LITERATURE SURVEY
AND
SCOPE OF THE WORK
CHAPTER - II

REVIEW OF LITERATURE AND SCOPE OF THE PRESENT INVESTIGATION

2.1. High temperature resistant coatings

Definitions of heat-resistant polymer vary considerably, means that a polymer can be used for short time period at temperature minimum from 150°C. The selection of polymers that have received at least some degree of commercial exploitation. Such that to details of their methods of preparation, their thermal and thermo-oxidative stabilities and modes of degradation, and their properties at elevated temperatures.

There are many applications for which heat resistant polymers are needed; among these their development has come from the aerospace field. Synthetic activity was at its height during the late fifties and early sixties, but has declined lately for a number of reasons. These include the cutback in aerospace expenditure, the basic difficulties encountered in producing useful materials, and the relatively small markets for and cost of these specialty products.

Progress in heat resistant polymers have been governed by the opposing requirements of thermal stability and processability. The types of chemical structures conveying heat resistance have tended to lead to insolubility and infusibility, and hence structural modifications must often be made for easy of
feasibility. As a consequence, relatively few of the many polymers that have been synthesized have achieved commercial importance.

In the past few years no completely new thermally stable organic polymer systems have emerged; efforts has been triggered off upon improved methods of synthesis of known structures, or upon modifications to these structures so that easier processing and fabrication are possible without a concomitant loss of stability. There is little evidence at present that any marked increase in thermal stabilities of organic polymers over those currently obtainable will be forthcoming. A survey of those materials available in commercial or development quantities is therefore appropriate, as it is considered probable that such materials are unlikely to be superseded in the near future. A good case could be made for a detailed critical review of some polymers that have been synthesized and evaluated with heat resistance in mind [1-2]. M.A. Uusitalo et al has employed in high temperature resistant coatings on low alloy ferric steel [3].

2.1.1. Background of heat-resistant polymer development

The specific need for heat resistant materials in the aerospace field is perhaps best illustrated as follows: For the major part of the flight somewhat over two hours, the skin temperature is approximately 110°C. Hence the materials of construction must be capable of withstandng exposure to this temperature for the aircraft’s flying lifetime, say 30,000 hours. The
temperature is a very important consideration in any discussion concerning the application of heat-resistant polymers. The other main aerospace use-guided weapons, reentry vessels, space shuttle service—may involve the imposition of very high temperatures (perhaps thousands of degrees), but for very short periods. Under such conditions, of course, nonmetallic materials are degrading rapidly, and it is the very breakdown that conveys insulating properties.

The conventional phenolic resin like Cashew Nut Shell Liquid (CNSL) has proved very successful as silicone resin for high temperature application. The requirements for use of a polymer at high temperatures may be stated as; Retention of mechanical properties-high softening point, high glass transition temperature, High resistance to thermal breakdown and high resistance to chemical attack. i.e., oxidation, hydrolysis.

Increasing the intermolecular forces between chains can raise the softening point and glass transition temperature. Incorporating polar side groups or sulphur to the main chain can do this. Pure thermal stability is influenced by the strength of chemical bonds and those combinations of atoms with known weak bond strengths should not be used. Table 1, lists some of the bond strengths for common combinations of atoms found in polymer structures [4, 5]. In the search for thermally stable polymers, undue emphasis upon the bond strength criterion led to an initial concentration of effort on the development of inorganic polymers. The higher bond strengths inherent in
These systems are, however, more often than not offset by chemical attack involving processes of relatively low activation energy, e.g., hydrolytic or oxidative cleavage reactions. As a consequence relatively few useful inorganic polymers have yet been developed. The most widely known and used polymers with fully inorganic backbone are the siloxanes, and these provide a high bond energies. In poly siloxanes the Si-O bond energy is 445 kJ/mole and that of the Si-C bonds 328 kJ/mole [6]. It would therefore be expected that cleavage would occur preferentially at Si-C bonds with the elimination of the alkyl, or aryl, framing groups. In practice Si-O

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bond breakage occurs with the formation of low molecular weight cyclic precuts because overall this is energetically favored [7].

2.1.2. Major criteria for high thermal stability [8]

- Only the strongest chemical bonds should be used.
- The structure should not allow easy paths for rearrangement reactions.
- There should be a maximum use of resonance stabilization.
- All ring structures should have normal bond angles Polybonding should be utilized as much as possible.

