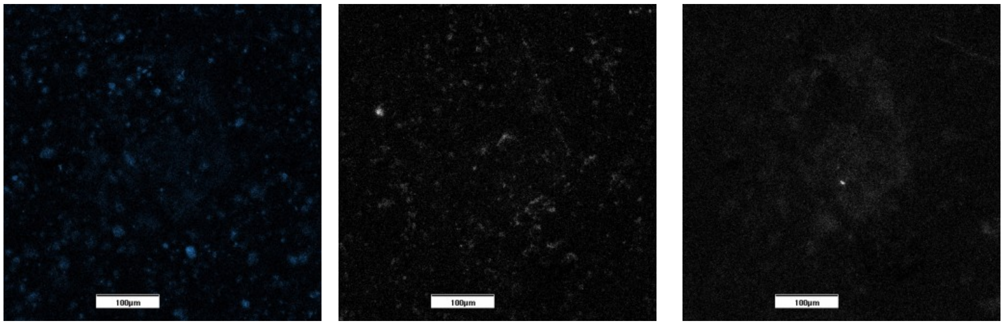
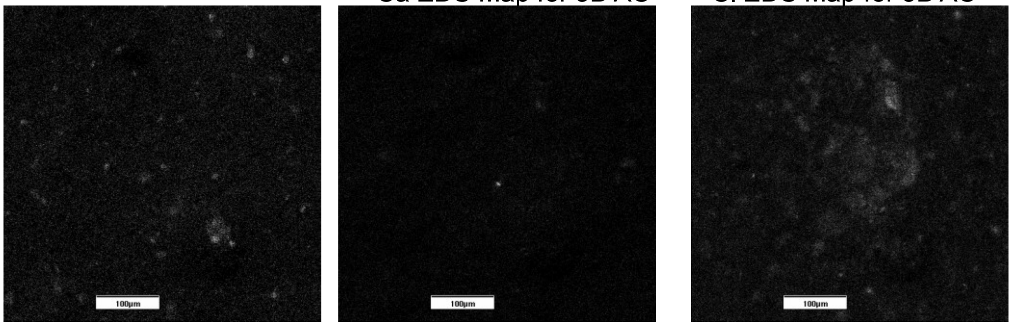


Figure 6.66 Optical profilometer image of topography of Sample 3B after leaching



Cu EDS Map for 3B AC Ca EDS Map for 3B AC Cl EDS Map for 3B AC



Mg EDS Map for 3B AC Na EDS Map for 3B AC S EDS Map for 3B AC

Figure 6.67 EDS maps of Sample 3B after leaching

The uniform porosity of the entire surface after leaching is indicative of uniform dissolution and leaching from all parts of the sample surface. The extent of corrosion and pitting is very small (few pits less than 10um in size) compared to the samples of Part I of the study. The salt deposit is also uniform across the surface and very small in extent as seen from the SEM images and EDS maps. The salt deposit could be due to corrosion or due to ion exchange between the salt water and the $-SO_3H$ groups of the ionomer.

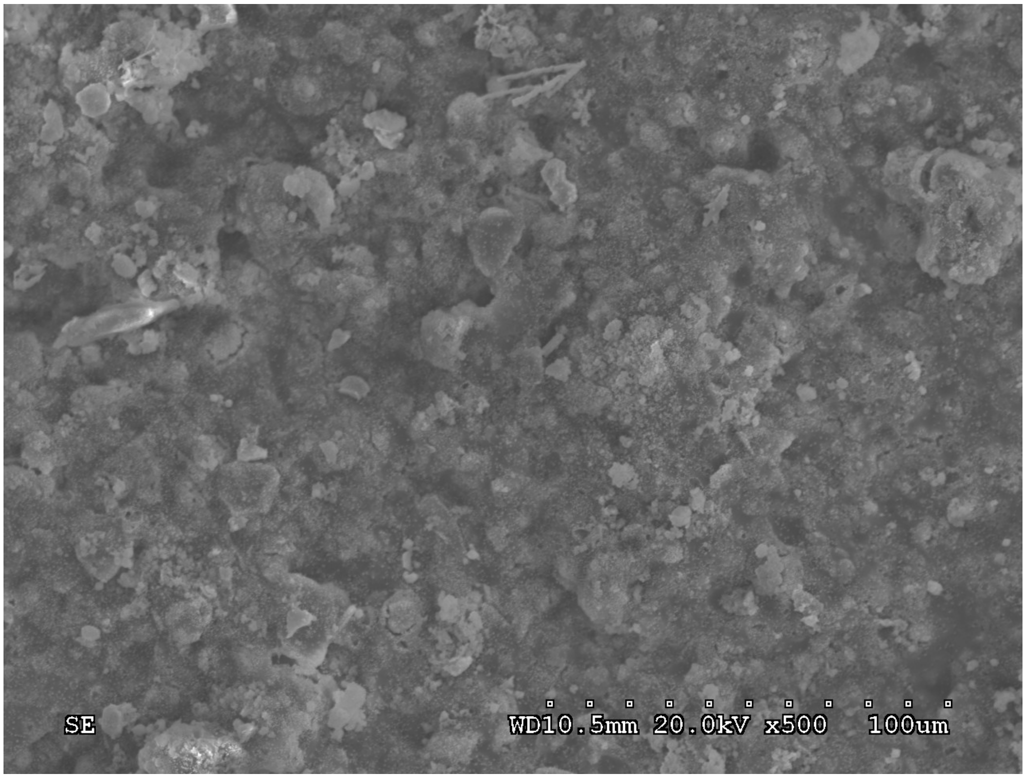


Figure 6.68 SEM Image of topography of Sample 5B after leaching

Surface Stats:

Ra: 5.68 um

Rq: 7.15 um

Rt: 74.92 um

Measurement Info:

Magnification: 5.00

Measurement Mode: VSI

Sampling: 1.98 um

Array Size: 640 X 480

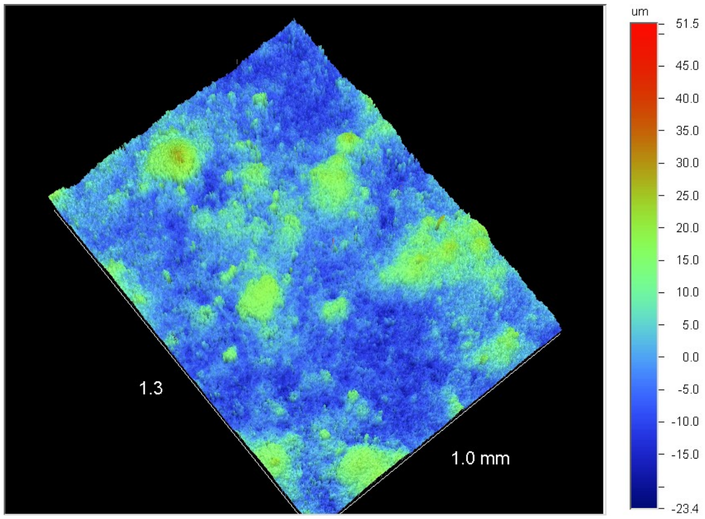
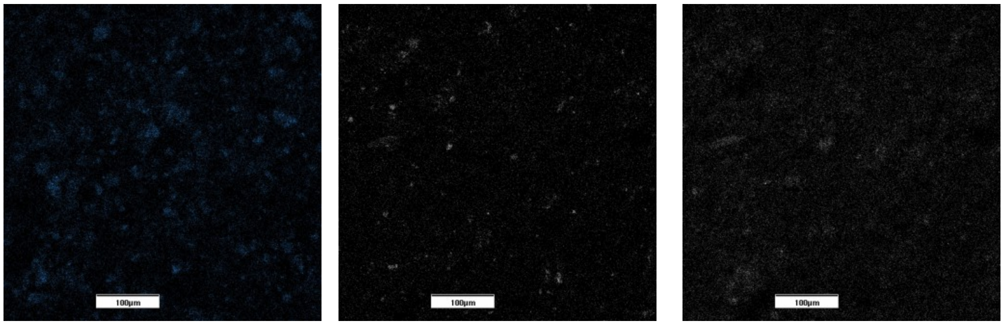
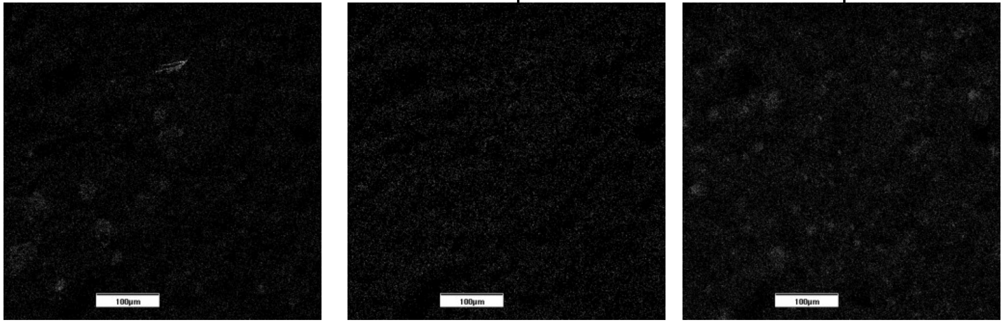


Figure 6.69 Optical profilometer image of topography of Sample 5B after leaching



Cu EDS Map for 5B AC Ca EDS Map for 5B AC Cl EDS Map 5B AC



Mg EDS Map 5B AC Na EDS Map 5B AC S EDS Map for 5B AC

Figure 6.70 EDS maps of Sample 5B after leaching

The EDS-maps reveal that the concentration of Mg, Ca, and Cl increases across the surface after leaching while the concentration of sodium decreases to some extent, indicating displacement of sodium from its –SO3H group in the ionomer by its heavier metal ions from the sea-water. This could be in addition to salt deposit occurring due to corrosion of the surface. The copper distribution across the surface becomes more scattered and diffuse versus patchy as compared from the EDS maps before and after leaching.

6.10.2 Mechanical properties of formulations after leaching

The changes in the mechanical properties like hardness and reduced elastic modulus of the different formulations as a result of corrosion is reflective of the corrosion resistance of the different samples and can be directly correlated to the behavior and concentration of the different additives.

Blend Series: The blend series demonstrated some interesting findings with the Nano-mechanical tests performed after the leach-study. A plot of reduced elastic modulus vs. samples can be seen below. From the plot it can be seen that the modulus of all sample except formulation 3B with 10% Ionomer and 5% Viscoplex had increased a little after corrosion.

This increase in modulus after corrosion can be associated to the amount of ionomer remaining in paint after dissolution in water, Viscoplex content, matrix content, the amount of copper leached from the sample and corrosion. The general trend was that;

- Greater the ionomer dissolution, less the amount remaining in the sample and higher the concentration of the paint matrix-so modulus increases. E.g. sample 1B , 2B and 5B had a higher concentration of ionomer to start with and lose so that the change in their modulus was higher
- Higher the concentration of the paint epoxy matrix after leaching, higher the modulus of the coating. This is directly related to the amount of copper leached from the sample. Copper leaching was facilitated and controlled by the

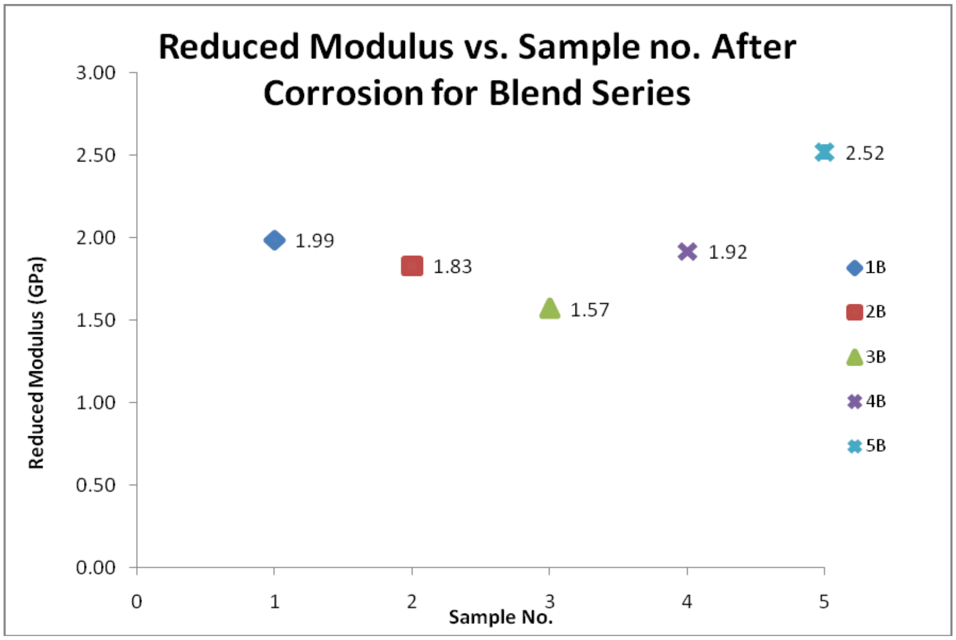


Figure 6.71 Reduced modulus of blend series for Part II study formulations after leaching

concentration of ionomer and Viscoplex in the paint. Higher leaching of copper involved greater loss of ionomer and enriched the epoxy paint content of the sample, thus raising its modulus. Eg. 5B lost the highest amount of copper in the seven days and had the highest modulus after the experiment while 3B which lost the lowest amount of copper had the lowest elastic modulus. Sample 4B and 1B also lost a high amount of copper to possess a higher modulus thereafter.

The hardness values of the blend series samples after the leach-study followed the same trend as the modulus again due to reasons described above. All samples except 3B increased in hardness after corrosion. A combined effect of all the above factors coupled with corrosion as seen from topography and scribe studies can be considered responsible for the changes in modulus and hardness after the leaching study.

