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WATER BASED SILANE COUPLING AGENTS FOR BONDING POLYACRYLATE RUBBER TO ALUMINUM

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ABSTRACT

This work mainly deals with the bonding of aluminum alloy AA5052 to polyacrylate rubber manufactured by Zeon Chemicals and ethylene/acrylic rubber (Vamac) manufactured by DuPont. Previously our research group has done a great deal of work on bonding rubber to metal by using solvent-based adhesives. Our research lab had earlier reported that the combination of bis-(trimethoxysilylpropyl)amine and bis-(triethoxysilylpropyl)tetrasulfide bond various type of rubber to metal. But the adhesive was solvent based and the present environment regulation by EPA restricts the use of solvents and chromating technology in rubber to metal bonding.

In this study a mixture of two silanes bis-[trimethoxysilylpropyl] ethylenediamine and vinyl triacetoxy silane in the ratio of 4:1 was found to give better bond strength with VAMAC rubber and AA5052 combination. This new water based silane treatment was found to be as effective as the solvent based adhesive phenolic adhesive used by Federal Mogul Corporation.

In addition to comparable bond strength, the silane system provides comparable corrosion protection as demonstrated using DC corrosion and polarization resistance measurement. Structure of silane mixture was studied in this thesis and a model is proposed for a possible bonding mechanism between VAMAC rubber and the silane-coated metal.

Infrared, XPS and TOF-SIMS techniques were used to investigate the reaction between the two silanes in the mixture and the silane film on AA5052 .The above mentioned techniques also helped me to study the surface cleaning method. This study also proposes a better cleaning method for aluminum AA5052 to improve the adhesion strength.

Though the silane mixture provides comparable bond strength to the existing solvent based adhesives, still further research has to be carried out to obtain 100% rubber retention on the metal surface and also a universal silane system to bond a wide range of rubbers and metals.

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1.0 General Introduction

Over the years rubber has found major applications in the automotive industry apart from the tire sector. A typical passenger car contains more than 600 rubber products. The complete range of non-tire automotive products made out of rubber includes vibration dampers, fuel flow controller, automotive seals, suspension systems, pressure regulators and cruise controls [1]. Rubber also finds application in hoses, conveyor belts, engine mounts and medical applications.

Due to the increased use of rubber in automotive, industrial and medical applications, the requirement for a strong and robust bond between rubber and metal has become more important and vital. Many papers have been published on rubber to metal bonding techniques, technology and applications [2]. One of the most widely used methods for bonding rubber to metal is by coating steel with a layer of brass. This method was primarily used in the tire sector to bond tire cords to natural rubber. Though this bond is strong and durable, it wasn't advised for automotive rubber components because of its expensive nature and also because of its narrow range of application (sulfur cured rubber) [2,3, 4, 5,6].

Failure of brass with other rubbers led to an alternative technique of bonding various metals to different rubber compound by means of liquid adhesives. Such adhesives, which are often two-layer systems, are traditionally solvent-based. Numerous adhesives developed earlier for the purpose of bonding elastomeric materials contained silane as the coupling agent and other ingredients such as fillers, antidegradants and thickeners **[3]**. But due to the highly organic nature of the organo-functional silane compounds, the traditional adhesive compositions have relied on organic solvents to form a stable and workable solution. The solvents are primarily

used for two major steps in the industry a) cleaning and degreasing of the metal b) coating of the metal by bonding agents [7].

The solvents used in all these adhesives are organic solvents, such as toluene, ethanol, xylene and others. But the need for a high concentration of organic solvents in these silane adhesive solutions for better adhesion has become a major obstacle because of the restriction imposed by Environmental Protection Agency (EPA) against Volatile Organic Compounds (VOC). A reduction in VOC is requested from environment regulatory boards all over the world for the sake of flammability and human safety. So in order to meet the target reduction of 67% solvent emission imposed by these boards, it is necessary to use only water-based adhesive for bonding rubber to metals in the near future [2]. In the past two to three decades increasingly more manufacturers (Lord Corporation, Henkel, Rohm & Haas and Chemetall) focused research on developing water-based adhesives, which are environment friendly. Though the aqueous adhesives can solve the environment crisis, these systems suffer from low bond strength, short shelf life and other production disadvantages.

In the recent years our research group has developed a series of pretreatments for metals prior to painting or rubber bonding that offer several advantages over existing solvent-adhesive systems. These systems are based on the use of certain organo-functional silanes that are applied to the metal as a very thin film using very low organic solvents, water, or from mixtures. All these silane systems were mainly used for the corrosion control of metals, except for the work by Jayaseelan et.al, which concentrated on rubber to metal bonding [3,4,5,8]. Silanes were selected because of the wide-ranging advantages over the existing metal pretreatments process for adhesion and corrosion performance.

The advantages of using silanes are as follows

- a) A silane pretreatment process consists of a very few steps, namely degreasing, alkaline cleaning and silane treatment.
- **b)** The coating process is carried out at room temperature as opposed to the phospating process that is carried out at elevated temperature.
- c) The silane treatment time can be faster than various other present techniques.
- d) Silanes are non-toxic.
- e) Silanes films can give outstanding corrosion protection to metal compared to the conventional chromating techniques [9].

1.1 **Objective of the study**

Federal Mogul Corporation, the sponsor of the project, manufactures rubber to metal bonded products for the automotive sector, using solvent-based phenolic adhesive systems. Such systems have the drawback of higher organic solvents and also higher solid content, which makes the adhesive very expensive and also a threat to the environment because of the higher VOC contents. So this project was devised to overcome this problem.

The objectives of the project were as follows:

- To formulate an aqueous silane adhesive to bond ethylene/acrylic rubber (Vamac) manufactured by DuPont and polyacrylate rubber manufactured by Zeon chemicals to aluminum (AA5052).
- Optimize the water- based silane adhesive replacing the solvent-based adhesive.
- To limit the solid content (silane concentration) to make the adhesive inexpensive.
- Optimize the silane system for improved corrosion performance.
- To replace the current metal pretreatment method (chromating or phospating) and to provide an environmentally compatible coating system.