2.1.3. Advantages of heat resistant coatings

- Good adhesion to the substrate
- High scratch resistance
- High temperature resistance
- Uniform coating thickness and good properties obtained by thinnest coatings
- High corrosion resistance for the most varied requirements
- Good inside-to-outside and outside-to-inside barrier action

2.1.4. High temperature polymer structure and properties

Variety of molecular weights with three types of polymer structures are exist

- Linear
- Branched
- Cross-linked
The method of increasing the softening point and glass transition temperatures of a polymer is by chemical cross-linking of the chains. The properties of such a system depend upon the structure of the main chains, the structure of the cross-links, and the number of the cross-links. Hence, many variants are possible. As the cross-link density increases, so normally does the heat resistance, but this is accompanied by decreases in impact strength, elongation a break, and reversible extensibility, and almost inevitable a compromise must be accepted. The cross-linking may be brought about either by addition or condensation reactions. The former have the advantages that no volatile by products are evolved during cure, thus allowing materials, and thick sections are much easier to fabricate. In theory all the functional groups should be used up in the cross-linking process, but in practice this not so.

The phenol–formaldehyde resins were the first of the thermosets developed (1909), depending upon the type and filler content, these may be rated for use at temperatures ranging from 120 to 260°C. In the surface coating industry, esters of titanium also used to protect metallic surfaces from high temperatures [9, 10]. The corrosion protection properties of the films have been studied using potentiodynamic scan and electrochemical impedance spectroscopy by V. N. Balbyshev et al [11]. The progress in CNSL resin development has attained a good position on the basis of phenol-formaldehyde resins.
2.2. Progress of metallic coatings - a review

Extensive electrochemical investigations have been carried out on the mechanism of corrosion prevention by zinc rich coatings on steel substrate in sodium chloride solution. This is being reviewed in this chapter. The literature review on the protective behaviour of Manganese, Aluminium, and Stainless steel pigmented coatings are also outlined.

Understanding the process of corrosion provides the key to steps that may be taken to prevent the reaction from occurring and to identify the role that paint coating can play in achieving this result. It becomes obvious that the meal can be isolated from a corrosive environment or made the steel potential sufficiently negative enough. The change in potential of the metal can be made by means of an impressed current or as a result of connecting a electrically more positive metal directly to the iron. This is called cathodic protection and it is achieved in the coatings technology by means of galvanizing, zinc metallizing, zinc rich primer and zinc plating [12]. Zinc dust is one of the widely used metallic pigments in the paint industry to formulate heat resistant as well as corrosion inhibitive coatings for the protection of metallic substrates.

2.2.1. Zinc dust pigments

The zinc dusts are usually available as a well pulverized bluish-gray powder in spherical shape with the particle size ranging from 3-8 μm. The appearance of this powder depends on the degree of zinc oxide contamination
and the size of the zinc pigment particles. The innovative technique of applying inorganic zinc rich coatings was done by means of hot dip galvanizing and it was first developed in the 1840’s in France. Victor Nightingale, the Australian originator of the inorganic zinc coatings were used in 1942 on the 250 mile Moragah-Wyalla pipe line in south Australia.

Marcel Leclercq [13], De Amo [14] had optimized the zinc content, particle size and the minimum thickness of the coating required for maximum protection life of the coatings on mild steel substrate and concluded that the protection achieved at 80-90% Zn content and the thickness of the coatings must be 80-95 microns. Similar type of work was done bye G.W.Kapse and K.M.Bela Rani [15] for organic and inorganic zinc rich coatings. They arrived at some conclusions but they found that in the case of organic coatings the amount of zinc to be used depends upon the binder.

As the cured inorganic zinc rich primer ages, the zinc continues to react with the environment, producing a variety of zinc corrosion products depending on the environment [16]. D. De la Fuente has found that zinc-rich (ethyl silicate) primer is provided the most effective protection against corrosion [17]. As this happens, the resultant corrosion current continues to render the steel totally cathodic and protected. After the zinc corrosion product occupies the interstitial areas between the zinc particles. Thereby sealing the primer film completely and producing a dense, hard, abrasion resistant film.
This behaviour of commercially available zinc coatings in different binders has been investigated by electrochemical methods. The duration of the cathodic protection given by the coatings are of shorter duration that the barrier protection period [18]. The mechanism of galvanic protection [19] and the barrier protection [20] period of the coatings have been explained by S.Felin et al.

For cathodic protection to be viable, a continuous film of electrolyte is needed across both anodic and cathodic areas. Only a thin surface film is necessary for dry atmospheric environment [21]. Similarly the organic and inorganic zinc rich coatings suitable for different environmental conditions [22-24] and the effect of atmospheric pollution on deterioration of the coatings have been discussed by Smieszek [25], Pereira et al [26].

In most cases, films are recoated quickly, after application and long before the primer films are sealed by corrosion products. This problem is reduced as the inorganic system ages and becomes sealed, and it does not occur in post-cured alkali silicate in which sealing is artificially induced during post curing.