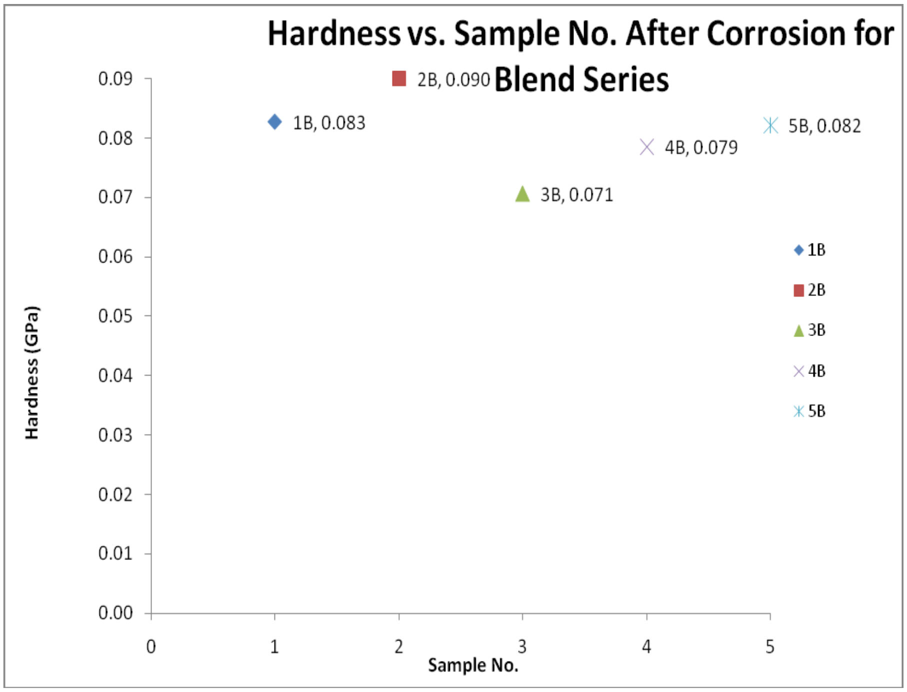


Figure 6.72 Hardness of blend series for Part II study formulations after leaching

Top-Coat Series: In case of the top-coat series, the concentration of the additives was the same with the difference that there was no copper oxide in the top coat. For the top-coat series the trend for hardness and reduced modulus is the same and is similar to the trend before the leach study.

The higher content of the paint matrix which became even higher after the dissolution of ionomer from the samples caused the modulus and hardness values to be slightly higher after leaching. However since the amount of ionomer dissolved and copper leached was very low, the net change in the matrix content after the leaching study did not change much and hence did not significantly change the hardness or modulus values or the trend among the different formulations after leaching.

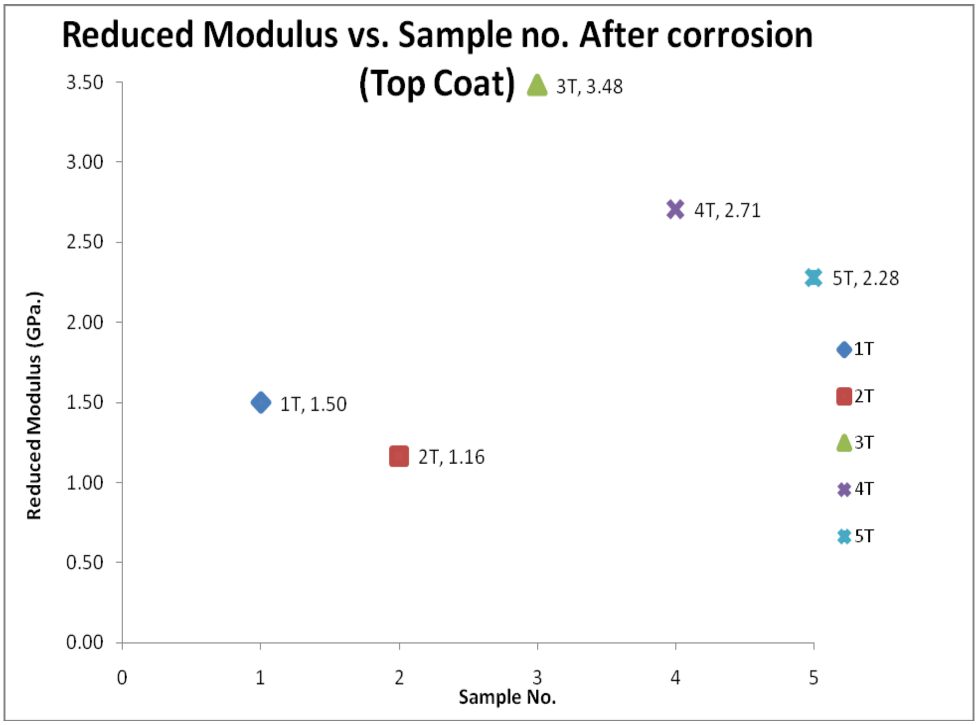


Figure 6.73 Plot of reduced modulus of top-coat for Part II study formulations after leaching

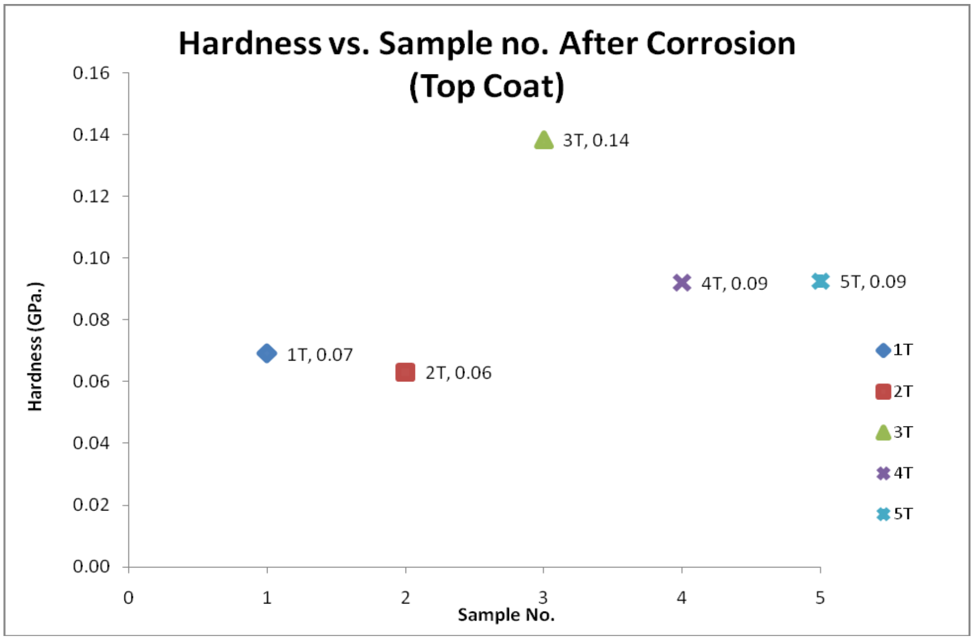


Figure 6.74 Plot of hardness of top-coat series for Part II study formulations after leaching

6.10.3 Weight and Thickness Measurement

The plots of the weight and thickness measurements of the different formulations for the Blend and Top-coat series in course of the leaching study are given below. As discussed in Part I of the study weight and thickness changes during the leaching study demonstrate the on-going processes which might be affecting the overall leaching process and they help understand the leaching mechanism better.

Blend Series: The observations for the blend series were as follows:

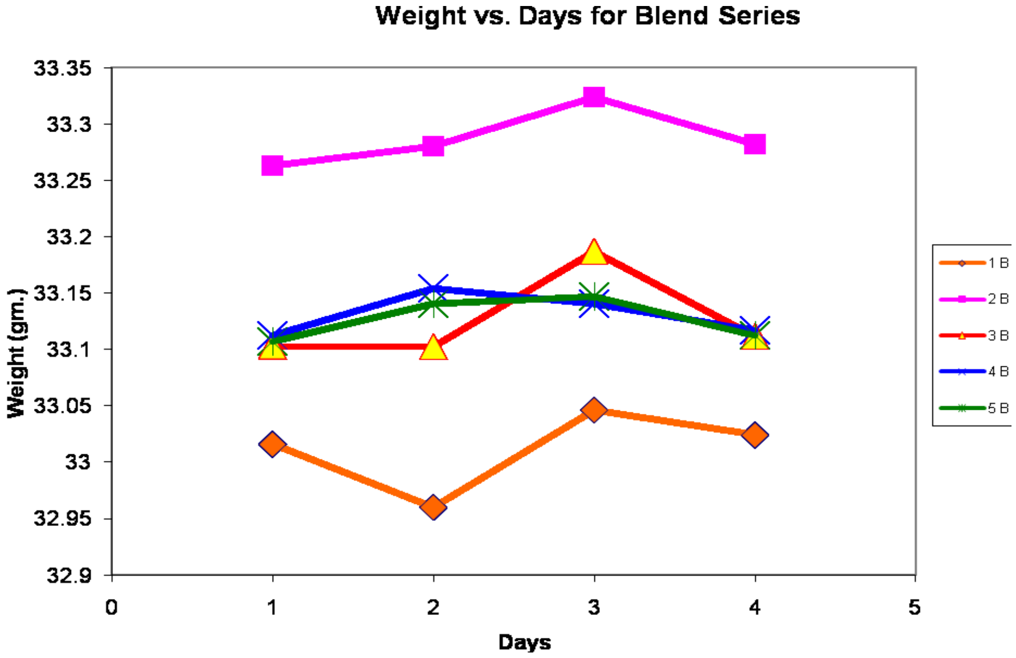


Figure 6.75 Plot of weight vs. Sample No. for Part II Study Blend formulations

- All samples showed s slight loss or constancy of weight after the 1st day of leaching.
- From the 1st-4th day of leaching; samples 1B, 2B and 3B showed an increase in weight. This could be due the absorption of water and swelling by the paint matrix or due to the build-up of diffusion barriers and deposit of corrosion products (salt deposits as seen from the SEM images after corrosion). This increase in weight is also in agreement with

the leach rates calculated which demonstrate drop in leach rate from the 1st-4th day of leaching.

- The observation for samples 4B and 5B were different between the 1st-4th days of leaching. Unlike the other three these samples display constancy in weight. This could be attributed to the balancing effects of increase in weight due to diffusion barriers, water absorption and corrosion and loss in weight due to ionomer dissolution and continuous copper release. These results are also in agreement with the leaching rates of copper which are much higher than the other formulations on the 4th day of release.
- All formulations exhibit a loss in weight from the 4th-7th days of leaching indicating that the weight loss by ionomer dissolution and copper release supersedes the weight build up factors. Once again these results display a congruency with the leach rate data where all rates increase on the 7th day demonstrating renewal of release rate from nascent surfaces of the coating.

The weight loss trend for the Top coat samples was found to be the same as that of the blend series samples with the difference that the weight build-up effects due to the reason described above for the blend series are seen even earlier (from the 1st day of leaching). This can be understood from the high matrix concentration (80-88%) of the top-coat samples which prevents diffusion and release of adequate amounts of water. However all samples display a downward trend from the 4th day of leaching.

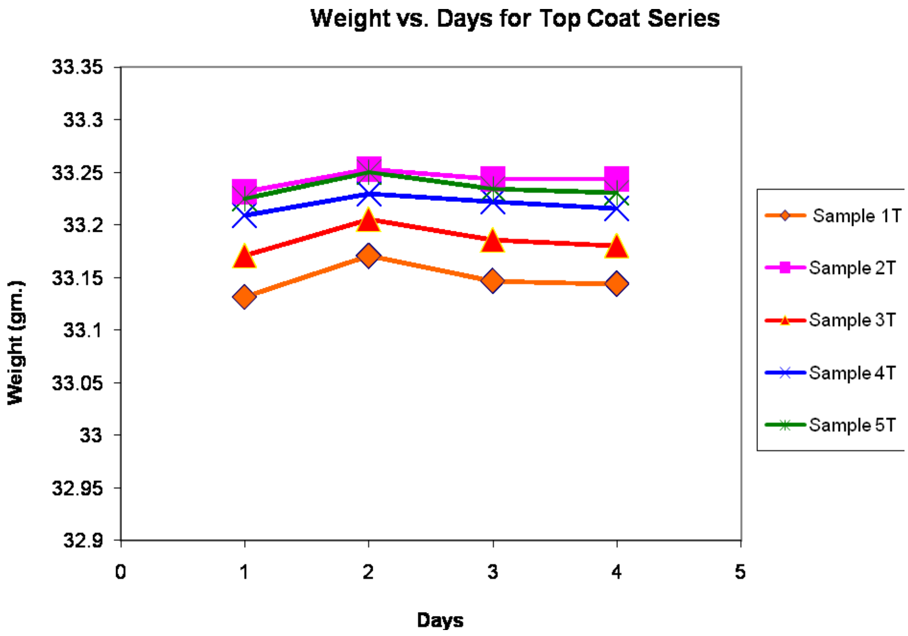


Figure 6.76 Plot of weight vs. Sample No. for Part II Study top coat formulations

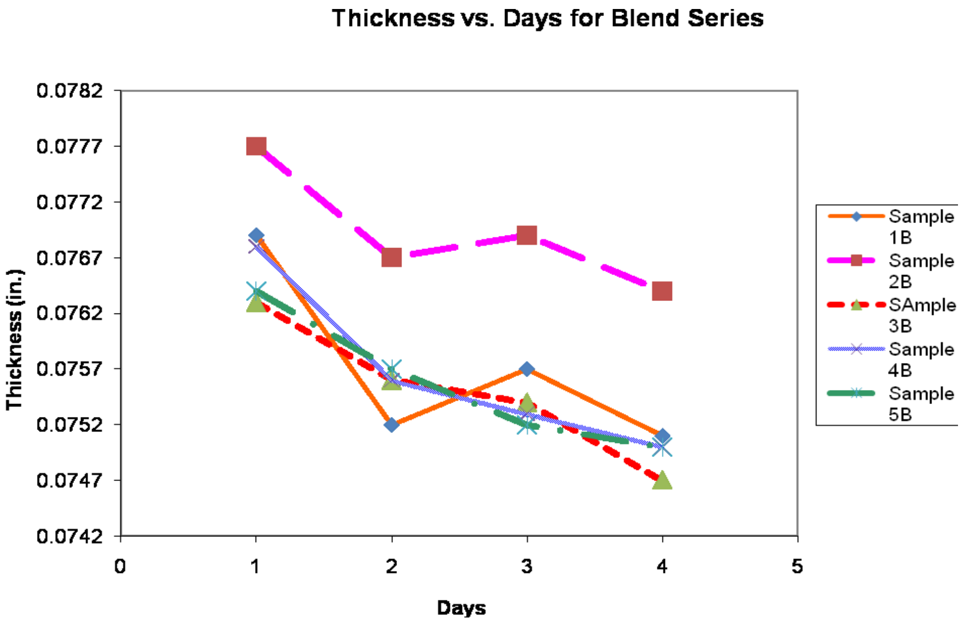


Figure 6.77 Plot of thickness vs. Sample No. for Part II Study Blend formulations