1.2 Metal substrate and its preparation

Metal plays an important role in bonding rubber to it. Even though we are not much interested in the metals structure within the mass of the metal, importance has to be given to what is happening in and on its surface layer. To obtain a long lasting bond between rubbers and metal it is essential to have an interface clean and free from contamination and defects. The presence of oil and grease has a major effect on the quality of the final product. A suitable pretreatment of metal is necessary in order to obtain a satisfactory bond between the rubber and metal. [2] It is difficult to underestimate the cleaning process of the metal, as it is fundamentally responsible for the success of the rubber to metal bonded products. This section is put forth to give an overview of the metal cleaning process in the automotive rubber to metal bonding industry. The metal cleaning process involves the treatment method such as degreasing, deoxidizing, acid and alkaline etching.

To achieve a successful cleaning cycle, we need to remove all or some of the following; a) Protective oils and greases which may have come from aluminum fabrication process; b) surface oxides; c) handling grease and finger prints; d) dust, dirt and foreign matter; e) moisture, as it helps corroding the metal and, f) oxide films **[10]**. The cleaning method adopted in rubber products industry is not universal and is carefully chosen depending on the nature of contamination, but the primary aim is to obtain a chemically clean surface.

Degreasing is the first step in the cleaning process as this process removes the oil and grease, which tend to affect the quality and bond strength of the product if not removed. Vapor degreasing has been used traditionally, but this doesn't give a chemically clean surface. Vapor degreasing is generally supplemented by chlorinated hydrocarbon solvents trichloroethylene or perchloroethylene or methylene chloride. The chlorinated solvents are highly recommended

because they have high solvency for organic materials, are chemically compatible with all materials, have high stability and are non-corrosive. The recent advancement allows vapor degreasing to be done in a closed chamber thereby eliminating loss of solvent vapor to the environment [11].

The chlorinated solvents have relatively low surface tension thereby making it easy to clean complex and porous by penetrating pores and crevices. The solvents will be more efficient in degreasing when the metal to be cleaned dwells in the solvent vapor till it reaches the temperature of the vapor. The vapor is heavier than air and remains in the cleaning tank. A cooling zone is created by means of cooling coils making the vapor to condense into pure liquid solvent on contact with the metal thereby dissolving the grease and oil **[2,11]**.

Ultrasonic cleaning is a cleaning method generally used for removing tough grease and oil. But it requires expensive equipment thereby making it feasible for smaller parts compared to larger parts. The cleaning process of 3 major steps involves pre-cleaning of the metal to remove dirt or dust on the metal, secondly immersing the part in the degreasing solvents (acetone, methanol, hexane) which are agitated ultrasonically and finally solvent spraying.

Many research groups [1,12,13] have studied ultrasonic cleaning in variety of solvents both acid and alkaline. Missel et al. [12] have recommended nitric acid at varying concentration for this purpose. They found optimum results are generally obtained when degreasing precedes this cleaning method and followed by a solvent and distilled water rinse [1]. Van Ooij et al. [3,5,14,15,16] have obtained good rubber bonding results by cleaning metal ultrasonically using solvents.

Alkaline Cleaning is the most important of all cleaning process. Aluminum being amphoteric, its easily attacked by alkaline solutions. The alkaline solution is generally used in a dip tanks for the purpose of cleaning. The nature of salt (completely and easily soluble), alkalinity of the solution (pH between 9 and 11 are preferred for aluminum), wetting power, temperature of the cleaning bath, dwell time of metal part in the alkaline cleaner is determined based on the requirement of the particular industry. Mixture of sodium carbonate, sodium metasilicate and trisodium phosphate are widely used in the industry to clean aluminum **[2,10]**.

Rinsing operation is an important step next to alkaline - acid cleaning. Hot and cold water rinses are used in the industry. They will generally speed up the drying process and the hot water rinse helps in keeping the metal **pores** open to permit removal of cleaning compound and emulsified oil.

Acid Cleaning can be *etching or non-etching*. The *non-etching* solution contains primarily nitric acid or chromic acid. Nitric acid is very slow while attacking aluminum. Nitric acid when combined with chromic acid crystals provides an excellent and extremely powerful cleaning medium, which will completely remove corrosion products or thick layers of grease. Another commonly used cleaner is a combination of chromic and phosphoric acid, which will rapidly dissolve any oxide without affecting aluminum and its alloys. The parts to be cleaned are generally immersed in an acid tank for about 20 minutes at a temperature of 40-65 °C. The process gives a very clean and slightly etched surface **[10]**.

Aluminum is typically *acid etched* using chromic V sulfuric acid [17] or dichromate/sulfuric acid [18]. Chromic V sulfuric acid etch is primarily used in Europe and dichromate/sulfuric acid etch commonly known as FPL (Forest Product Laboratory) etch is used in North America.

Sun et al. [19] were successful in showing that FPL etching eliminates MgO formed on aluminum 2024 alloys during thermal treatments. But Environmental concern limits the use of chromates /fluorides in etching operation. This has resulted in a number of formulations [17,20,21] that are acid-based but not containing chromates or fluorides. These formulations primarily contained various combinations of sulfuric acid, phosphoric acid, hydrofluoric and nitric acid.

1.3 Rubber to Metal Bonding

Rubber to metal bonding was discovered when natural rubber bonded to brass accidentally during the vulcanization of rubber in the middle of 19th century **[2]**. But even today this process is the basic idea behind rubber to metal bonding. Rubber to metal bonding can be classified broadly into two categories a) direct –rubber metal adhesion b) adhesive bonding.

1.3.1 Direct rubber – metal bonding

Rubbers vulcanized by sulfur are able to successfully bond with metals like brass, zinc and nickel **[1].** Strong bond between rubber-brass is established during the vulcanization process of the rubber. The mechanism of rubber-brass bonding was investigated and documented in detail by Van Ooij et al. **[22,23].**

Vanooij refined the rubber-brass adhesion model based on various recent studies **[24]** for easy understanding. Following are the various stages involved in the rubber-brass bonding.

- a) Formation of active sulfur-containing intermediate products from accelerators interacting with rubber molecules.
- b) Adsorption of accelerator fragments on the surface of the metal after stearic acid treatment of brass surface (stearic acid dissolves surface oxides)
- c) (Me S) bond formed opens the S₈ ring and helps in sulfur insertion.