The physical and chemical properties of zinc corrosion layers are well established by T.C. Gradel [27]. The surface morphology of the organic and
inorganic zinc rich coating were evaluated by Scanning Electron Micrographic (SEM) and energy dispersive x-ray spectroscopic methods [28, 29].

Single coat of inorganic zinc can effectively and economically prevent corrosion of carbon steel structures in marine environments and also in high temperature environment [30-32]. New coatings are continually appearing on the market, but none can match the inorganic zinc in long term atmospheric marine exposures.

Drying oils were the first type of materials used, which were not entirely successful, but for some formulations, linseed oil used for a primer or a finish coat galvanized steel. During 1930s, many other resin and oil types were used with zinc dust. These included, polystyrene, chlorinated rubber, vinyl resins, and similar products. The degree of variation in the performance of coatings depended primarily on the vehicle. In general, the performance is indirectly proportional to the resistance of the vehicle to corrosive conditions.

During later 1940s, epoxy resin become available and was soon found to provide a good vehicle for zinc rich coatings. Nowadays, three types of organic vehicles namely epoxy, chlorinated rubber and phenoxy make up and used in the majority of the organic zinc rich products. All the three coatings have good dielectric properties provided that sufficient quantity of zinc is present in the coatings for particle-to-particle contact throughout the film. Tremendous attempts have been made to specify optimum weight of zinc to be
present in the coating and it is found to be between 80% and 95% by weight of the dry film [33-35]. The zinc particles must be in contact with the base metal in order for the coating to be conductive and to prevent corrosion by cathodic protection.

There is little chemistry involved in the formulation of organic zinc rich coatings other than to provide a resistant vehicle, which does not react with the zinc metal. The formulations of paints consist of dielectric constant of the vehicle, presence of wetting agents, thixotropes, auxiliary pigments, particle size, and its proper distribution. The physiochemical properties have been discussed by several authors [36].

Zinc is a heavy pigment and tends to settle rapidly in paints to prevent zinc settling thixotropes are used. Inhomogenized zinc material may result in widespread variation in the zinc content of an organic zinc rich film [37]. For this reason, manufacturers recommend continuous agitation of zinc rich materials throughout the application process.

Epoxy zinc rich coating has its own advantages and disadvantages. Medium molecular weight epoxy-polyamides have achieved the widest use in organic zinc rich primers. They exhibit a property similar to chemically curing epoxy thermosets and provide strong adhesive films. They are two component system and require the complete mixing of two before the application.
Phenoxy systems, usually single pack ready mixed zinc primers, may be too solvent resistant for good inter coat adhesion with certain topcoats such as vinyls [38].

In Japan zinc rich coatings based on epoxy ester have not often been used on steel bridge structures but extensively used in the automobile industry in U.S. [39]. Epoxy ester based zinc rich paints have better adhesion to poorly prepared substrates than do other zinc rich systems. Nevertheless, the evolution of alkali at the steel cathode with this system would attack the ester groups of the epoxy vehicle. The effects of partial replacement of the zinc by di-iron phosphate extender in zinc rich epoxy polyamide coatings for the anti-corrosive properties were studied by several authors [40, 41].

Silicone

The organosilicon compounds were first prepared by Friedel and Crafts in 1863 [42], but Silicones were produced first commercially in 1940’s and used as high temperature electrical insulating materials in USA [43]. Their use in surface coating applications followed soon after words.

Silicones are synthetic semi-inorganic polymers, which can be produced in several forms, such as fluids, rubbers and resins etc. Silicones exhibited its structure on orderly alternate arrangement of silicone and oxygen atom in inorganic skeleton. This skeleton, which bears a close structural resemblance to silica, is responsible for the inertness of the silicones and for their stability
over a wide range of temperatures. In the semi-inorganic silicone polymers, the substituent groups are mainly organic, the methyl groups are mainly incorporated in fluids and rubbers, in the case of resins, methyl and phenyl groups are present.

In recent years the utility of silicon in organic chemistry and in the field of polymers are a great advancement. Silicon containing polymers are known to exhibit superior thermal withstanding properties. Lot off efforts [44-46] have been given to modify bismaleimides by introducing silicone linkages into the backbone to enhance their toughness. An available way [47, 48] of extending bismaleimides thermal shocking tolerance by silicone monomer have been investigated in detail and reported [49, 50] that poly (siloxanes-imides) with unique properties were prepared by Diels -Alder intermolecular polymerization of bismaleimides and bisfuranes. Such polymers possess either outstanding thermal stability assigned to the forming of an imides ring after aromatization. Hence it should be valuable to synthesize polybismaleimide oligomers by this method to improve their process ability and the toughness of their cured reins, moreover without sacrificing the thermal stability.