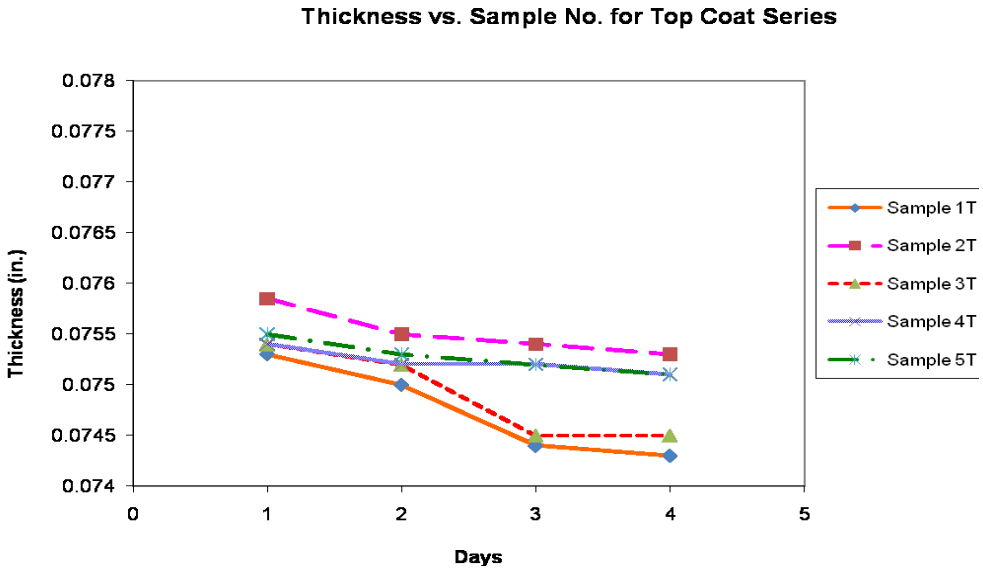


Figure 6.78 Plot of weight vs. Sample No. for Part II Study top coat formulations

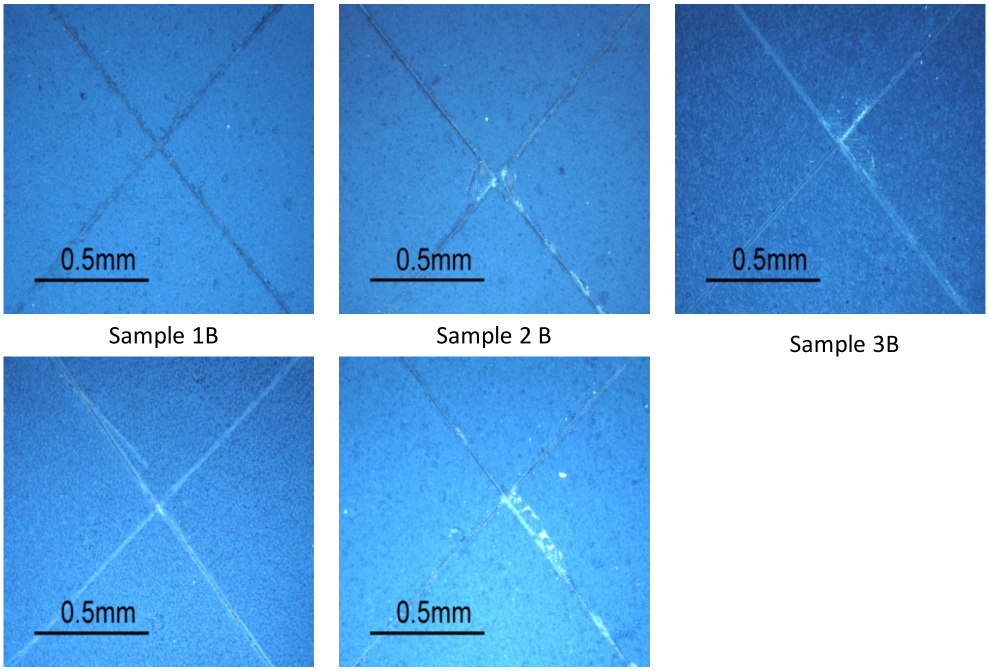
The trend for thickness change for all samples of the blend and top-coat series was found to be the same as that of weight change and the same reasons can be attributed as for the weight change.

Thus the weight and thickness study data are follow the same trend for all formulations and are in agreement with the leach-rate calculations for copper. Based on these results it can be said that all formulations require a thresh-hold time after which they can overcome the diffusion barriers and sustain the release rate by enhanced ionomer dissolution. The formulations 5B and 5T which demonstrated a continuous release rate also showed a constant decline in the weight and thickness of the coating proving their capability in overcoming barriers to diffusion and releasing continuous supplies of copper by ionomer dissolution.

6.11 Corrosion study of scribed samples

The corrosion study on scribed samples for the optimization study was restricted to the blend samples. The top coat samples need further optimization of the concentration of the ionomer to produce the desired leach rates. Hence based on the leach study observations, the scribe study was performed only on the blend series.

As seen from the optical images the scribed samples before immersion in water had a continuous surface free from pitting, salt deposits, rusting or any other kind of corrosion.



Sample 1B

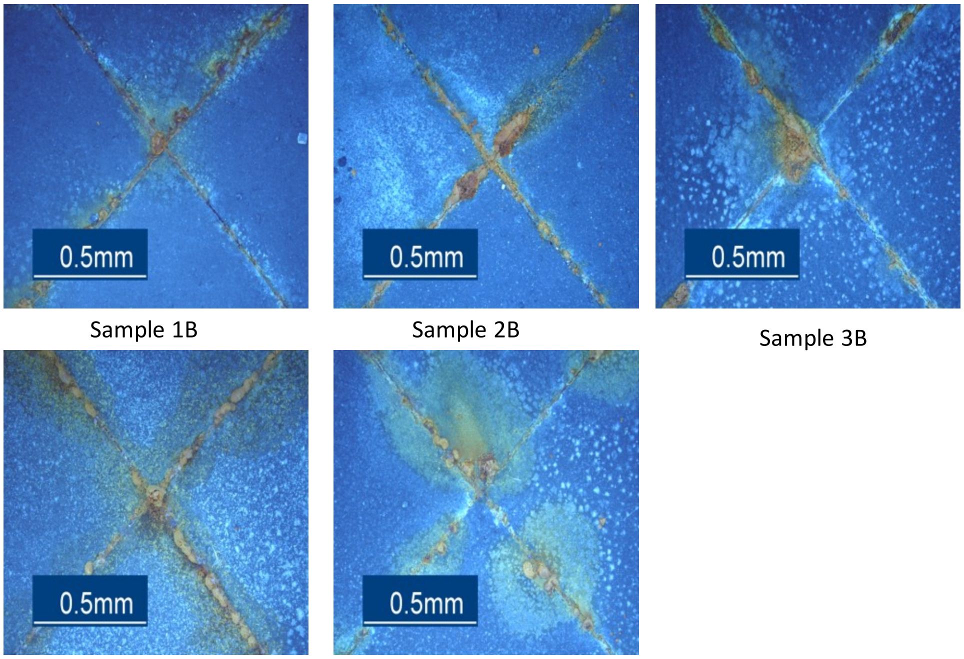
Sample 2 B

Sample 3B

Sample 4B

Sample 5B

Figure 6.79 Optical images of scribe samples of blend samples before leaching



Sample 1B Sample 2B Sample 3B

Sample 4B Sample 5B

Figure 6.80 optical images of scribe samples of blend series after leaching

All samples after the leaching study were corroded and rusted in the scribed region. However the samples with higher proportion of Viscoplex like 1B, 3B and 5B with almost 5% Viscoplex and a high amount of ionomer i.e. 1B, 2B and 5B with 15% ionomer had incomplete coverage of the scribed region. Sample 4B with lowest concentration of both ionomer and Viscoplex showed the highest amount of corrosion and rusting of the scribed region. This confirms that both Viscoplex and ionomer have some contribution to preventing corrosion and rusting of scratches which expose bare metal. Both Sample 1B and 2B which had a high amount of ionomer (15%) showed low corrosion and salt deposits on the coating surface indicating that the ionomer contributes more to protecting damage to the coating versus protecting the bare metal.

6.12 Polarization Study

Polarization study was conducted (as per procedure discussed section 4.8.) on five different chemistries to evaluate their corrosion resistance. The details of the chemistries and their polarization results have been included in Table 6.8

Table 6.8 Corrosion Current and Potential for Samples before leaching

SAMPLE	Corrosion potential (Ecorr) Before leaching (V)	Corrosion Current (icorr) Before leaching (A/cm2)
Sample 1 (IRCUFIB)	-0.39	2×10^{-7}
Sample 3 (AM30CU)	-0.65	2×10^{-6}
Sample 5 (AM30CU5VIS)	-0.71	8×10^{-7}
Sample 6 (AM30CU15 IO T)	-0.66	7×10^{-7}
Sample 5B (AM30CU12.5 IO 3.5 VIS B)	-0.68	5×10^{-7}

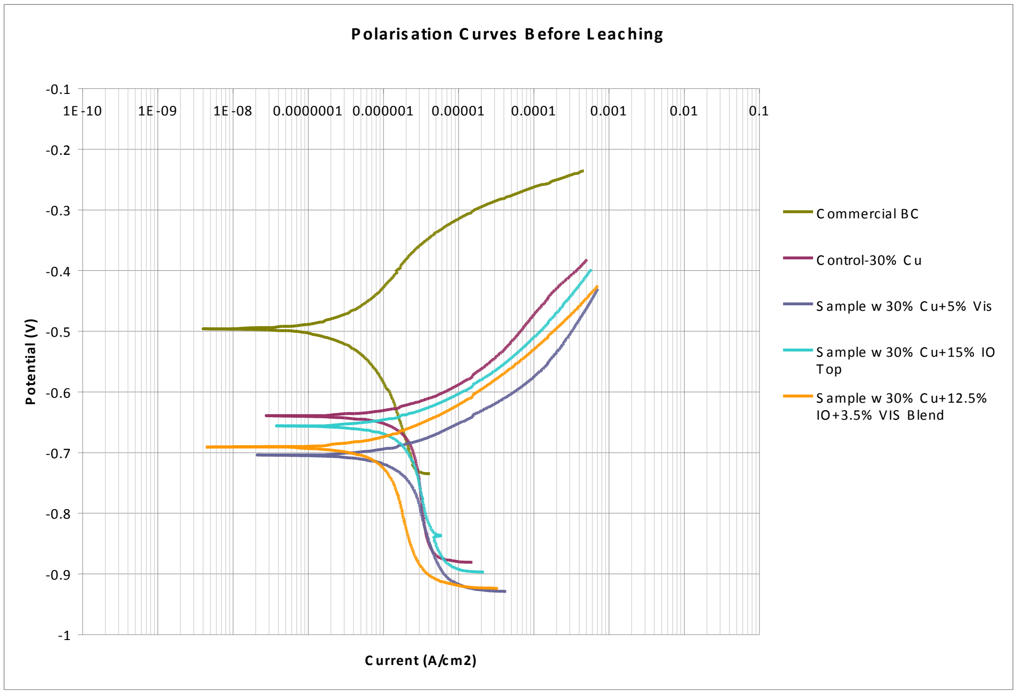


Figure 6.81 Polarization curves of samples before leaching

The polarization plots before and after the 24 hours immersion in salt water can be seen below. Some interesting observations can be made from the polarization plots (Fig.6.82) and the corrosion current and potential values listed in Table 6.9

The commercial sample (Sample 1 IRCUFIB) shows the highest potential(-0.39V) and low corrosion current (10^{-7}A) before 24 hours immersion in sea water; but drops significantly to about -0.65 V after one day of copper leaching in salt water. The corrosion current also increased by an order of magnitude, indicating the high corrosion vulnerability of the coating. The high corrosion potential before immersion could be due to the high concentration of cuprous oxide (43%) in the paint. After 24 hours of immersion in sea-water, the sample must have lost a high amount of copper due to burst release as seen from the leach study results in section 6.4. This coupled with the loss in coating integrity both by leaching and corrosion could be responsible for the drop in corrosion potential after the experiment.