- d) At higher temperature complex decomposition takes place to form sulfide film, which consists of Cu_xS at the sulfide-rubber interface and ZnS at the sulfide-metal interface [3].
- e) During vulcanization process the Cu_xS crosslinks with the rubber matrix. The crosslink density of rubber adjacent to the metal is increased, which contributes to the strong adhesion between brass and rubber.

In summary, all transitions metals, which form a covalent bond of the type Cu-Sulfuraccelerator, will typically bond to sulfur vulcanized rubbers. This is not the case with other metals as the sulfide growth is very slow and the metals are passive. As mentioned above the bond between rubber and brass is strong and resistant to high temperature and dynamic loading.

In spite of the overwhelming advantages of brass, it also has several drawbacks and limitations mainly due to corrosion. Brass is prone to galvanic corrosion in conjunction with steel. Also the brass-rubber bond is very sensitive to the formulation of rubber compound. High sulfur content and delayed action accelerators have to be used in the rubber formulation, which aids the formation of copper sulfide. Though this change in formulation improves bond strength, there is a reduction in the thermal and mechanical properties. This causes the rubber vulcanizates to fail prematurely in the cord region due to flexural fatigue **[2, 4, 25]**.

Some authors [7,23,26,27] have suggested that the use of cobalt adhesion promoters is necessary to obtain the stability of rubber-brass bond in aging conditions. But once again cobalt is very sensitive to reversion and causes degradation of rubber modulus on oxidative aging. Also cobalt being an expensive metal, it makes the process expensive.

But the advantages like thermal stability, dynamic loading resistance, crack growth resistance of natural rubber outweighs the above-mentioned limitations. Thus brass is still extensively used in tires for bonding rubber to tire cords.

1.3.2 Adhesive Bonding

As early as 1869, ebonite, the first adhesive developed, was found to impart good bonding between natural rubber and steel and this is still being used in application like tank lining, rubber rollers and castor wheels. Ebonite, containing certain amount of sulfur is applied as a solution on the metal surface. During vulcanization the sulfur migrates to rubber and forms an interpenetrating network. So there is a restriction on the amount of sulfur in the solution as high sulfur content gives poor physical properties for the product. Also due to heat softening at around 80 °C, ebonite is restricted in many applications [1].

The automotive industry does not use the brass-plating method or the above mentioned ebonite because of the various limitations mentioned earlier and also because there is a wide range of metals and rubber compounds (not only NR), which are formulated for specific products such as seals, gaskets and hoses. These products must have the ability to withstand high temperature, better resistance to solvent and high corrosive environment and good mechanical properties. There is also a wide variation in the cure systems used for these rubber compounds from the traditional sulfur curing systems used for the natural rubber. Due to the enormous variations in rubber compound formulation and metal substrates a single adhesive system to bond different rubber-metal combination has always eluded the adhesive market.

Adhesive systems can be broadly classified into solvent-borne adhesive and water-borne adhesive.

1.3.2.1 Solvent-based adhesive

The main principle [7] involved in the bonding process using a conventional solvent are 1) coating the metal with a one or two layers of primer and a top coat, the formulation being proprietary, 2) solvent evaporation has to occur before the metal part can come in contact with the rubber, 3) the molding of the metal to the uncured rubber to obtain simultaneous bonding and vulcanization. The major reason for using solvent is because of its ability to wet the metal surface easily. Dilution of the highly viscous bonding agents on the factory sites has also made the use of organic solvents necessary.

Conventional solvent-based adhesives have always been two-coat systems consisting of two layers - primer and cover cement. The primers generally contain resins like phenolics, isocynates and other specific ingredients dissolved in organic solvents like toluene, perchloroethylene and xylene. The main requirement for the primer is to obtain good wetting of the metal surface. The topcoat or the cover cement is formulated using mostly halogenated polymers with specific additives like silanes, fillers (carbon black) and organic solvents. The topcoat has to react with the rubber to give good bonding between the metal and rubber. This was proved earlier by Milczarek et al. **[28]** and Packham et al. **[29]**, who could observe a reaction between the natural rubber and the cover cement during vulcanization by a diffusion/cross bridging mechanism.

Rubber to metal bonding also occurs by means of an adsorption mechanism, which was showed by the results obtained by Moore **[30]**. His results proved that a rapidly curing cement after complete curing bond to rubber (basically due to adsorption) and gives good adhesion strength.

Polyisocynates was earlier used for bonding NR, SBR to various metals because of its ability to interact with hydroxyl groups at the metal surface and the rubber compound. **[1,31].** But they were very sensitive to moisture and start complex adverse reaction with rubber chemicals such as the accelerator in the rubber compound.

In the middle of 1950's, the chemical product division of Lord Corporation, Erie, PA came with a revolutionary bonding agent, Chemlok 220 based on the US patent by Coleman et al. **[32].** They came up with this adhesive which comprised of a heat activated chlorinated rubber and at least 1%, by weight, of a poly-C-nitroso aromatic compound dissolved in methanol. This was the first kind of a solvent adhesive, which produced rubber-tearing bonds (cohesive failure- failure within rubber). This system was stable and had longer shelf life when stored in a can at ambient temperature **[2].** Unlike the isocynates they did not react with the moisture and gave outstanding bond strength. This system was able to bond to any metal and a wide range of rubbers available at that time.

Later in 1963 De Crease et al. **[33]** came up with a novel composition containing chlorosulfonated polyethylene, certain isocyanates and dinitrobenzene. This composition was successful in bonding natural and synthetic rubbers, such as ethylene propylene, non-conjugated diene terpolymers, neoprene, styrene butadiene rubber, butyl rubber and various other rubbers to metal substrates. This adhesive was not helpful in bonding silicones and fluorocarbons.

Today varieties of solvent borne adhesives (Chemlok, Chemosil, Thixon, Megum, Cilbond, Metalok and Parlok) are available which can bond to various rubbers and metal as reported by several manufacturers **[34]**.

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But nowadays the use of organic solvents is not accepted environmentally because they create health hazard in the factory atmosphere and are expensive. But industries have to be extremely careful in eliminating these solvents, as they are highly flammable. So there is always a continuing effort to obtain an ultimate waterborne adhesive for bonding elastomers to metals, which can eliminate the solvents.