Silicone containing polyamides, which are stable and are also been synthesized [51-55]. Since epoxy resins have excellent heat, moisture, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates, they widely used in the field of coatings,
adhesives, casting, potting, composites, laminates and encapsulation of semiconductor devices. Kovaes et al [56] have reported that the silicone containing benzimidazole, hydrazide and oxadiazoles. Incorporation of silicon in CNSL-sulfur would definitely yield and entirely new type of interesting class of polymers. Hence, the present work has been undertaken to prepare silicone-containing CNSL-sulfur. Polyester containing silicone were prepared from the reaction of silicon containing diacids [57] or diols [58].

The silicone based coating materials have been increased their attraction in the field of protective coatings for high temperature applications [59-62]. One of the governing factors is the thermal stability of the protective coatings. The heat stability limit of a commonly available coating system falls well within 333 K (60°C). As the operating temperature rises, deterioration becomes rapid. However, a novel class of protective coatings, based on silicone resin, was developed in the early 50s [63-66]. The practical considerations of these protective coatings have recently been reviewed by Staples [67].

The reactions of silicone are quite slow (1 to 2 hours at 500 F or 260°C) and are usually catalyzed to cure at approximately 400F (240°C C), which may take 45 to 60 minutes. Silicone resins reacted with hydroxyl -terminated organics such as alkyds, polyesters, and epoxies. These reactions are cost effective and upgrade the heat resistance and exterior durability of the organic
coatings. Owing to its chemoselective, mild, and rapid characteristics, quite a few applications of hydrosilylation reaction have been developed in industry [68-71]. On the basis of these requirements, several types of compounds such as acetylenes and olefins have been developed and evaluated for their characteristic properties with the help of the platinum catalyst [72, 73].

Recently, several systems, including melamine/polyester, methylmethacrylate /methacrylic, styrene/n-burylacrylate, silicone-modified alkyds [74, 75], and others were developed and discussed by so many authors. The actual revolution in the prevention of substrates commences only in the 1940’s in Australia and in the 1950’s in United States [76]. In 1950’s a number of coatings were developed from silicates. The reaction products on the steel surface resemblance with sodium silicate coatings. When zinc is added to the system, a silicon-oxygen-zinc polymer is created. This combination is insoluble and forms the strong matrix surrounding the zinc powder to produce the coating.

The self-cured water based silicate coatings are being used from past few decades as a binder for the zinc and applied by an organic solvent instead of water. A stable solution of ethyl silicate-silicic acid mixture was obtained by hydrolyzation of ethyl silicate in presence of acid medium and it was first patented [77]. The inorganic zinc rich coatings are not only cohesively strong and are extremely adhesive on well-prepared surfaces. The adhesive strength is
due to the formation of primary valence-bonded between iron ions from the steel surface as well as zinc ions from the pigmentary surface matrix. Unlike organic systems the zinc silicate matrix is electrically conductive [78]. The life of the protective coating is also dependent upon the amount of zinc metal employed in the coating formulation [79]. The importance difference between the organic silicate and the alkali silicate is that the elimination of the hydrolyzed product of ethyl groups from the ethylsilicate polymer proceeds gradually and for this process acquire several months [80].

The development of titanium esters for use in surface coatings and related field is analogous to that of the silicon esters. Among these binders silicone is the commonly used carrier vehicle in the anti-corrosive primers of industrial, high temperature and marine environments [81]. The structures of these compounds are confirmed by I.R. spectroscopic analysis [82].

The silicone is mixed with modified phenolic resin and pigmented with zinc and aluminium, which possesses heat resistant as well as anti-corrosive properties like titanate [83, 84]. Gottfried have reported methyl phenyl siloxanes and ketone-formaldehyde polymeric resin containing polymer and its role in heat resistance surroundings [85]. A comparative study of galvanic protection and the impedance behaviour of the titanate zinc rich coatings with the organic zinc rich coatings show that the titanate based coatings protect the carbon steel substrate for longer duration by galvanic protection mechanism
The performance of inorganic zinc rich coatings depends upon the formulations to a certain extent on the metallic zinc content; a comparison of performance of inorganic zinc silicate primers in marine atmosphere is in the following order,

Post-cured > Water base > solvent base-2 component > solvent base- one component systems.

S. Feliu et al [87] studied this character through impedance method and concluded that the di-iron phosphide in ethyl silicate medium does not impose the barrier effect. On the other hand the partial replacement of zinc by di-iron phosphide in epoxy polyamide media reinforce their barrier effect. In the case of galvanic effect reverse is the true.