Table 6.9 Corrosion Potential and current for samples after leaching

SAMPLE	Corrosion potential (Ecorr) After leaching (V)	Corrosion Current (icorr) After leaching (A/cm2)
Sample 1 (IRCUFIB)	-0.65	2×10^{-6}
Sample 3 (AM30CU)	-0.64	4×10^{-5}
Sample 5 (AM30CU5VIS)	-0.67	9×10^{-7}
Sample 6 (AM30CU15 IO T)	-0.66	7×10^{-7}
Sample 5B (AM30CU12.5 IO 3.5 VIS B)	-0.73	7×10^{-7}

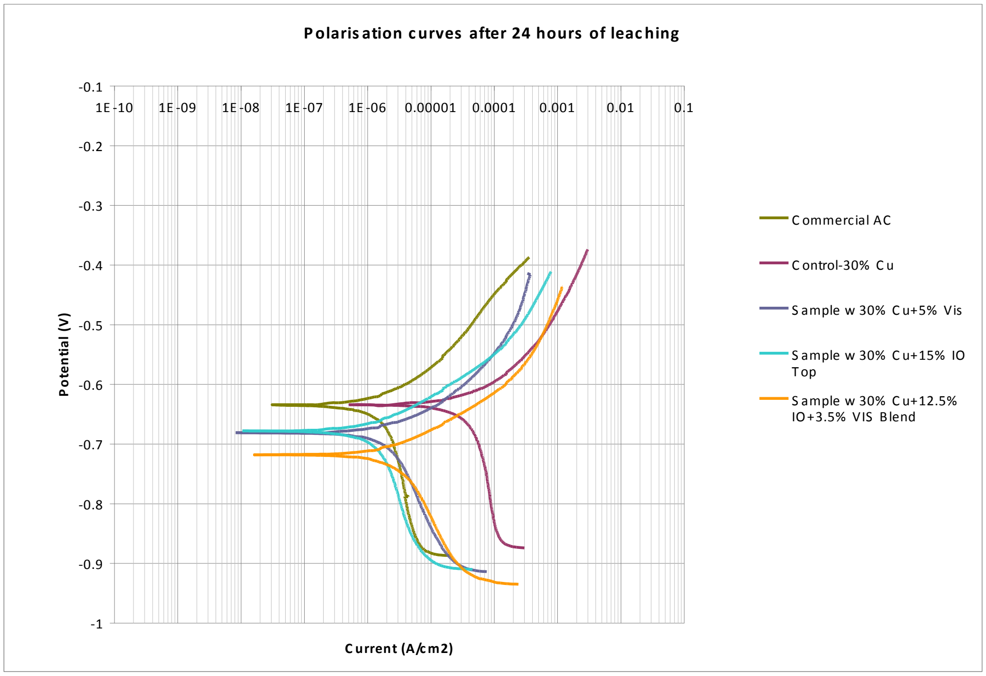


Figure 6.82 Polarization curves of samples after leaching

The control sample (Sample 3 AM30CU) without any additives and just copper oxide shows a higher corrosion current and lower potential. Its corrosion current/rate also increases by an order of magnitude after leaching but the corrosion potential doesn't change as drastically as the commercial. These results clearly indicate that the in the absence of any binding additive the coating is unstable and corrodes rapidly with the leaching of copper to allow more current to pass through with no signs of passivation.

All formulations with viscoplex and Ionomer show similar performance with a low corrosion potential (-0.68V) but a low corrosion current (icorr) $7x10^{-7}$ A/cm^2 before leaching. An interesting fact is that while the commercial and control samples changed much after one day of leaching, these three did not show any increase in the corrosion current/rate and changed very little in corrosion potential. This is indicative of the stability in the structure and the passivating tendency of the additives. Also all of these samples produced a much lower corrosion current (icorr) $7x10^{-7}$ A/cm^2 compared to the control sample 3, both before and after the leaching period. Since all of these formulations had the same concentration of copper, the passivation would be a contribution if the ionomer and viscoplex. Another interesting observation is that, the corrosion potential and corrosion potential and current for sample 6 (AM30CU15IO T) with ionomer only and no copper or viscoplex in the top coat; and sample 5B (AM30CU12.5IO3.5VIS) in a blend had similar corrosion current and corrosion potential both before and after the 24 hours immersion, indicating a domination of the ionomer in controlling the corrosion behavior of the samples. As seen from the scribe test results in section 6.6 and section 6.11, it can be said that the ionomer and the viscoplex demonstrate some ability to protect the coating against corrosion.

CHAPTER 7

DESIGN OF EXPERIMENTS

7.1 DOE for Optimization Study

The Design of Experiments (DOE) is a powerful statistical tool that is used to optimize a product or process. It offers a wide variety of features which allow the identification of the critical factors which affect a particular process so that significant process improvements can be made and higher yield/outcomes can be attained. The Design Expert (version 7.1) software by Stat-Ease was used for making comprehensive interpretations and predicting a model based on critical factors affecting mechanical properties like reduced modulus and hardness and also the copper leach rate from the optimization blends prepared in Part II of the study. This software offers the ability of creating various types of mixture designs using the mixture design techniques and discovering and predicting the ideal recipe for a product or formulation.

In case of the optimization study a DOE matrix of was used for combining the ionomer and viscoplex with a fixed concentration of Cu_2O. Along with the variation of the components, two different cases like a blend series and the top-coat series (Chapter 4.4) were also examined. Also it was realized that in addition to the concentration of ionomer and viscoplex, the matrix concentration which also varied depending on the former two factors had a strong influence on the copper leach rate and the mechanical properties. Thus to get a comprehensive view of the individual and combined influence of the three variables; viz. ionomer, viscoplex and paint matrix concentration and the effect of presence or absence of a fixed concentration of copper, it was necessary to create a design for mixtures and study the affected parameters like leach rate, hardness and reduced modulus as responses to the variables in the design.

7.2 DOE for Blend Series

As discussed in section 4.4 this series was designed to examine the effect of ionomer and viscoplex in controlling the copper release rate and the changes in mechanical properties or corrosion resistance in the presence of cuprous oxide. Hence all additives as listed in Table 7.1 were combined in blends to prepare five different formulations. The responses studied for this series include reduced modulus and hardness both before and after leaching and the leach rates of copper on the 1st, 4th and 7th day of leaching. The D-Optimal design for a mixture with three variables; ionomer, viscoplex and paint matrix concentrations in % weight adding up to a concentration of 30% by weight in the paint recipe (since the remaining is 30% Cu_2O fixed for all formulations) was used to study responses.

The responses were obtained in the form of a triangular contour plot and 3D plot as seen in fig.7.1 and 7.2. The apexes of the triangle indicate maximum concentration of the three components which decrease along the median. The parallelogram contour plot shows the matrix components.

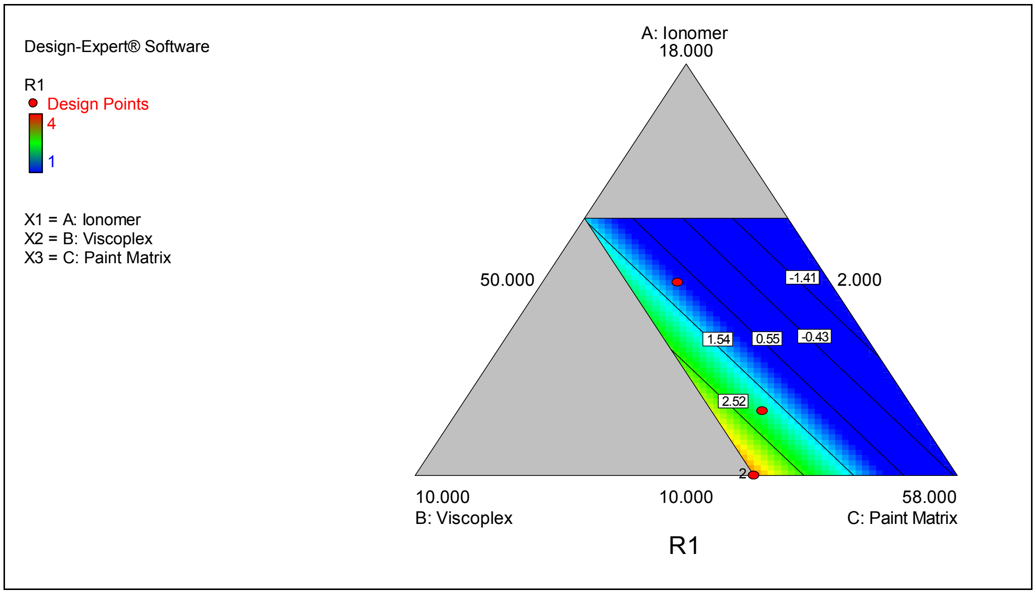


Figure 7.1 Example of contour design plot for a mixture of three with sum of 70%

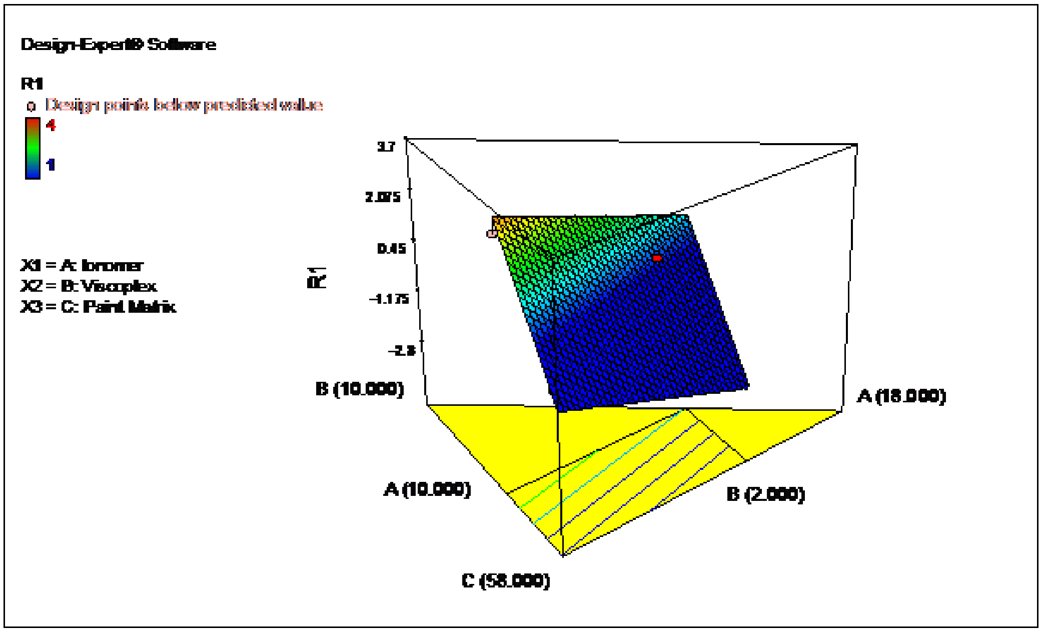


Figure 7.2 Example of 3D-design plot for a mixture of three with sum of 70%

Table 7.1 DOE Matrix for D-Optimal design of Blend Series

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Cu_2O Fixed Qty.
Sample 1B	15%	5%	50%	30%
Sample 2B	15%	2%	53%	30%
Sample 3B	10%	5%	55%	30%
Sample 4B	10%	2%	58%	30%
Sample 5B	12.5%	3.5%	54%	30%

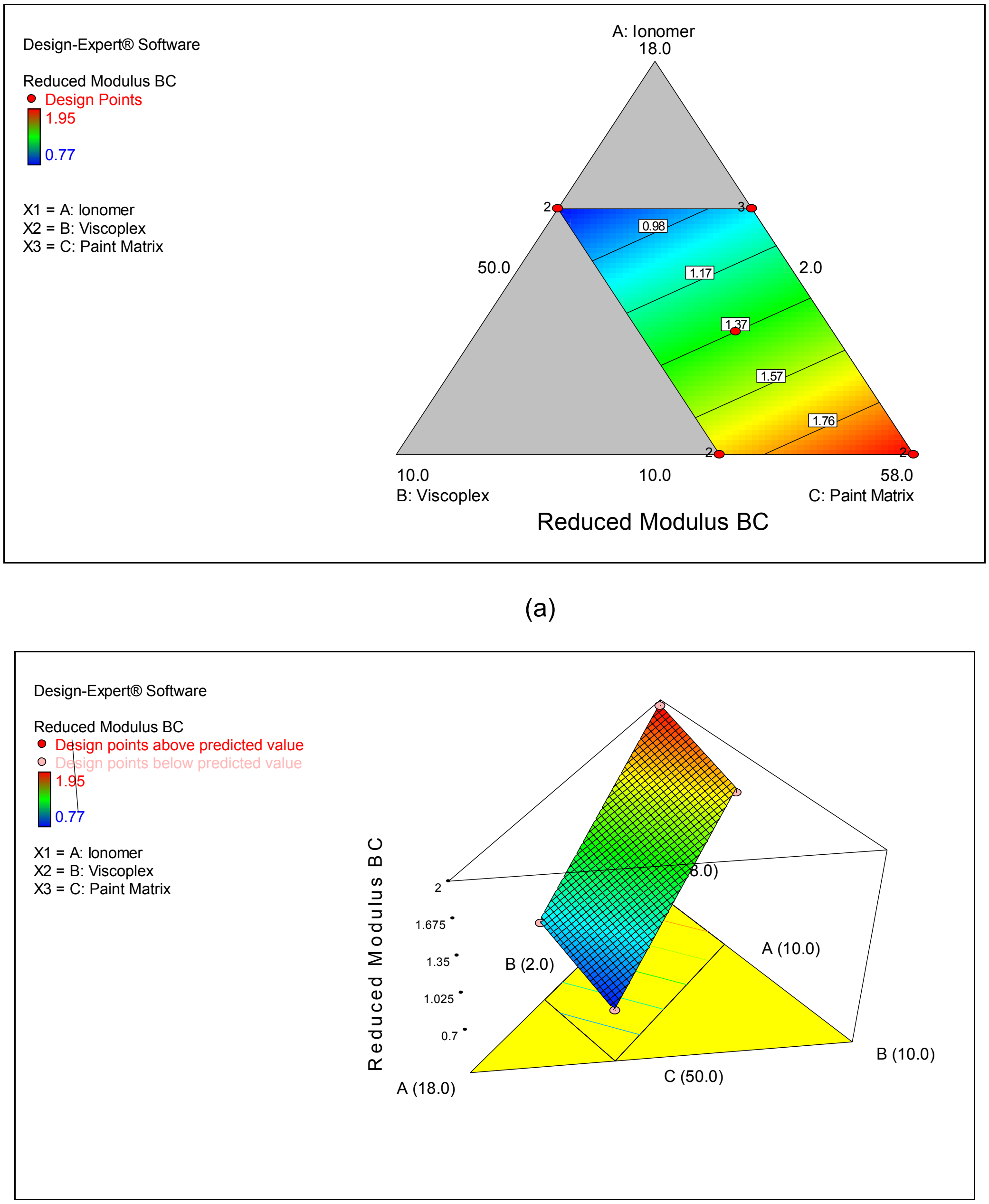
7.2.1 Design plots for Reduced Modulus and Hardness before leaching

The nano-mechanical studies performed before leaching by single indentation tests on the blend series samples gave the following results for as listed in table 7.2.