1.3.2.2 Water-based adhesive

Bonding agent manufacturers have tried hardly for the past 3 decades to come up with a single coat bonding system or a water-borne adhesive because of the increasing concern for the elimination of solvents. Solvent-based adhesive are generally composed of two components, the primer and the cover coat, but in the water-based adhesive both primer and the cover coat are in emulsion form [7]. Film formation using a solvent-based adhesive is very simple as the film formation occurs when the solvent evaporates, but for a water-based system, the film formation is more complex. These systems are emulsions of small particles namely micelles. After air-drying, the micelles, which are uncured, become separated and only have surface cohesion between the particles. The micelles coalesce to form a dense and continuous film.

But the main problem faced by water-based adhesives are that they need to be applied to warm metals which help in breaking down the micelle structure in the system to produce a continuous film. Otherwise the adhesive will flake of **[2]**. Many water-based adhesive were developed in the past 30 years, which are discussed below.

In 1977, Jazenski et al. **[35]** came up with a storage stable, heat-reactive waterborne composition, which contains a water dispersible novolak phenolic resin, a methylene donor

such as an acetal homopolymer or acetal copolymer. This adhesive was useful in direct bonding of natural and synthetic resins to rigid and non-rigid substrates and also as primers to rubber-to metal bonding adhesives.

In 1983, Sadowski et al. **[36]** invented a terpolymer latex which was prepared by emulsion polymerization of 2, 3-dichloro-1, 3-butadiene and a mixture of at least two different unsaturated monomers. This latex provided adhesive strength comparable to commercial solvent-based adhesives in bonding natural and synthetic elastomer to metal substrates.

An aqueous dispersion formulated by Rullmann et al. **[37]** contains an organic polymeric film forming substance (like polyvinylacetate, polyacrylic acid), an aromatic poly nitroso compound and a coactivator (like isocyanurate, 1,3-butyleneglycol dimethacrylate). This additive improves the crosslinking of the organic film-forming substance and results in higher bond strength between natural rubber and metal substrates.

In 1993 Treat et al. **[38]** bonded nitrile rubber to metal using a novel aqueous adhesive composition, which contained chlorosulfonated polyethylene latex, a polyhydroxy phenolic resin copolymer and a high molecular weight aldehyde polymer. The trihydroxy aromatic compound is the reason behind the effectiveness of the phenolic resin copolymer (prepared by combining monohydroxy and di/trihydroxy aromatic compound) in bonding nitrile rubber to metal.

Mowrey [39] developed a water-based adhesive for bonding peroxide-cured elastomers to metal substrates. He formulated his adhesive using maleimide compound, acid scavengers, a polymeric film former and precipitated silica, optionally phenolic resole or isocyanatosilane.

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This adhesive bonded all elastomers (like homopolymer of conjugated diene compounds such as isoprene, butadiene and chloroprene) cured by peroxide to metal substrates, but failed when tried with sulfur-cured elastomers. Above-mentioned adhesives are few examples for the continuing effort shown by the adhesive industry to come up with ultimate water-based adhesive to bond elastomers to metal substrates.

Today a variety of waterborne adhesives are available in market **[7, 34]**, which form stable, and durable rubber-to metal bonds. However no detailed information is available on the formulation of these adhesives. These water-borne adhesives available in the market are tabulated **[Table 1.1]**. These bonding agents include specific primers and cover a wide range of rubbers: unsaturated (NR, NBR, CR) or saturated (EPDM) or polar (ACM, VAMAC) and even fluorinated and silicone rubbers. Recently some systems have also been developed which are one-coat system (examples: Thixon 3010 and Megum W 2502).

Even though waterborne adhesives assist in compliance to solvent emission regulation and in some cases provide better durable bond strength compared to the traditional solvent-based adhesives, there are some deficiencies to be eradicated for complete replacement of solventbased adhesives by water borne adhesives. Those deficiencies are listed below:

- a) Stability of the aqueous adhesive
- b) Necessity to preheat the metal to apply the adhesive
- c) Bond durability against highly corrosive fluids and solvents.
- d) Under-bond corrosion or porous adhesive layer due to incomplete evaporation of water from the adhesive at normal temperature.

1.3.2.3 Silane adhesive for bonding rubber to metal

The chemistry, usage and development of silane coupling agents as adhesion promoters, cross linkers for organic polymers and as surface modifiers for substrates have been outlined over the years in several excellent review articles and different books by different authors [3, 4, 5, 6, 14, 40-42]. Alkoxyorganosilanes were known to adhesive chemists for a long time for its ability to enhance adhesion of organic polymers to inorganic substrates such as glass and metals. In the recent years organosilanes have penetrated into varied industries such as the automotive sector, building construction, aerospace and even electronics. It is hypothesized that alkoxysilane having the following structure $X_3Si(CH_2)_nY$, in which X represents a polar hydrolyzable silanol group and Y an organofunctional group, promote adhesion through a broadly reviewed mechanism. [43]

Though there are many potential organosilanes in the market, which can give good adhesion strength in rubber to metal bonding, these silanes are deemed failures because of the inability of the chemist to control the hydrolysis before, during or after the adhesive product manufacturing process. The silane solution pH plays a vital role because the hydrolysis occurs only in a particular pH range and even a slight variation in those values causes condensation of silane. Water molecule is eliminated during condensation and we obtain a cross-linked siloxane network. **[3, 43]** So obtained condensed silane is insoluble in water and makes the system unstable. In general silanes are hydrolyzed before application and cross-linking mechanism occurs after the deposition of the hydrolyzed silane on the metal substrate. Importance of silane hydrolysis are proved by several authors **[43]**.

After a certain degree of hydrolysis of silane in water or water/alcohol mixture, the silane molecules contain hydrophilic silanols groups (-OH). Silane molecules are adsorbed on a clean

metal surface, as they are hydrophilic. Metallo-siloxane bonds (Me-O-Si) are formed after adsorption, though this reaction is controversial. This reaction is speeded by heating the coated metal substrate. In the adsorbed film, silanols reacts with each other to give a siloxane network (-Si-O-Si-), which is the reason for superior corrosion protection [40,42,44]. Though the above mentioned bonds -Me-O-Si- and -Si-O-Si- can be hydrolyzed, this reaction is very slow because of the very low water concentration in the silane film. Thereby the hydrolysis equilibrium is not driven to the left for most metal. This is proved by the previous work done by Van Ooij et al. [44-46]. The organofunctional group "Y" of the silane later reacts with polymer matrix to give the Me-O-Si-R-Polymer linkage to give a strong bonding between the metal and the polymer [3].