**Cashew nut shell liquid (CNSL)**

CNSL preparation involves the reaction of phenol like compound with formaldehyde have been discussed by several researchers [88, 89]. The thermo-oxidative stability of phenol-formaldehyde resins can be further improved by chemical modification. Inorganic polybasic acids e.g., phosphoric and boric acid, are used to esterifies phenol novolacs and this increases both heat and flame resistance properties. Reaction of phenolic resins with metal halides, metal alcohohates, or metal organic compounds containing metal elements such as molybdenum, titanium, zirconium, tungsten, or aluminium are also reduces the rate of decomposition at elevated temperatures.
The original polysulfide rubbers were solid materials with very high sulfur contents. Early development work treated these compounds as being similar to other rubbers and cures was achieved by the addition of sulfur and zinc oxide. The introduction of liquid polysulfide polymers in the 1940’s that accelerated the use of alternative curing agents, although it is only recently that the mechanism has been studied in depth. Stronger oxidizing agents such as the permanganates and dichromate yield a very high modulus material and in the latter case one with improved thermal resistance [90].

CNSL is available as a by-product from the cashew nut industry in India. It lends itself to polymerization by physical and chemical methods and the resin obtained could be used for the production of surface coatings [91]. The utilization of CNSL in surface coating has been studied by Harvey and Caplan [92, 93] in U.S.A. In India, some work on the preparation of surface coatings from CNSL has been published [94, 95]. The drying property of CNSL resin is improved by condensation with hexamine and aldehydes or treatment with drying oils. The extraction, properties, and the application of the polymers obtained from the CNSL have been reviewed by L.C. Anand [96] and P.H. Gedom et al [97]. The inhibitive primer formulated from CNSL resin is comparable with other inhibitive primers properties [98-102]. Anti-corrosive paints based on linseed oil or DCO alkyds modified with 20-50% CNSL resin are found to give better protection to metals from atmospheric corrosion [103]. In recent years, electrophoretic deposition is dominating in the
automobile painting works. Hence, the CNSL resin is water soluble and pigmented with inhibitive metal particles and the anti-corrosive properties of the coatings are studied by M. Selvaraj and S. Guruviah [104, 105].

Paints formulated using the CNSL based epoxy resin and bitumen as binders with aluminium powder, mica and zinc chromate as pigments are found to be very effective anti-corrosive coating for steel structures in marine atmosphere [106]. Similarly the primer formulated from salicylic acid CNSL-formaldehyde resin pigmented with red lead, iron oxide and talc is comparable with zinc rich epoxy primer coatings. This is due to the formation of the CNSL resin complexes with iron ions, which have a coordination number 6 [107]. Earlier S. Ramanujan has taken Indian Patent for the preparation of zinc rich paints based on CNSL polymers [108]. This zinc rich coating is also equally comparable with other organic zinc rich primer formulations.

In the organic zinc rich primers, polyamide epoxies, chlorinated rubbers and phenoxy resin are commonly used along with Vinlys and styrene-butadiene resins. The vinyl ZRP coatings are still available, whereas the styrene - butadiene is no longer used. Alkyds and epoxy ester based zinc rich primers are widely used in automobile industries, but are not recommended as suitable vehicle for field application as industrial maintenance primers. So many literatures are available using phenol-formaldehyde as a heat resistant polymer.

**Inter penetrating polymer networks (IPNs)**
Numerous investigations have been conducted over many years, in an attempt to develop a process and procedure that would allow significant improvements in toughness to be achieved with minimal loss of mechanical properties [109-111]. Of a few ways to obtain better performing polymeric binders, alloying the incompatible polymers through ‘compatibilization’ is fast-emerging with a number of promises. Interpenetrating polymer networks are one of its kinds. The fracture toughness values of thermosetting resins such as epoxy and unsaturated polyester resins used as a matrix are generally less than those found in thermoplastic resins. Efforts have been made to improve this disadvantage. Improvement by blending with rubber particles is widely considered to be a useful method. The properties of such blends have been investigated by many researchers [112-114], who have reported some of the dominant mechanisms of energy absorption when toughening polymers.