Table 7.2 Responses for reduced modulus and hardness of Blend Series before leaching

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Cu_2O Fixed Qty.	Response 1 Reduced Modulus Gpa	Response 2 Hardness Gpa
Sample 1B	15%	5%	50%	30%	0.77	0.03
Sample 2B	15%	2%	53%	30%	1.01	.03
Sample 3B	10%	5%	55%	30%	1.67	.07
Sample 4B	10%	2%	58%	30%	1.95	.07
Sample 5B	12.5%	3.5%	54%	30%	1.54	.05

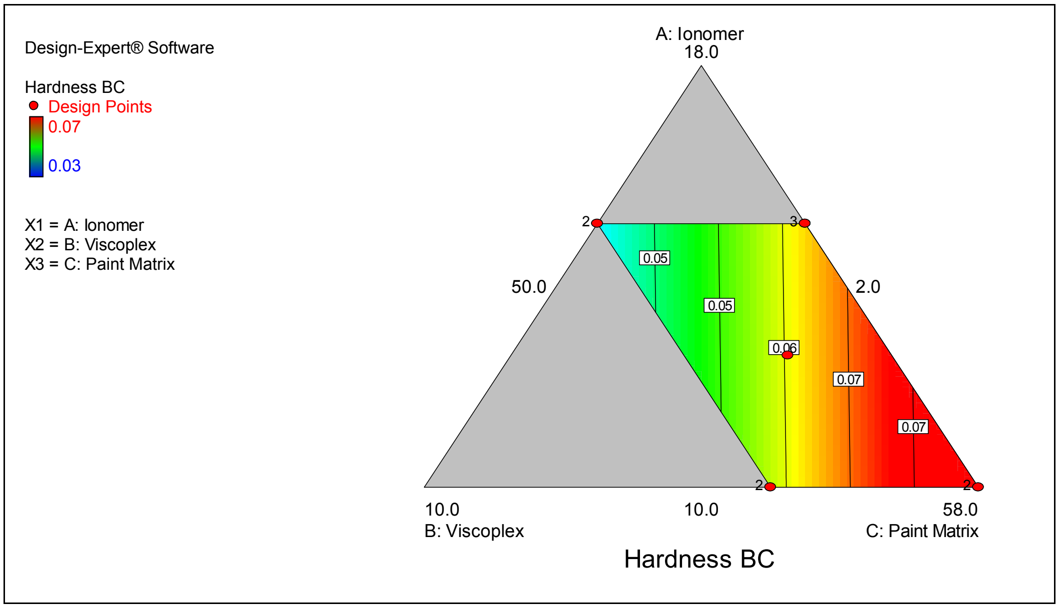
From fig.7.3 (a) & (b) it can be seen that the reduced modulus before corrosion increases with decreasing concentration of Ionomer as marked by the red region of the contour map which has high paint matrix content but low proportions of ionomer and viscoplex. Also from the direction of the contour lines it can be seen that the reduced modulus is inversely related to ionomer content as the modulus values decrease along the apex ‘A’ of the triangle. It also shows that the matrix concentration is directly proportional to the modulus. The modulus seems to be independent of viscoplex concentration (contour lines are parallel to the viscoplex median/axis).



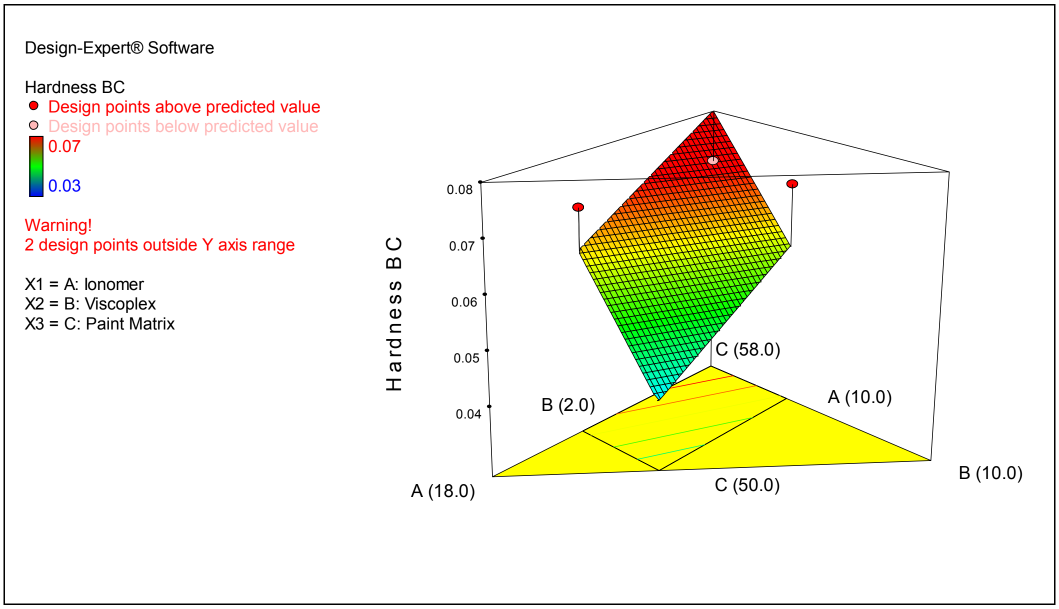
(a)

(b)

Figure 7.3 (a) Contour plot (b) 3D plot for reduced modulus before leaching



(a)



(b)

Figure 7.4 (a) Contour plot (b) 3D plot for hardness before leaching

From fig.7.4 (a) & (b) it can be seen that the hardness before corrosion increases with decreasing concentration of viscoplex as marked by the red region of the contour map which has high paint matrix content but low proportions of ionomer and viscoplex. Also from the direction of the contour lines it can be seen that the hardness is directly related to paint matrix content as the hardness values increase along the vertex ‘C’ of the triangle. The hardness seems to be independent of ionomer concentration (contour lines are parallel to the viscoplex median/axis).

7.2.2 Design plots for Reduced Modulus and Hardness after leaching

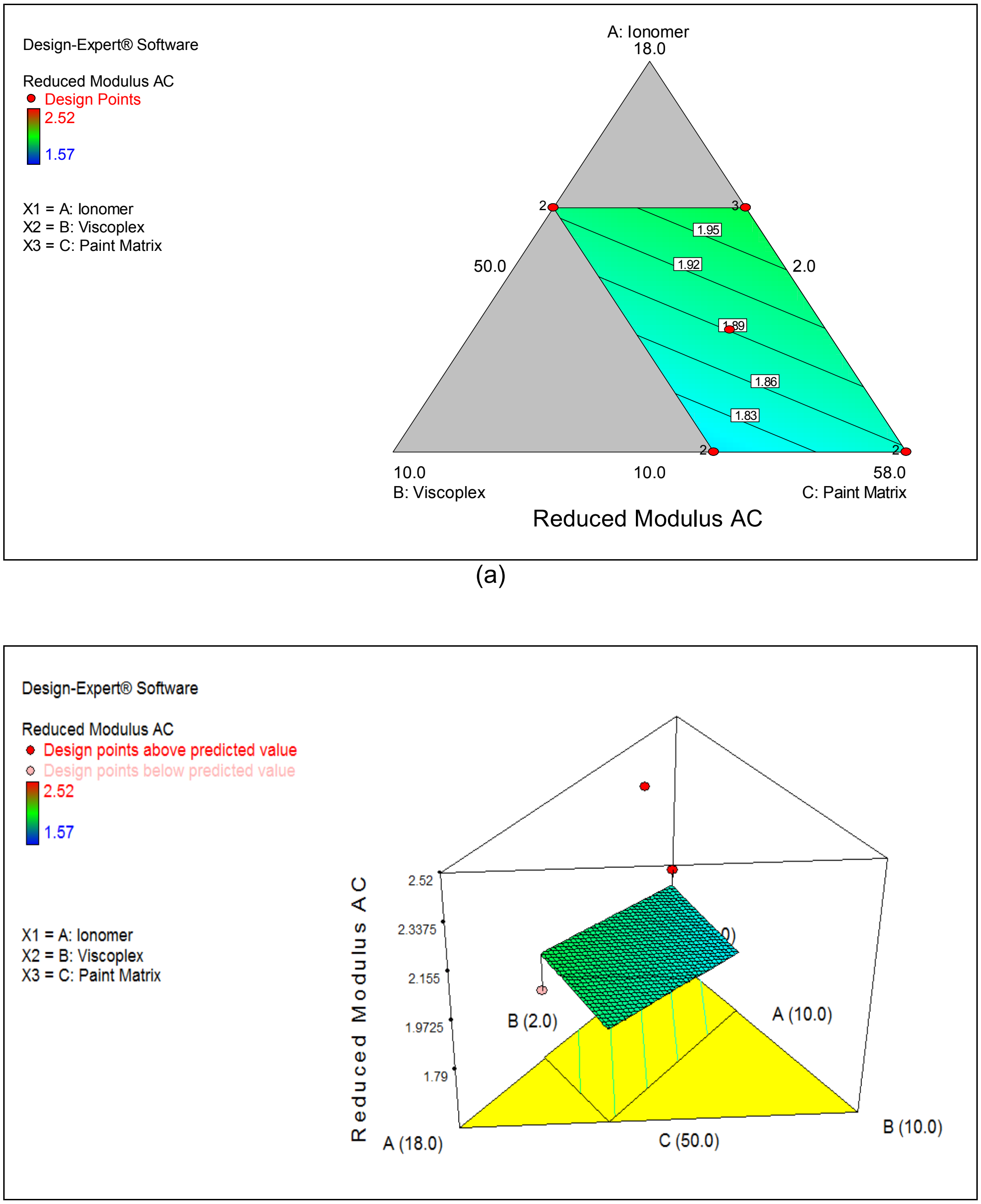
The nano-mechanical studies performed after leaching on the blend series samples gave the following results for as listed in table 7.3.

Table 7.3 Responses for reduced modulus and hardness of Blend Series after leaching

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Cu_2O Fixed Qty.	Response 1 Reduced Modulus Gpa	Response 2 Hardness Gpa
Sample 1B	15%	5%	50%	30%	1.99	0.08
Sample 2B	15%	2%	53%	30%	1.83	0.09
Sample 3B	10%	5%	55%	30%	1.57	0.07
Sample 4B	10%	2%	58%	30%	1.92	0.08
Sample 5B	12.5%	3.5%	54%	30%	2.52	0.08

While interpreting the results for reduced modulus and hardness by the DOE method an important fact should be taken into consideration. When the samples were subject to the leaching test several variables were introduced namely; differential leaching of copper which initially (before leaching) constituted a fixed 30 weight % of the paint matrix. Along with the leaching of copper there would also have occurred leaching of differential proportions of the ionomer, viscoplex and paint matrix based on the binding and releasing forces of the coating.

Sea water salt deposit, corrosion and deposition of corrosion products would also have occurred during the leaching time period.

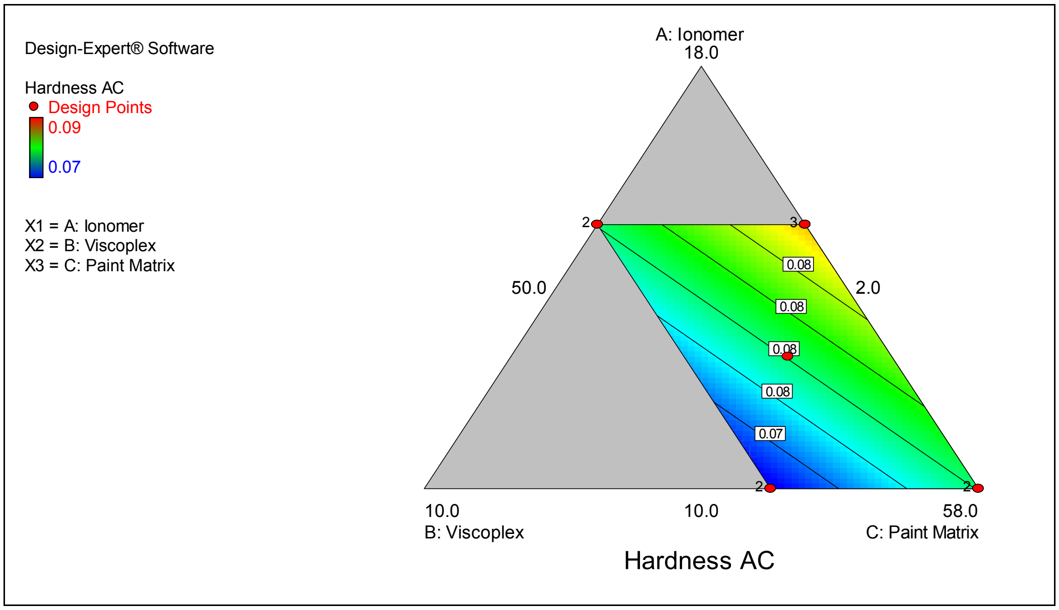


(a)

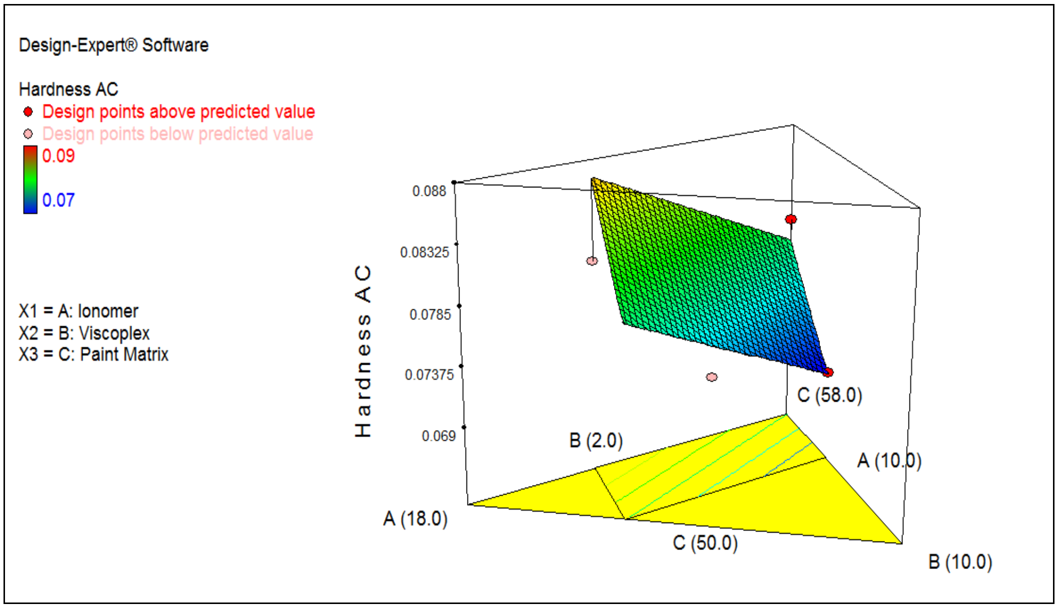
(b)

Figure 7.5 (a) Contour plot (b) 3D plot for reduced modulus after leaching

The design plots for the reduced modulus after leaching changed significantly from those before leaching.