So the mechanism of bonding will depend on several factors discussed above: the relative pH at the interface, the thermodynamic compatibility of the silane with the polymer and its condensation product and the organic functionality of the silane molecule. If the organofunctional group is a primary amine, no external acid is necessary for hydrolysis, as the amine will catalyze auto-condensation in the presence of water. **[43, 46]**

The choice of particular organofunctional group gives a silane the maximum reactivity with the polymer. Gent et al. **[47]** proved the above fact by using various types of silanes to bond polybutadiene with glass. He was successful in treating glass with vinyl and ethyl silanes and also obtained higher peel strength with increasing amount of vinyl silane in the mixture. In the past 5-10 years many chemists **[4, 5, 48-52]** have come up with different silane adhesive for bonding different range of rubber to different metals.

In 1957 Jenkins et al. **[48]** came up with a silane adhesive composition comprising a mixture of unsaturated silane (like vinyl triethoxy silane) and amino alkyl silane (like gamma aminopropyltriethoxysilane). This adhesive was successful in bonding silicone rubber to various substrates. Bonding occurred when the rubber and silane-coated metal were cured at higher temperature and pressure.

Gervase et al. **[49, 50]** patented a solvent-based silane mixture made with an isocyanate functional organo silane in combination with polyisocyanate and aromatic nitroso compound. This adhesive was found to have good storage stability and was a single coat adhesive. Though the reason for good stability was not clearly explained, it was experimentally proved that the inclusion of aromatic nitroso compound improved the stability. The adhesive could bond to a variety of metal substrates and elastomers.

Van der Aar et al. **[1, 4, 6]** came up with a combination of organofunctional and nonorganofunctional silanes for bonding peroxide cured rubber (like EPDM and fluoro elastomers) to metal. It was a two-step process in which the first coat was applied on the metal using BTSE [bis- (triethoxysilyl) ethane] silane and later a topcoat using vinyl silane. The vinyl silane was oxidized by the peroxide-cured rubber compound to from a covalent coupling and there by a strong bond was formed. This was one of the earliest attempts to successfully bond peroxide cured rubber with metals.

Jayaseelan et al. **[3,5,8]** later attempted to bond sulfur-cured rubber to metal using two functional silanes in their unhydrolyzed state. The silanes bis (trimethoxysilylpropyl) amine and bis (triethoxysilylpropyl) tetrasulfane were mixed in a particular ratio to successfully bond sulfur-cured rubbers to metal substrates. It was the first attempt to try non-hydrolyzed silanes

as an alternative to bond rubbers to metals. It was also seen that the silanes individually did not give promising bond results. This silane system also offered outstanding corrosion protection. It was postulated that the presence of the sulfur functionality in the sulphur silanes, helped the crosslinking reaction between the sulfur cured rubber and the silane to give higher bond strength.

In light of the continuing effort to eradicate volatile organic solvents from all chemical formulations for environmental purpose, there is always a need for water-based silane adhesive composition, which is free of volatile organic solvents. Some of the attempts are discussed below.

In 1993 Sexsmith **[54]** proposed a silane adhesive formulated using a low molecular weight alkoxy silane and an unsaturated acid compound. The adhesive preparation was very simple involving mixture of two silanes in certain ratio in water. The resulting mixture can be later diluted with water for coating the metal. This adhesive composition was very effective against non-sulfur-cured elastomeric materials such as polyol and peroxide-cured elastomers.

Later in 1996 Sexsmith **[55]** once again came up with a stable aqueous adhesive comprising water-immiscible organofunctional silane (like vinyltriethoxy silane) and a phenol resole (phenolic bisphenol A resol in water stabilized with poly vinyl alcohol). In this case the silane is dispersed in a stabilized aqueous dispersion of a phenolic resole. The resulting composition possessed unique adhesion qualities through the synergetic action of silane and resole mixture, enabling its use as an adhesive for vulcanization bonding of specialty elastomers and also as a primer or overcoat in protecting metals against corrosion. The solid contents in this

formulation make up from about 5% to about 40%. This could eventually make the adhesive expensive.

Wang **[56]** studied and later patented an aqueous silane adhesive, which was termed more versatile than the other commercially available silane during that time. Wang used a mixture of vinyl silane and water-dispersible polyisocyanate. Though the vinyl silanes are insoluble in water and unstable in aqueous solutions, the water dispersible polyisocyanate of the aqueous compositions can disperse and stabilize the organo silane in the aqueous phase. The silane adhesive tends to exhibit low VOC emissions and can be used to bond vulcanizable rubbers to a variety of substrates.

In this present work we have discovered a process for bonding amine-cured ethylene acrylic rubber to metal using a water-based silane. The process involves a mixture of two silanes, bis (trimethoxysilylpropyl) ethylenediamine and vinyltriacetoxy silane, used in a particular ratio and completely hydrolyzed in water. In this thesis we present some results for adhesion of amine-cured ethylene acrylic rubber (VAMAC – duPont's trademark for ethylene acrylic elastomer) [57]. Though some of the silane adhesives mentioned earlier [55, 56] in this review could bond ethylene acrylic rubber to metal substrates, they still needed a primer coating to give an outstanding corrosion protection for the metal parts and simultaneously strong rubber to metal bond [58]. The silane adhesive mentioned in this work showed a comparable bond strength and better corrosion resistance.

1.4 Corrosion protection of metals using silane coupling agents

Chromates have been used as anticorrosive inhibitors in surface pretreatment of metals like aluminum and its alloys, zinc and other metals. But the hexavalent chromate ion is reported to be toxic and carcinogenic, so EPA regulates their use [59]. The studies on silane coupling agents are carried with the primary aim to replace conventional chromating process in the metal finishing industry.

Silanes can provide outstanding corrosion protection for many metals because of the uniqueness of silane molecules in reversing the hydrophilicity to hydrophobicity as compared to other surface pretreatment methods using coupling agents, titanates, zirconates and others.