Recently, the introduction of incompatible materials such as siloxanes to other resins is better in the industry. In this study, two polymer alloys of Interpenetrating Polymer Networks (IPNs) based on silicone-CNSL-Sulfur polymers have been developed in the laboratory and the coatings were subjected to different accelerated tests. They have been found to possess far superior physical and chemical and corrosion resistance properties compared to commercially available silicone resins. The search for polymers providing better qualities and properties is ever lasting.
Epoxy resin is one of the most important thermosetting polymers. It exhibits many desirable properties, such as high strength and modulus, excellent chemical and solvent resistance, thermal stability and strong bonding properties. However, epoxy resin is generally brittle because of its highly cross-linked structure. Many efforts have been made to improve the toughness of the cured epoxy resin. The modification of epoxy resin with silicone rubber improves the toughness of the cured resin with no damage to the heat resistance. However, if epoxy resin is directly modified with silicone rubber, the silicone is completely separated from the epoxy resins, because silicone rubber lacks compatibility with epoxy resins [115, 116]. Therefore, to improve the toughness of epoxy resin by modification with silicone rubber, an increase in the dispersibility of silicone into the epoxy matrix is needed.

In this aspect, Interpenetrating Polymer Networks, (IPNs), a class of polymer alloys promises a number of advantages in coating properties like corrosion resistance, chemical resistance and improved mechanical properties. In order to achieve compatibility of polymer alloys in two or more immiscible polymers have been studies [117-127].

2.2.2. Progress of manganese coatings

In recent years manganese powder has been incorporated in zinc pigmented coatings and the corrosion protection behaviour was studied by Roland et al [128] and found that the coatings acquire greater compactness and
higher alkali resistance. The partial replaced (∼ 60%) zinc coatings by manganese powder due to their hard and brittle behaviour as well as acid and alkali resistance and it is explained by Tadeusz Szauer et al [129].

The manganese ore has been used as a pigment in non-aqueous medium, however the stability of the particles in the medium is determined by the particle to particle and the particle to medium interactions [130, 131]. The stability of the Egyptian manganese ore in the medium and the effect of surface treatment of the ore particles on painted films are investigated by A.A. Add and El. Hakim et al [132, 133]. They have also studies the character of the primers formulated with treated and untreated manganese ore with alkyd and epoxy resins. The results showed that the mechanical and corrosion properties of painted films improved very well with the arrangement of the ore particles in the coating formulation. The cathodic protective behaviour of the manganese pigmented inorganic coatings is more reported by V.M.Kelker in 1964 [134]. Afterwards no major work has been done using the manganese pigments.

In 1989, M. Selvaraj and S. Guruviah [135] carried out he electrochemical behaviour of the pigment in organic and inorganic binders and concluded that this pigment is performed well in organic medium. Similarly the protective behaviour of the manganese filled organic coating was studied by A.V. Kyazimov et al [136] and reported the performance of the coatings. In 1996s highly efficient heat resistant paint formulations based on Egyptian
manganese ore (high and medium grades) doped silicone resin were prepared and physicochemical properties of the coated paint films were evaluated. The manganese ore imparts heat resistance protection for the painted substrate up to 450°C. The anticorrosive properties of the paint formulations were moderate, but their efficiency can be improved by adding melamine in to the paint formulation.

2.2.3. Progress of stainless steel coatings

In recent years a new metallic pigment was brought to the attention of paint formulators namely stainless steel. This metal composed of iron, nickel and chromium is known to resist most types of staining, tarnishing, oxidation and chemical attack. The stainless steel flake pigment can be produced from any type of stainless steel, but the shape of the particles is in irregular flake. The use of stainless steel flake pigment in the coating industry is mainly due to its inertness [137].

The stainless steel pigmented coatings show much greater resistance to abrasion than the other metallic pigmented coatings [138]. The chemical inertness of the stainless steel pigmented coating suggests to its use in high temperature applications and in highly corrosive environments [139]. Structural evaluation and localized corrosion behaviour of stainless steel pigments are evaluated by E. Angelini et al [140]. Unlike other metallic pigments, stainless steel pigment could be used in alkyd, epoxy, vinyl, phenolic, acrylic, fluoro
carbons, polyurethane, chlorinated rubbers and other systems. This pigment is used as a primer pigment as well as a component of any multi pigment systems for both protective and decorative coatings [141].

Norman [142] studied the properties of the stainless steel pigmented coatings and concluded that the stainless steel is not considered as corrosion inhibitive pigment by itself, unless used with extremely higher concentrations. However, stainless steel flakes offers a reinforcement property to most pigment combination. It is possible to combine with the anti-corrosive pigments so as to get a complete coating system. The optimum results are obtained with a primer coat of iron oxide and zinc chromate applied to a dry film thickness of 1.5 mils and the similar thickness of topcoat with stainless steel pigment.

Tim Race et al have [143] used the stainless steel pigment as a sealant in vinyl and epoxy polyamide coating and studied the performance in dam applications and concluded that the pin-point rusting was noticed after 10 months duration, the performance as sealant was not good. But increase in the thickness of the coating would prevent the penetration of the corrosive ions into the thick continuous coatings. The properties of the stainless steel flake pigments in different binder system is also explained by Hirsohi Ito [144].