(a)



(b)

Figure 7.6 (a) Contour plot (b) 3D plot for hardness after leaching

The contour lines in fig. 7.5 (a) indicate that the reduced modulus after leaching is almost independent of the concentration of the paint matrix (lines running parallel to the CA) and are more dependent on the concentration of the both the ionomer and viscoplex. Increasing concentration of ionomer and decreasing concentration of viscoplex increases the reduced modulus. However, due to the variations in sample configuration owing to leaching and corrosion of different elements, the statistical confidence calculated from the ANOVA (analysis of variance method) was very low, decreasing the reliability of this model.

The statistical design models for the hardness of the blend formulations after leaching (fig. 7.6 a & b) were found to follow the same trend as that of the reduced modulus after leaching. The hardness values were similar for all formulations but scaled higher from the hardness values before leaching. The statistical confidence for the hardness model as calculated by the ANOVA method was very high 98%.

7.2.3 Design plots for Leach rates of blend samples at different intervals

The copper leach rates for the blend series during the seven day leaching study are listed in table

Table 7.4 Responses for leach rates of Blend Series

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Cu_2O Fixed Qty.	Response 1 Day 1 ug/cm^2/day	Response 2 Day 4 ug/cm^2/day	Response 3 Day 7 ug/cm^2/day
Sample 1B	15%	5%	50%	30%	37	7	12
Sample 2B	15%	2%	53%	30%	33	7	11
Sample 3B	10%	5%	55%	30%	35	9	7
Sample 4B	10%	2%	58%	30%	35	13	14
Sample 5B	12.5%	3.5%	54%	30%	39	12	16

The design models prepared for the leach rate dependence of blend formulations on concentrations of ionomer, viscoplex and paint matrix concentration can be seen below (fig. 7.7-7.9).

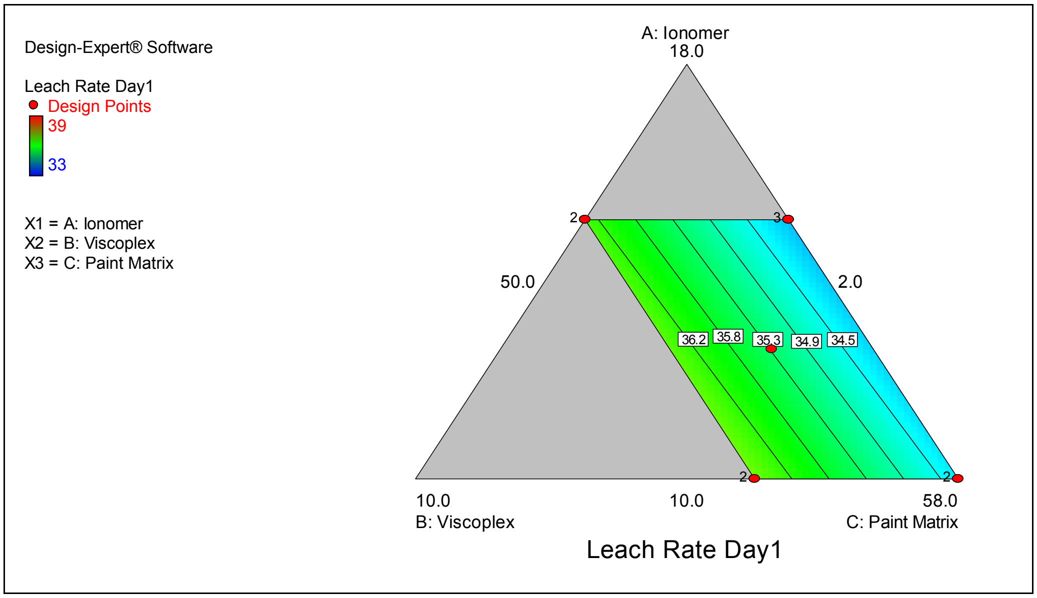


Figure 7.7 Contour plot for leach rates on day 1

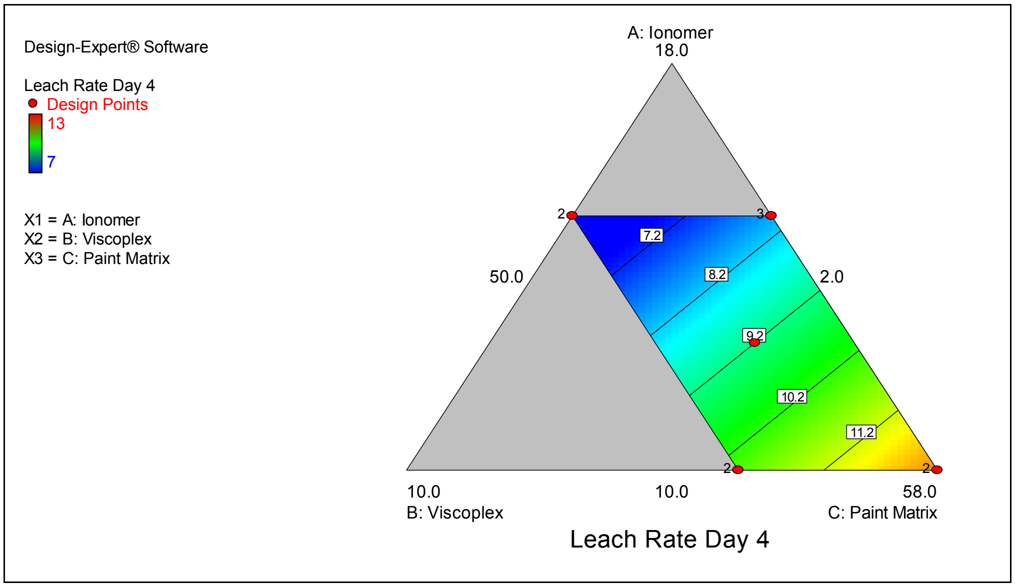


Figure 7.8 Contour plot for leach rates on day 4

As discussed in section 7.2.2 due to the varying forces that come into play when the leaching phenomenon occurs; the statistical confidence on the models below reduces to a certain extent. This can be understood from the fact that Cu2O which is considered as a fixed quantity in designing the models below becomes a variable during the leaching study and varies for different formulations. In addition the corrosion process introduces several other variables which cannot be included in the design model and hence reduce the statistical confidence on the same. It can be seen below that the contour plots on day 1 and day 7 of leaching when the leach rates were significantly high are similar and are different from leach rate variance trend on day 4 where the leach rates for all samples had dropped.

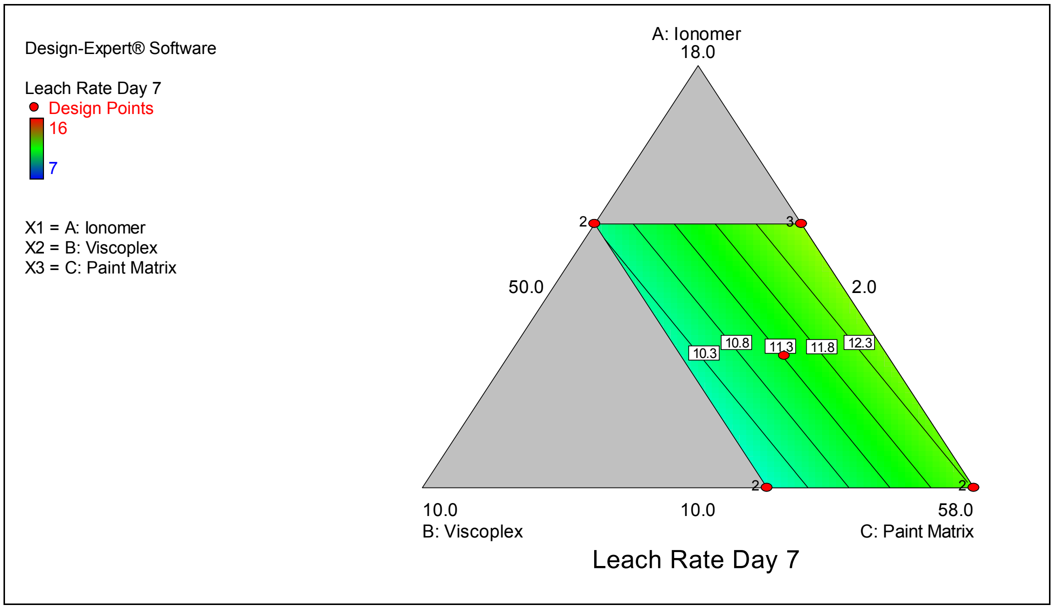


Figure 7.9 Contour plot for leach rates on day 7

Day1 and Day 7 contour plots indicate that decreasing the proportions of viscoplex and paint matrix contributes to increasing the leach rate. The contour plots for day 1 and day 7 when the leach rates were high also indicate that increasing proportions of the ionomer tend to increase the leach rates.

The low statistical confidence of the design plots clearly indicates that repeat tests with the formulations are desired before making any conclusive interpretations.

7.3 DOE for Top-Coat Series

The top-coat series was designed to examine the influence of ionomer ED-SPAN and viscoplex in controlling the leach rate of copper when the latter is embedded in an underlying layer and is not free to leach out from the surface but instead restricted pathways created by ionomer dissolution/paint matrix disintegration as a medium for its release. The DOE compositions for the top-coat series can be seen below:

Table 7.5 DOE compositions of top-coat series

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3
Sample 1T	15%	5%	80%
Sample 2T	15%	2%	83%
Sample 3T	10%	5%	85%
Sample 4T	10%	2%	88%
Sample 5T	12.5%	3.5%	84%

The D-optimal mixture method was used to create and predict design models reflecting the critical effect of the responses like reduced modulus, hardness and leach rates. The models for each of these responses have been discussed in the subsequent sections.

7.3.1 Design plots for Reduced Modulus and Hardness before leaching

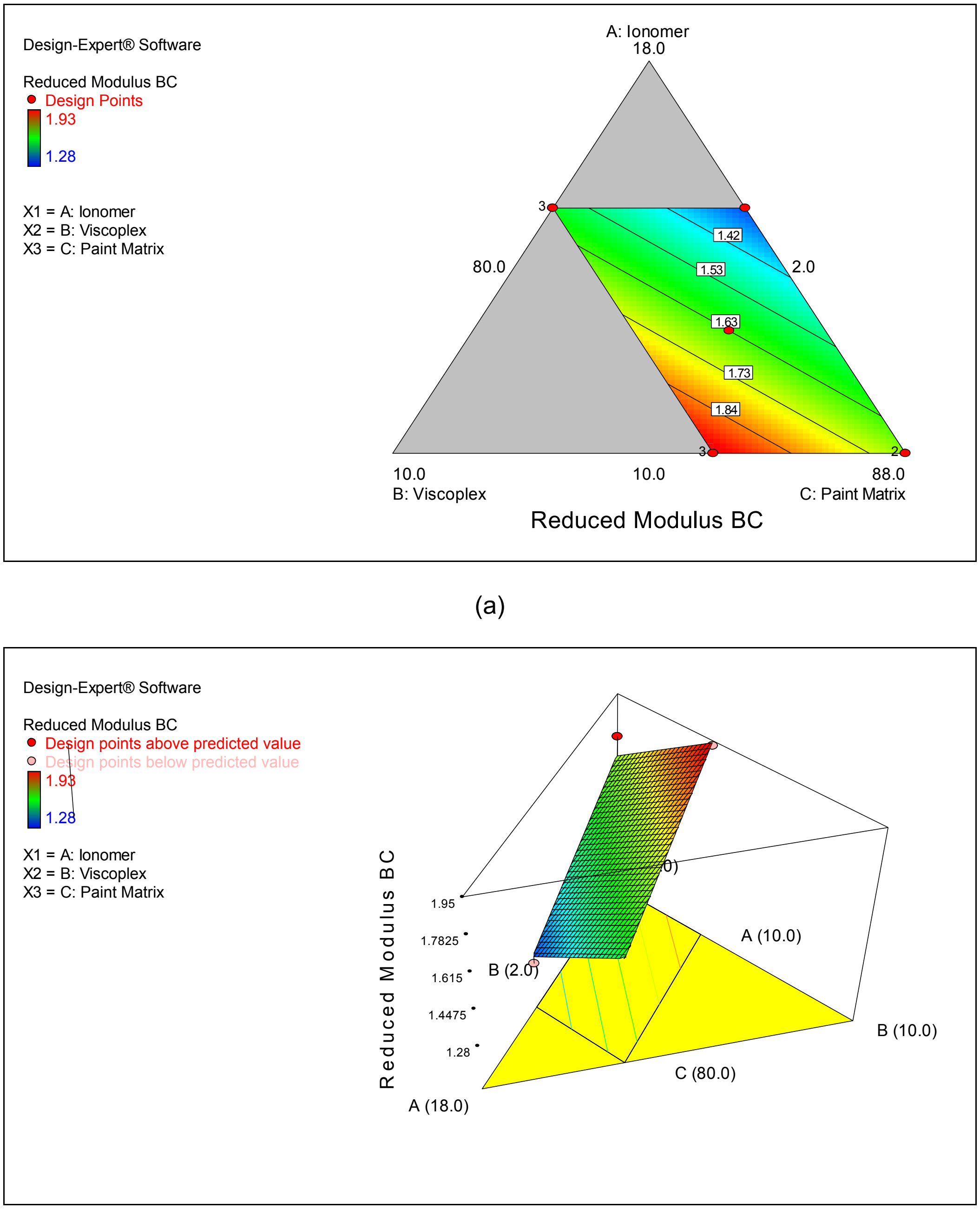
The nano-mechanical studies performed on top coat samples before leaching by single indentation tests on the blend series samples gave the following results for as listed in table 7.6.