Van Ooij et al. **[16,44,45,46]** carried out studies intensively relating to corrosion protection of metals by silane treatments during the past few years. It is believed that the Al-O-Si and Si-O-Si bonds grow into a very strong network on the metal surface, which protects the metal against corrosive liquids & environment **[16,46]**.

Corrosion protection of cold-rolled steel using plasma-polymerized thin films of hexamethyl disiloxane (HMDS) of approximately 20 nm was studied by Conners et al. **[60].** This film could successfully pass the ASTM D-160 test to assess the corrosion protection

Some of the mono-silanes of the type X- $(CH_2)_3$ -Si $(OH)_3$ (where X is a functional group such as vinyl or otherwise), which are initially used as coupling agents in glass-reinforced polymeric composites or as adhesion promoters for metals-paint systems, can also serve as efficient corrosion inhibitors for a variety of metals Examples of this type of silanes are vinyltriethoxysilane (VS) and γ -ureidopropyltriethoxysilane (γ -UPS) [44].

Silanes can be deposited in various different ways: solution deposition, vapor deposition, plasma deposition and electrodeposition [16]. But solution deposition was the widely used

method in this project because of the ease with which we could coat silane on the metal surface.

Corrosion performance of metals coated by solution deposition of silanes was studied by Beccaria et al. [61] and Van Ooij et al. [44,45,46,62,63]. However surface deposition of silane by immersion produces non-uniform and uncontrolled thickness of silane coating which can affect the performance of metal in corrosion protection [16].

Petrunin et al. **[64]** studied silane films formed by vapor deposition. Petrunin et al. found vinyl triethoxy silane (VTES or VS) and trimethyl ethoxy silane (TMES) anodically inhibits steel, magnesium and aluminum against corrosion.

Recently Singh et al. **[16]** came up with a process to deposit silanes on metals by pulsed electrodeposition. He achieved coating of uniform thickness. He could demonstrate improved corrosion protection properties compared to solution deposition method (immersion method)

Zhu et al. **[44]** found that bis-type silanes, with the general formula of Si-(OH)₃-(CH₂)₃-R-(CH₂)₃-Si(OH)₃ (where R is an organofunctional groups such as secondary amine), like bistriethoxysilyl]ethane (BTSE), bis[3-(triethoxysilyl)propyl]tetrasulfide (or bis-sulfur silane), bis-[trimethoxysilylpropyl]amine (or bis-amino silane) and their mixtures, can provide much improved corrosion performance on a wider range of metals, as compared with the earlier mentioned mono-type silanes .

They also came up with a water-based silane solution (mixture of bis- [trimethoxysilylpropyl] amine and vinyltriacetoxysilane), which gave outstanding corrosion protection among various

other water-based silanes. The advantage of this system was that the silane mixture hydrolyzes instantaneously and that it is alcohol free **[44,65]**.

During the past few years Palanivel **[44]** also demonstrated that films of silanes on metal could be modified extensively by certain addition of additives namely silica nanoparticles, corrosion inhibitors and color pigments (dyes). These modifications tend to duplicate the unique attributes of chromate films, having a color and exhibiting superior correction protection by self-healing mechanism.

Silane coupling agents are expected to replace the conventional chromating process and solvent-based adhesives for better adhesion and corrosion performances. But after reviewing lot of published works on silane, its properties and applications, the author concludes there is still a need for an universal waterborne silane adhesive, which could bond all rubbers to different metal substrate and at the same time give outstanding corrosion protection.

2. Experimental

2.1 Materials

2.1.1 Mold for Bonding Rubber to Metal

The rubber compounds used in this project were bonded to metal substrates using a specially designed mold based on the drawing provided by Federal Mogul Corporation. Cold-rolled Steel (CRS) was the material used to manufacture the mold. A local company helped us in fabricating the mold shown in **Figure 2.1 a, b**.

2.1.2 Metal substrate & substrate cleaning

Federal Mogul Corporation supplied us with 2.54 cm x 7.62 cm x 0.16 cm metal coupons made out of aluminum alloy AA5052.Its composition was (in wt%) 2.46 Mn, 0.22 Fe, 0.19 Cr, 0.1 Si, 0.02 Ti and remainder Al [66]. The metal coupons received were cleaned in our lab during the initial stages of the project. Later we cleaned the metal coupons with alkaline cleaner at Federal Mogul facilities in a specially designed tank (Figure 2.2 a, b) for alkaline cleaning.

Initially the metal substrates were alkaline cleaned using the *Oakite Aluminum Cleaner NST*. This cleaner was supplied by Chemetall Oakite, Houston, Texas. The alkaline cleaner in the tank is maintained at 45°C and the substrates are dipped in the solution for 5 minutes. Immediately after that, the metals are cleaned in hot water for 5 minutes, followed by cleaning the substrates with cold water and de-ionized water. The metal is then kept in an oven at warm temperature to dry the metal substrate.

2.2 Sample Preparation

2.2.1 Silanes used

Several silanes (**Table 2.1**) were initially tried in this project. The silanes bis-(3-trimethoxysilylpropyl) ethylene diamine and vinyltriacetoxysilane (VTAS) were the final choice of silanes used in this project with successful results. Both the silanes mentioned above were obtained from Gelest Inc. (Tullytown, PA). The silanes were used without further purification.

2.2.2 Silane treatment of metal substrate

The silane treatment of metal was completed in one step. The water-based silane solution was prepared by mixing the bis - diamino and VTAS silanes in the ratios of 4:1, i.e., 4 parts of bis-diamino and one part of VTAS by volume. About 1 vol% of this mixture was hydrolyzed with 99-vol% of DI water. The pH of the silane solution was adjusted using acetic acid to a value between 6.5 and 7. The solution can be immediately used, as the hydrolysis is fast and complete. Amino silane is mixed with VTAS in certain ratios to increase the pH to a value where the silanol groups have a higher stability

2.2.3 Rubber compound used

Federal Mogul Corporation uses a variety of rubbers for their rubber-metal bonded product .Two of the common polyacrylate rubber compound used by them and in this bonding study are 1) L75 – ethylene acrylic rubber (VAMAC) supplied by DuPont and 2) KO6 – polyacrylate rubber supplied by Zeon Chemicals. The typical formulation of VAMAC is given in **Table 2.2**.