Nowadays, the metallic pigments are incorporated with fluoro polymers and used as topcoats. The fluoro polymer based metallic pigmented coating
consists of a wide range of pigment percentage (70-95%), and it depends upon the end use [145]. A composition of a primer with topcoat which remains weldable consists of an anti-corrosive pigment with graphite powder as primer and a top coat containing stainless steel powder in a fluoro polymer [146]. Stainless steel as a pigment offers exceptional inhibitive action in organic coatings to protect metal surfaces from corrosive environments. Once the initial coat factor has been overcome, it could prove in the long term a more economical product. Pigments, such as metal oxides, graphite, carbon black, powdered Aluminium, bronz, and stainless flakes, are reviewed as heat resistant coatings by C.A. Smith et al [147].

2.2.4. Development of aluminium pigments

Aluminium pigments are incorporated with silicone resins for high temperature resistant coatings. Aluminium flake pigments are of two kinds, one is leafing and other non-leafing. The two types of aluminium flakes differ mainly in the nature of the lubricant on the surface of the flakes, but they give very different impact in paints. The leafing variety in a correctly formulated paint, is carried during the drying process to the paint film surface, and gives the appearance almost of a continuous film of metal. The non-leafing variety remains within the film and produces a polychrome effect, when used in conjunction with semi transparent coloured pigments. The pure grades give better resistance to attack by acids. The particle size of the flakes generally varies from 1.2 μm to 80 μm diameter, and the thickness from 0.03 μm to 0.3
μm. Doshi, L. Kantilal [148] developed the solvent-based, aluminium paste containing paint resistant to peeling at 600°C as a sealant in silicone coating. The structure of silicone resins, pigmentation, heat resistance, and applications were reviewed and discussed by L. Thomas, W. Chemie et al [149]. A waterborne silicone/aluminium coating is developed to offer heat resistance at temperature in excess of 600°F and corrosion resistance at film thickness of less than 0.5 mils in the recent years. The waterborne system also drastically reduces volatile organic compounds, (VOC) content, eliminating the need for emission control equipment [150]. Inorganic anticorrosive aqueous paints and their preparation have been done by Y.Feng, F.Z.Shenqing, et al [151]. Kielska, Blandyna [152] suggested the chemical inertness of the aluminium pigmented coating and its use in high temperature (at 450°C) are manufactured from compositions containing methyl phenyl silicone with Zn dust and Al powder.

Heat-resistant, anticorrosive paints for metal structures are prepared by mixing Al or Zn dust with butyl titanate binder and coated on a pickled steel surface to give a coating that allowed no brown rust formation after 20 days at 70-80°C in 3% NaCl solution and had negligible weight loss after 20 days at 200°C [153]. Heat and corrosion resistance paint drying at both room temperature and under heating is composed of poly vinyl butyral with Zn dust and Al powder were prepared and characterized by J. Nagrodzki. Potentiodynamic polarization studies of aluminium and it properties were
explained by A. K. Maayta et al [154]. Zhang et al have been synthesized a brominated polystyrene for fire retardant polymer in heat-resistant resins [155].

2.2.5. Development of ceramic pigments

Ceramic components are frequently made by sintering of powders. Alternatives for sintering melt processing are chosen but this process is uneconomical, because many ceramics have very high melting points or sometimes decompose before melting. These are also very reactive with container materials, which imposes the disadvantages on available handing out methods. A rule of thumb in ceramic processing is that the quality of a ceramic part is not better than the quality of the powder from which it is made. Thus, much effort has been directed to enhancing the properties of ceramic powders. Improvements in the ceramic paints are higher purity, finer particle size, less agglomeration, and better control of compositions and distributions of dopants.

Raw materials for ceramic processing range from relatively impure clay materials to ultrahigh purity powders prepared by chemical synthesis. Naturally occurring ceramic materials such as silica, SiO₂, sand, quartz and talc are used as extensively as raw materials in the manufacture of traditional ceramics.

Chemical synthesis provides a means of producing powders for manufacturing advanced ceramics. However, chemically synthesized raw
materials are expense and difficulties in scale-up and availability. Additionally, ultra fine particle-size powders produced by chemical synthesis pose some unresolved processing problems in the areas of handling and mixing.