Table 7.6 Responses for reduced modulus and hardness of Top-coat Series before leaching

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Response 1 Reduced Modulus Gpa	Response 2 Hardness Gpa
Sample 1T	15%	5%	80%	1.63	0.05
Sample 2T	15%	2%	83%	1.28	0.04
Sample 3T	10%	5%	85%	1.93	0.08
Sample 4T	10%	2%	88%	1.77	0.05
Sample 5T	12.5%	3.5%	84%	1.37	0.06

The contour and 3D plots for the reduced modulus of the top-coat formulations before leaching can be seen below Fig.7.10 (a) & (b). the contour lines are almost parallel to the axis for paint matrix concentration indicating that the modulus is almost independent of the paint matrix concentration. However, it was seen that due to higher concentration of paint matrix in all of these formulations as compared to the blend series; the reduced modulus and hardness values were higher than the blend series. The plot also indicates that the reduced modulus is a function of both viscoplex and ionomer concentration. The color scale of modulus values of the contour lines indicates that lower ionomer contributes to higher reduced modulus. This is in agreement with the blend series as well.

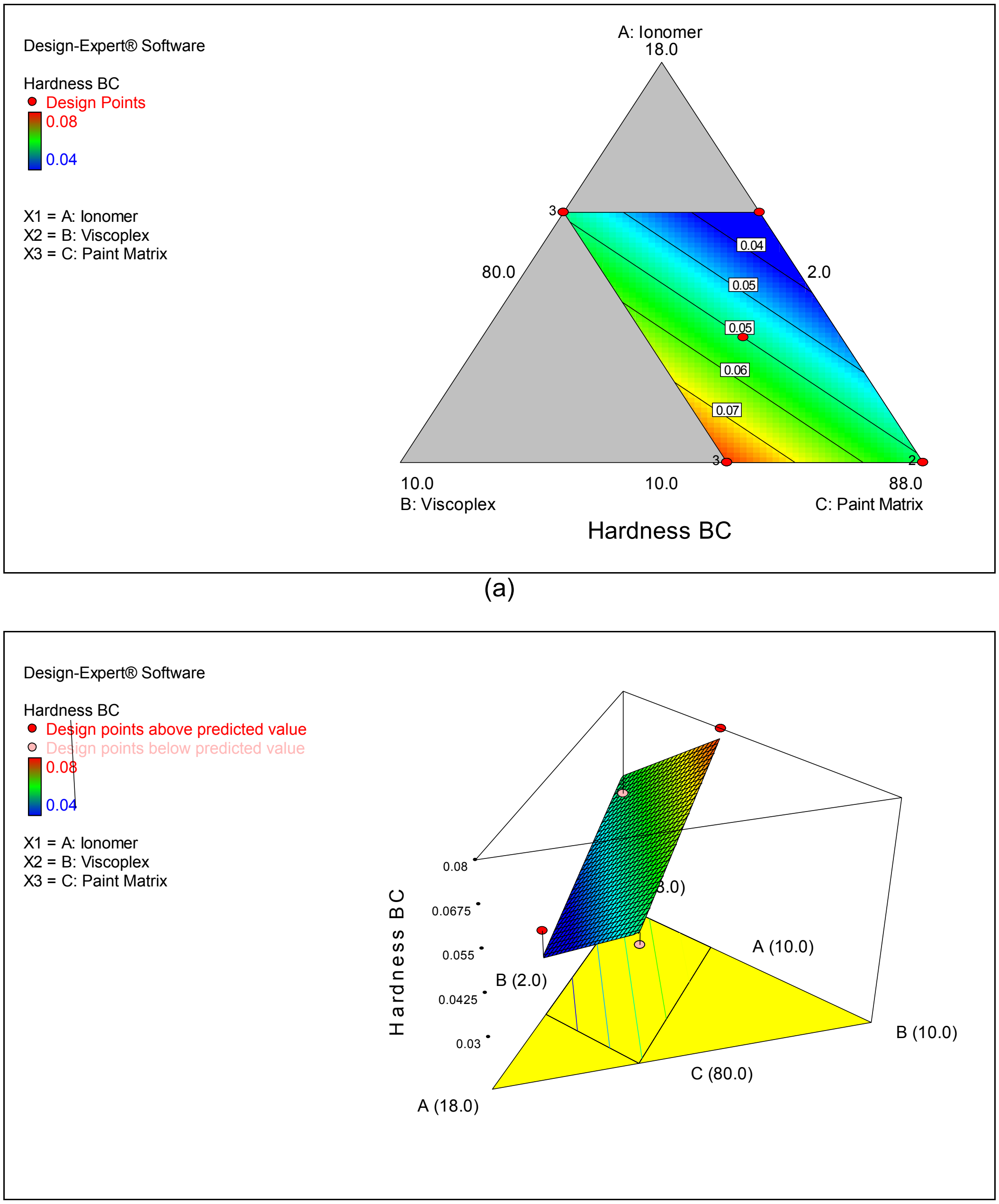
The design plots for the hardness values of the top-coat formulations before leaching were found to follow the exact same trend as that of the reduced modulus as seen in fig 7.11 (a) & (b)



(a)

(b)

Figure 7.10 (a) Contour plot (b) 3D plot for reduced modulus before leaching



(a)

(b)

Figure 7.11 (a) Contour plot (b) 3D plot for hardness before leaching

7.3.2 Design plots for Reduced Modulus and Hardness after leaching

The reduced modulus and hardness (table 7.7) for the top-coat samples after leaching were higher than that before leaching. This is understood from the fact that during leaching process, dissolution of ionomer which is a modulus and hardness reducing component, enriches the coating with paint matrix content.

Table 7.7 Responses for reduced modulus and hardness of Top-coat Series after leaching

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Response 1 Reduced Modulus Gpa	Response 2 Hardness Gpa
Sample 1T	15%	5%	80%	1.50	0.07
Sample 2T	15%	2%	83%	1.16	0.06
Sample 3T	10%	5%	85%	3.48	0.14
Sample 4T	10%	2%	88%	2.71	0.09
Sample 5T	12.5%	3.5%	84%	2.28	0.09

The design plots for the reduced modulus and hardness after leaching follow the same trend as was before the leaching.

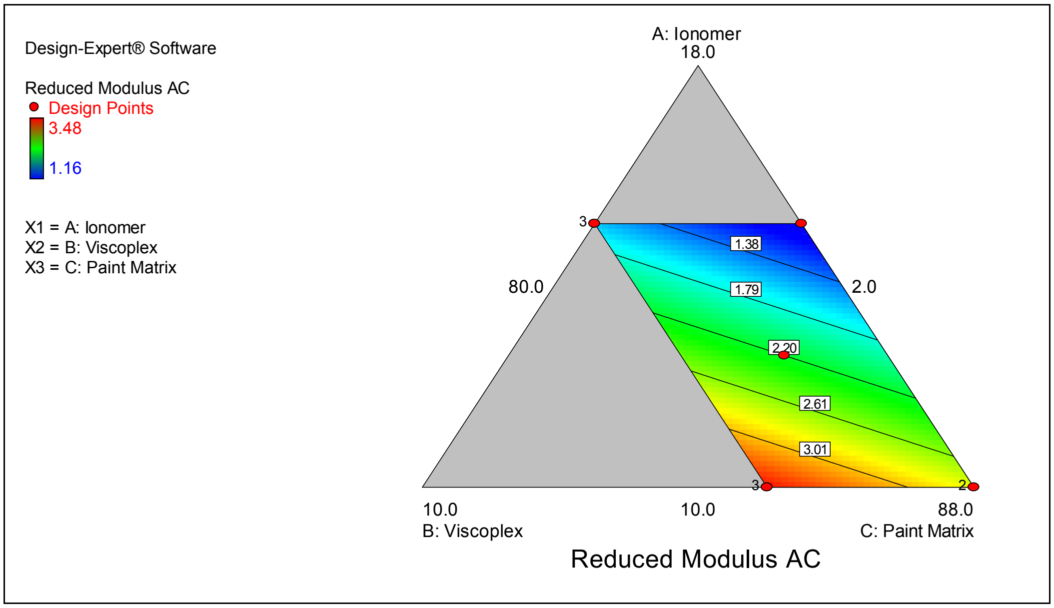


Figure 7.12 Contour plot for reduced modulus after leaching

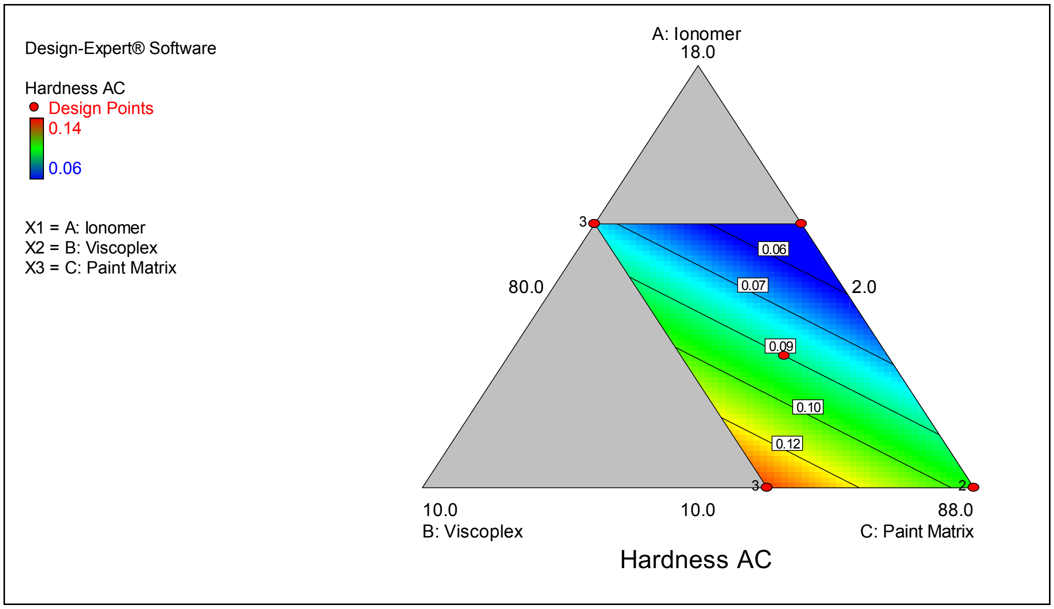


Figure 7.13 Contour plot for hardness after leaching

This can be seen by comparing the contour plots 7.12 & 7.13 to those before leaching. The low leaching rates of copper indicate little disintegration of the coatings thus supporting very little change in mechanical properties. The contour lines in both the plots indicate that the modulus or hardness is almost independent of paint matrix content (since the paint matrix axis is parallel to that of the contour lines). A lower concentration of ionomer increases the mechanical properties while the influence of viscoplex is somewhat reverse. These plots reveal that the influence of ionomer in reducing the mechanical properties of the paint is higher than that of viscoplex. The reduction in mechanical properties by the ionomer and viscoplex can be understood by the high molecular weight and bond flexibility introduced in the molecular structure and polymer chains by the presence of hetero atom linkages like C-O or C-S. The increase of mechanical properties slightly after leaching of these components further supports this belief.

7.3.3 Design plots for leach rates of top coat samples at different intervals

The copper leach rates for the blend series during the seven day leaching study are listed in table 7.8 below.

Table 7.8 Responses for leach rates of top-coat series

Formulation	Ionomer (ED-SPAN) Variable 1	Viscoplex Variable 2	Paint Matrix Variable 3	Response 1 Day 1 ug/cm^2/day	Response 2 Day 4 ug/cm^2/day	Response 3 Day 7 ug/cm^2/day
Sample 1T	15%	5%	80%	4.3	`1.3	1.1
Sample 2T	15%	2%	83%	5.5	1.9	1.4
Sample 3T	10%	5%	85%	2.7	1.0	0.8
Sample 4T	10%	2%	88%	3.9	1.0	0.8
Sample 5T	12.5%	3.5%	84%	5.1	1.0	1.4

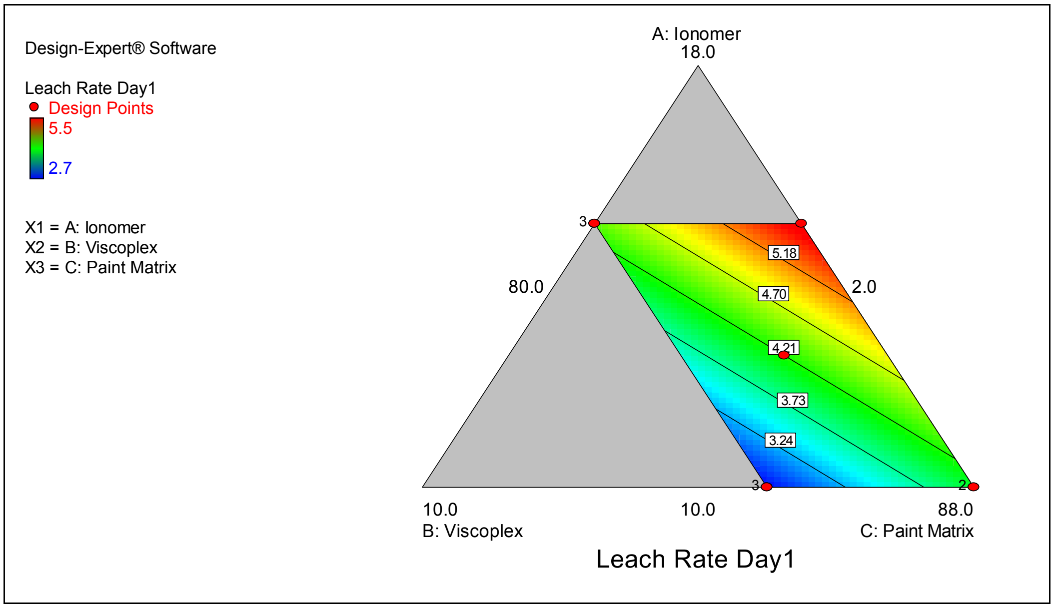


Figure 7.14 Contour plot for leach rates on day 1

The contour plots for the leach rates on day 1, 4 and 7of leaching for the top–coat series follow the same trend. Unlike the blend series where the trend on the 4th day differed from the 1st and 7th day, in this case all days demonstrated similarity in behavior. This can be explained again from the fact that, the low amounts of copper leaching point to very little matrix degradation affirming the retention of properties by the coating at all stages of the leaching study.