The basic structure of the most acrylic rubbers is the ethylene group with a carbalkoxy branch structure $CH_2=CH-(COOR)$.

VAMAC is categorized as a terpolymer with the ethylene-methyl acrylate in the ratio of 2:1.The cure site monomer is usually less than 5%. The carbalkoxy ($-CO_2-CH_3$) group imparted the oil-resistance property of the VAMAC.

2.2.4 Sample molding and adhesion testing

Silane treated metal substrates were bonded to the rubber compounds at Federal Mogul Corporation according to the cure conditions specified by the company manual. The adhesion test performed by Federal Mogul is different from the common ASTM D429 B test. Samples produced after curing are similar to the one shown in **Fig 2.3**.

The sample molding is completed as per the following Federal Mogul sample molding procedure.

- 1. Apply silane solution to the bonding edges.
- 2. Mill a fresh sample of the rubber compound.
- 3. Adjust rolls to produce 0.285 cm to 0.292 cm slab thickness.
- Cut the preps so that the compound train is parallel to the direction of the pull. Preps should be cut immediately after milling.
- Trim excess compound from preps to adjust their weights according to the following formula:

Overflow flash = (2 to 6 grams) x specific gravity of compound

6. Spray the preheated mold with a releasing agent, if needed.

- 7. Assemble the test pieces and preps in the mold. Each test piece should be mounted on one of the dowel pins in the mold cavities with the end to be bonded towards the center of mold. Place prep between the test pieces.
- 8. Mold according to the curing time and temperature recommended (**Table 2.3**) for the specific compound under test. Prepare 3 test specimens for each sample batch.
- Remove test specimens from mold using extreme care to avoid hot tear at the bonding edges.

Adhesion Testing

- 1. Modify the Instron Tester as follows:
 - a. Replace lower clamp with specimen holder adapter.
 - b. Cross head speed 5.08 cm per minute.
 - c. Measure the thickness and width of the metal coupon.
- 2. Mount the test specimen, clamping the rubber not more than 1.27 cm and no closer than 0.635 cm from the bond area.
- Pull to rupture. Spark at maximum tension at failure. (Total tension is recorded directly in Newton.) Discard any data resulting from stock tear rather than from bond tear.

Why edge pull test

The adhesion test performed in this thesis is different from the common ASTM D429 B test. Federal Mogul Corporation proposed this test to us keeping in mind the application of their product (gasket) .In real time application the bond strength for a gasket with

metal is measured at its edge. So our edge pull test was able to simulate the exact conditions mentioned above. Also all the customers of Federal Mogul Corporation universally accepted this test.

Visual Inspection of De-Bond Surfaces

1. Carefully inspect the de-bond surfaces after pulling the bond butts in the tensile tester. Look for visible bare metal surface. In some cases, there might be complete rubber coverage leading to no visible metal surface. That should be interpreted as 100 % rubber coverage.

2. A situation where no rubber is found on the metal surface may be interpreted as 0% rubber coverage. There may be intermediate cases.

3. In cases where the surfaces are partly covered with rubber, the % rubber coverage must be estimated. This can be best done using a low powered microscope (about 5X) or a magnifying lens. Carefully estimate the area of bare metal compared to the total bond area. Determine the % rubber coverage from that.

Calculations

- 1. Record total tension in Newton for each test specimen.
- 2. Calculate mean total tension for the 3 test strips of the current batch.

Mean Tension =T / N, Where T = sum of maximum total tensions and N = number of test strips, 3.
3. Analytical techniques in this research

3.1 Surface analysis techniques

3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The technique is extremely useful for studying the chemical composition and molecular structure of thin films on the surface of metals. RAIR measure the reflectance, i.e. the ratio between the reflected and incident intensities of the radiation. When a sample to be tested is placed in the beam, various wavelengths of infrared radiation are absorbed by the sample as the beam is scanned, and the result recorded as the infrared spectrum of the sample. A typical IR spectrum is composed of several absorption bands that correspond to various vibration modes of the molecule. Each of these vibrations can occur in any molecule, but they all occur at different frequencies.

Advancement in the field of computers led to the development of FTIR. FTIR consists of a high-speed scanning Michelson interferometer, and a high-performance computer that runs a Fourier transform algorithm. FTIR has made it possible to run real time measurement of changes in surface states with high resolution [71].

FTIR spectroscopy was used for the identification of functional groups of individual silanes and mixtures used in this study. The transmission infrared spectrum of silane mixture was obtained using a Nicolet Magna 760 FTIR spectrometer. KBr powder was pressed into a transparent disc using a hand die and a drop of the silane was placed onto the disc. The spectrum of the silane mixture /individual silane was obtained by subtracting the spectrum of a KBr disc from the spectrum of the same KBr disc with a

drop of silane on it. The spectrum of individual silane / silane mixture was obtained by averaging 256 scans of the sample at a resolution of 4 cm^{-1} . [67]

Reflection-absorption infrared (RAIR) spectra of silane films deposited on aluminum substrates were obtained using the same spectrometer and a Nicolet FTS-85 external reflection accessory that provided one reflection at an angle of incidence of 85° . Each spectrum was collected by averaging 256 scans of the sample at a resolution of 4 cm⁻¹. The spectrum of a film was obtained by subtracting the spectrum of an uncoated substrate from the spectrum of a film-covered substrate. The spectrum was corrected for water and CO₂. Numerous spectra were obtained for silanes films of varying pH and concentration.

3.1.2 SEM/EDAX

This technique was used for micro structural characterization and analysis of the silane film on AA5052. A Hitachi S-3600 SEM was used for the analysis. The coated samples were also characterized using Energy-Dispersive X-Ray Analysis (EDX), to determine the elemental constituents of the film. The samples were metallized by gold sputtering to prevent any charging of the surface. This technique was applied for the analysis of the locus of failure of rubber-metal bonds after destructive test. The maximum incident energy of the beam was 20 keV.