Ceramic compounds can be formed by reacting constituent oxides and thermally decomposed salts at an elevated temperatures in a solid state process described as calcination. The chromium oxide is a gray-green colour and has low tinting strength but good opacity, good heat resistance, excellent light fastness, and extremely good resistance to chemicals properties. It is also substantially non-toxic (the chromium is in the trivalent state; toxicity is associated only with hexavalent chromium). Cobalt chromium aluminate is a type of ceramic pigment with a mixed phase cobalt and aluminium oxide in the spinel crystal form. They are transparent and bright blue with low tinting strength, but are very lightfast and resistant to heat, solvents, and chemicals. They are used where high stoving temperatures and excellent durability characteristics are demanded. The spinel structure of MgAl$_2$O$_4$, can be formed by reacting magnesia MgO, and alumina, Al$_2$O$_3$. Because solid-state diffusion is inherently slow, fine, well-mixed powders are required to ensure that reactions go to completion and that chemical and structural homogeneity are achieved during calcination. Often multiple calcination, grinding, and mixing steps are performed to ensure homogeneity for ceramic powders. Purity of the product is limited because it depends the purity of the constituent raw
materials, and also by the impurities introduced during the grinding processs. Ceramic powders formed by calcination are typically less expensive than those formed by liquid or vapour techniques, but are also typically less pure and larger in size.

Calcination \[156, 157\] involves heat treating a powder or mixture or powders at a temperature well below its melting point to effect decomposition, ie, to liberate unwanted gases and chemically bound waste, solid-state reactions, and structural transformations to produce the desired composition and phase product. For example water is liberated and the crystallographic structure changes when $\alpha - \text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ is calcined to form $\alpha - \text{Al}_2\text{O}_3$.

Calcination is used extensively to dehydrate cements and hygroscopic materials to produce a less water sensitive product. It is also used to decompose metal salts to base oxides and to produce multi component or mixed oxide powders for manufacturing advanced ceramics. Sieve sizing \[158\] utilizes gravitational forces acting on particles translating across a screen. The process can be enhanced by vibrating the sieves. Dry forced air and sonic sieving are used to size dry powders from 850-to 37-\(\mu\)m size. Wet sieving eliminates electrostatic particle-particle and particle-sieve attractive forces to size particles down to ~5 \(\mu\)m.
2.3. SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Widespread utilization of coating materials demand the production of them that are durable, low-cost and efficient for selective environmental applications. The focus of the present investigation is to formulate a paint system that has high temperature and corrosion resistance property. Towards this end is the judicious choice of binders and pigments. The polymeric binders as well as pigments must be stable at high operating temperatures and resistant to atmospheric corrosion of the paint formulation are meant for such environments.

Out of these coatings generally inorganic based paints (mostly silicone or silicates binders) are preferred due to their high stability in such specialized atmosphere. However, these materials are higher in cost and their preparation procedures are much more involved than for many organic materials of similar nature. Keeping this in mind in the present investigation it is aimed to synthesize new organic based binders from Cashew Nut Shell Liquid oil (CNSL-S) and compare its performance with silicone resins, which is specially meant for high temperature applications. Further the CNSL-S resin is a polymeric phenolic binder and can be prepared from a naturally available abundant source through eco-friendly process. The material is cost effective and possess huge durability, very high thermal and corrosion resistance property almost equal to inorganic binders owing to its chemical structure.
An Interpenetrating network of polymer system (IPN) is to be tried by blending the inorganic (silicone resin) and organic (CNSL-S) polymers in the right proportion to overcome some of the drawbacks of the organic polymer and to make it perform almost equal to the inorganic polymer.

Metallic pigments such as zinc and manganese as metal powders are reported to have extensive corrosion resistance properties by their cathodic protection through galvanic coupling with the substrate metal mostly mild steel in wider application. The mechanism of protection that is offered by aluminium and stainless steel metal pigments are claimed to be due to the passivation mechanism and inert nature coupled with their higher melting points. In addition, these metallic pigments acquire a good adhesion to steel surface due to their high interfacial forces of metal-metal bond. Hence, the developmental studies involve the use of these metallic pigments in the formulation.

Normally metal pigmented paint formulation may not have much of the mechanical properties such as abrasion and wear resistance. To achieve this, ceramic pigmented topcoats application will be helpful. Hence, new ceramic blue and ceramic green pigments are to be synthesized and applied as finish coat in silicone resin primers. Such a multi component system may be expected to give still further high temperature and corrosion resistance properties.
The methodology of evaluation of the pigmented primer coats and primer coats with finish coats is to include electrochemical studies like potential-time measurements, potentiodynamic polarization studies and Electrochemical impedance spectroscopy studies in 3% NaCl medium.

Further the studies is to include evaluation for the mechanical properties like abrasive, impact and scratch resistance, flexibility etc.

The evaluations are meant to understand the corrosion resistance and heat resistance properties of the coatings.
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