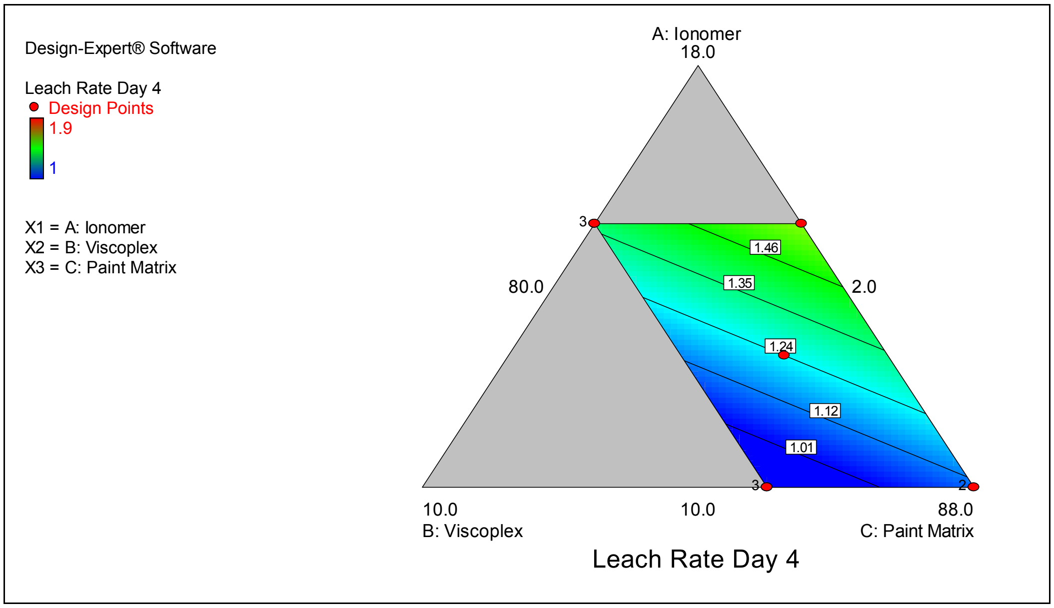


Figure 7.15 Contour plot for leach rates on day 4

The leach rate design plots display contour lines parallel to the axis for paint matrix concentration, once again indicating a negligible dependence on the same. The color contrast and leach rate values of the contour lines suggest that increasing concentration of ionomer and decreasing concentration of viscoplex produces a higher leach rate. This observation from the design model is in agreement from hypothesis made from the leach rate results in chapter 6. Thus from the design plots it can be said that ionomer concentration facilitates matrix disintegration and leach rate renewal probability and contributes to higher leaching which might be helpful in sustaining the leach rates. Also viscoplex may be considered as a suitable binder for reducing the release rate of copper.

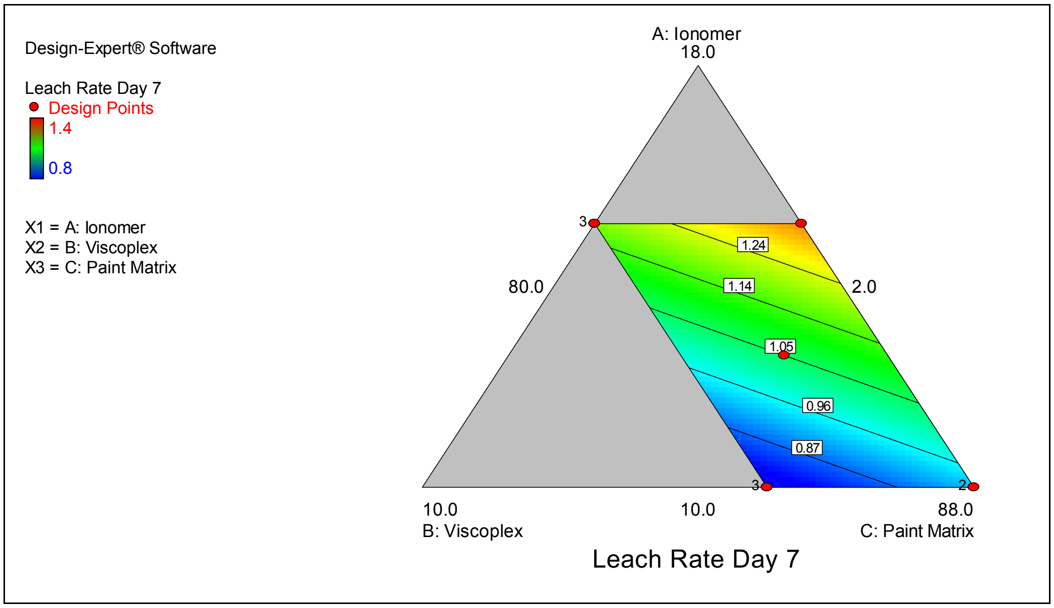


Figure 7.16 Contour plot for leach rates on day 7

Together viscoplex and ionomer in an optimized concentration can both be efficient in controlling the leach rate of copper at the desired level and help facing the dual challenges of burst release reduction and sustained release maintenance.

CHAPTER 8

CONCLUSIONS

From all the experiments conducted in Part I & Part II of this study and the results obtained; the following conclusions can be summarized:

1. Viscoplex (PAMA in mineral oil) has been found to be a suitable additive for binding the particulate additives in the paint recipe and is capable of reducing the burst release rate of cuprous oxide from paint. This has been confirmed from the leaching studies and accelerated leaching study where the control sample gave a higher release of cuprous oxide in the absence of any binding additive but the sample 5 (of Part I study) containing 5 % wt. of Viscoplex reduced the cuprous oxide release significantly. It also shows a good resistance to corrosion. This was realized from the findings in the characterization study using SEM/EDS, optical microscope and optical profilometer (discussed in chapter 6). The sample with Viscoplex showed smaller pits, lower surface roughness fewer salt deposits at the active sites. The nano-mechanical studies also confirmed that sample with Viscoplex were of low modulus and hardness and these properties did not change after leaching too. Also from the scribe experiments it was seen that the corrosion of the scribed area was low compared to other samples and the release rate of cuprous oxide did not increase in spite of the introduced scribe. Finally in the polarization study performed using 3.5% NaCl salt solution, sample 5 showed a low corrosion potential but lower corrosion current 10-8 A/cm2 compared to the commercial and control samples and which did not increase even after exposure to drastic marine conditions for 24 hours.

2. CuDDP was found to be unsuitable for use as an additive for marine systems because of its poor compatibility with the paint recipe and other additives and even poorer resistance to corrosion. CuDDP demonstrated some ability to restrict the burst release of cuprous oxide from paint as found from the leaching study. In spite of ability to control burst release, it was considered unsuitable for optimization study due to tendency to corrode. The visual observations, SEM/EDS, optical profilometer images and accelerated leaching test confirmed the poor corrosion resistance of CuDDP sample. The sample showed extensive rusting (of scribed and non-scribed areas), salt deposits. Also the Nano-mechanical studies and visual observations revealed that the CuDDP containing matrix turned brittle after corrosion to flake off easily. In addition the sample showed increased cuprous oxide release in case of the scribed sample leaching study compared to the release rate of non-scribed sample leaching study. This leads to the belief that in actual situations where scratches are likely to be introduced to a marine system in water, CuDDP would be unable to protect the substrate and in turn would generate uncontrolled release of cuprous oxide. Based on these findings CuDDP was disregarded for the optimization study (Part-II)
3. Ionomer (ED-SPAN) was found to be a suitable additive for controlling the release rate of cuprous oxide from biocide based antifouling paints. When used in 15% concentration with base paint as a top coat of sample with undercoat of 30% Cuprous oxide in paint, it was capable of dissolving in water and degrading the matrix to produce some leaching of copper. Again when combined with other additives it produced a very high leaching rate of copper. From these findings it was believed that Ionomer concentration of 15% alone (with 85% paint matrix) would be insufficient to generate sufficient release of copper for antifouling but if blended with other additives so as to lower the matrix concentration, the leach rate could perhaps be optimized to the desired value. The SEM/EDS and profilometric images confirm that the sample with ionomer

generates pores through ionomer dissolution which aid in the controlled release of copper. The scribed sample leaching study and accelerated leach study demonstrate that the ionomer sample has a good chance to generate appropriate leaching rate for at least 6 months and also shows good resistance to corrosion. The copper leach rate of the scribed sample was almost constant and comparable to that without scribe. Also in the polarization study the sample showed low corrosion current (compared to commercial and control samples) which did not change after 24 hours marine condition exposure. Based on the above arguments the Ionomer was considered appropriate for optimization study.

4. The optimization study conducted with a DOE matrix of Viscoplex and Ionomer additive with 30% Cu_2O in base paint was separated into two parts; one comprising of Top Coat systems and the other comprising of the blend systems. The leach study of both systems confirmed that the top-coat systems comprised of a high concentration of the base paint and were incapable of producing adequate leach rate of 15 ug/cm^2/day necessary for antifouling. For the ionomer top coat systems to work well a higher concentration of the ionomer is essential and blending that into the paint recipe can be challenging. From the corrosion stand point the formulations work well as seen from the visual observations and SEM/ profilometer images which show less pitting and any other evidence of corrosion.
5. The optimization study conducted with the blend systems demonstrated good performance in terms of establishing control on the copper release from the paint. Viscoplex was effective in controlling the burst release and Ionomer in renewing the copper release by breaking the diffusion barriers by bringing about matrix degradation through self-dissolution in water after an optimum thresh-hold period of four days. This was gathered from the copper release rates calculated from the leaching study with the entire DOE of blend samples with varying concentrations of Viscoplex and Ionomer. All

samples from the blend as well as top coat series showed similar trend with drop and in copper release rate till the fourth day and a rise thereafter. Similar behavior was demonstrated from the weight and thickness plots. The results of the nano-mechanical studies, SEM/EDS images, visual observations and optical profilometer images confirm that corrosion is not significant during the leaching study and there is no significant change of properties before and after the study. The polarization study results confirmed that the corrosion current (10^{-9} A/cm^2) or potential does not change significantly after corrosion (10^{-8} A/cm^2 after corrosion). Based on the leaching study the composition containing 12.5% Ionomer, 3.5% Viscoplex and 30% cuprous oxide was found to be keeping with the current expectancy of controlling the leach rate, renewing it with time, and keeping it around the desired value of 15 ug/cm^2/day; even with a much lower concentration of cuprous oxide compared to the commercial paint (43%). Although the burst release rate for the blend release was a little high, it demonstrated better control than the commercial on sustaining the release rate to the desired value and preventing it from dropping below the critical limit. This is very crucial as we see from the literature a period of 72 hours could be sufficient for the surface to get covered and once fouled, there is not much that can be done.

CHAPTER 9

FUTURE WORK

The following things were considered as out of scope for this study due to time constraints and availability of resources. However, conducting a future study on these would be interesting and a prime requirement in complete understanding of the antifouling application feasibility of the optimized formulations. From the conclusions of Part I & Part II of this study the composition with 30% Cu_2O, 12.5% Ionomer and 3.5% Viscoplex in base paint (5B) was considered as a suitable candidate for all future studies. The following studies are recommended to weigh out the antifouling feasibility of this formulation:

1. Although the formulation described above was considered suitable for all future trials, it is worth mentioning here that the top-coat systems could not be further experimented due to time and resource constraints. If proper equipments are available for homogenizing a composition with larger concentrations of Ionomer, to create a fine-texture formulation which can be easily applied; then a suitable recipe for the top-coat system capable of producing a desired controlled leach rate could be attempted. Also if larger samples with proper coating systems (suitable for large samples) were to be used then a higher concentration of Ionomer suitable for top-coat systems could be tried. This would help to separate the coating layers containing copper , Ionomer and Viscoplex and hence would provide better control over burst release perhaps passivate corrosion further.
2. Conducting a laboratory study with a marine set-up and marine organisms like barnacles, zebra mussels etc. and painted samples of the above described blend

formulation (5B) to calculate the extent of fouling of the surface. If the formulation performs well in this laboratory set-up, the experiment needs to be extended to actual environment.

3. Conducting a long-term leaching study in a large enclosure of natural environment like harbors to calculate the leaching rate of copper from the painted formulation and evaluate the extent and nature of corrosion on the samples. If the formulation exhibits good antifouling behavior from leach-rate, biofouling resistance and corrosion-resistance standpoint, then the experiment needs to be extended one step further so that paint is implemented on actual application systems.
4. Conducting long-term real environment leaching and fouling resistance study with actual systems for which the paint is designed e.g. Ships, pleasure crafts etc. Such study would require the paint to be applied on large vessels which are to remain in sea-water for long-time under differing conditions and to calculate at intervals what the antifouling performance and the biocide leach rate is like.

If the formulation provides an outstanding performance in all of the above described experimental studies, it would be considered suitable for commercial application and would have to go through the procedure for product registration and then commercialized.

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BIOGRAPHICAL INFORMATION

The author Hansika Parekh was born and brought up in Kolkata, India. She procured her fascination for chemistry by dint of her sister, Kajal Parekh. She completed her Bachelors in Science with Chemistry Honors from St Xavier’s college, Kolkata. Later, she pursued Polymer Science and Technology (B.Tech) from the University of Calcutta, owing to her deep interests in Applied chemistry. Here she was awarded for excelling in academics. After completing her Bachelor’s in Polymer Science in May 2007 she joined Masters in Materials Science and Engineering at the University of Texas at Arlington. With her proclivity in polymer processing, synthesis and characterization of polymer blends she joined research under the supervision of Prof. Pranesh Aswath in formulating paints for marine applications. Currently she is working in a polymer compounding company (Ingenia Polymers) and specializing on the processing needs and quality issues of commodity plastics. She wishes to pursue research and development in the area of Polymer Science & Technology and contribute significantly to the area in the years to come.