3.1.3 Contact angle analyzer

Wettability of pretreated aluminum substrates and silane-coated substrate was determined by the contact angle (θ). Advancing contact angles were determined using water and methylene iodide with a Video Contact Angle System. Measurements were made on several drops, which were placed in various locations on the surface. Surface energy (γ) with its polar (γ^{p}) and dispersion (γ^{d}) components was obtained directly from the instrument software by using the equations given below

Young's equation:
$$\gamma_{1s} = \gamma_{sv} - \gamma_{1v} \cos\theta$$
 (1)

Kaelbe's equation:
$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\gamma_{sv}^{d} \gamma_{lv}^{d})^{1/2} - 2(\gamma_{sv}^{p} \gamma_{lv}^{p})^{1/2}$$
 (2)

From (1) and (2)
$$-1 + [2(\gamma_{sv}^{d} \gamma_{lv}^{d})^{1/2} + 2(\gamma_{sv}^{p} \gamma_{lv}^{p})^{1/2}]/\gamma_{lv} = \cos\theta$$
 (3)

Where, γ_{ij} are the interfacial tensions between "S" solid, the "L" liquid and the "V" vapor Values of polar (γ^p) and dispersion (γ^d) components of surface energy for water are 22.0 and 50.2 mJ/m², respectively whereas for methylene iodide the values are 48.5 and 2.3 mJ/m², respectively [67].

3.1.4 Water break test [68]

This test method helps us in the detecting the hydrophobic (nonwetting) silane film on the metal surface. The surface (in a vertical position) to be tested is withdrawn from a container overflowing with water. The pattern of wetting helps in interpreting the nature of the film. In absence of a hydrophobic film, the draining water will remain as a uniform film over the substrate. In areas where hydrophobic materials are present, the draining water layer will break into a discontinuous film within a minute.

3.1.5 Ellipsometry – Silane Thickness Measurement

The approximate thickness of silane films deposited on aluminum, AA5052, was determined using variable angle spectroscopic ellipsometer (VASE) from J. A. Woolam

Co. This technique is more like an IR spectroscopy, which is a non-destructive optical technique, which provides information about layer thickness and optical constants of single and multilayered samples such as metals and polymers **[71]**.

The ellipsometer was used with monochromatic light at wavelength of 5461 nm. Optical parameters Δ and Ψ were collected from 300 to 1000 nm at 10 nm intervals and for 60-75° angles of incidence at 5° intervals. A computer program WVASE32 was used to fit a mathematical model to the experimental data. More detailed explanation about this useful technique is given in [71]

3.1.6 XPS [69]

A Perkin-Elmer model 5300 XPS spectrometer was used to examine the silane coated metal substrate. Mg K_{α} X-rays (hv = 1253.6 eV) at a power of 300 W and 15 kV were used as the excitation source. The chamber pressure was maintained at 10⁻⁸ to 10⁻⁹ Pa. Photoelectrons were analyzed with a concentric hemispherical analyzer. Survey spectra were obtained between 0 and 1100 eV binding energy at pass energy of 89.45 eV while high-resolution spectra were obtained at pass energy of 35.75 eV. Unless otherwise indicated, all spectra were obtained at a take-off angle of 45°, which is the angle between the specimen surface and the optical axis of the analyzer. High-resolution spectra were corrected for charging by referencing the C_{1s} hydrocarbon peak to a value of 284.4 eV due to the presence of Si-C bonds. [70] The atomic composition was determined from the area under the peaks in the high-resolution spectra using sensitivity factors included in the instrument software. The peak shape 90/10 % gaussian/lorentzian was used for curve fitting the core level spectra. XPS was also used to determine the composition of

aluminum substrates because acid and alkaline pretreatments produced aluminum oxide layer of varying thickness and chemical reactivity on the aluminum alloys. Highresolution spectra were corrected for charging by referencing the C_{1s} hydrocarbon peak to a value of 284.6 eV.

3.1.7 TOF-SIMS [71]

Top few nanometers of substrates are analyzed using this ion beam equipment. Primary ions of energy 0.5-20 keV, commonly O⁻, Cs⁺, Xe⁺, Ar⁺, Ga⁺ and O²⁺ are used to erode the sample surface .The secondary elemental or cluster ions formed from the target atoms by the impact are extracted from the surface by an electric field and the energy and mass analyzed. The ions are then detected by a Faraday cup and the resulting secondary ion distribution is displayed as a function of mass, surface location or depth into the sample. Some of the advantages of this technique are

a) Excellent sensitivity (<1 ppm) and a wide dynamic range for most elements

- b) Different isotopes of the same element can be distinguished
- c) Information on chemical structure can be obtained at the surface by monitoring molecular ions.

In SIMS analysis with a time-of-flight spectrometer it is essential that the ions to be analyzed enter the flight path simultaneously or at least within the shortest possible time interval because this results in the simultaneous generation of secondary ions, which are then accelerated by a constant voltage over a short distance. Ions of different mass will have different velocities and consequently a mass separation will occur. Hence the mass separation is given by the flight time, t, from the sample to the detector.

The sample analysis was performed using a CAMECA Ion-Tof Model IV instrument equipped with a 25 kV liquid metal (Ga) ion gun. The area analyzed was approximately 50 x 50 µm and a flood gun was used for charge neutralization. Positive and negative spectra along with depth profiling were obtained for silane-treated AA-5052 panels.

3.2 Corrosion studies

3.2.1 DC–Polarization test

DC polarization tests were carried out on silane-treated panels in a neutral 0.6 M NaCl solution. The silane-treated panels were pre-immersed in the electrolyte for some time before testing, in order to achieve a steady state. The bare panels were tested immediately after exposure to the electrolyte. On average, 3–4 replicates were tested for each condition. The data were recorded at potentials $E_{corr} \pm 250$ mV, with a scan rate of 1 mV/s. SCE and a platinum mesh were used as the reference and counter electrodes, respectively. The exposed area was fixed at 0.78 cm². The corrosion current and Rp obtained were converted to corrosion rates in mpy (mm/year) using the formula

 $CR = I_{corr} K EW / d A$

(70)

Where

CR is the corrosion rate.

 I_{corr} is the corrosion current in amps

K is a constant that defines the units for the corrosion rate

EW is the equivalent weight in grams/equivalent *d* is the density in grams/cm³ *A* is the sample area in cm² *E*_{corr} is the corrosion potential or Open Circuit Potential (OCP) *R*_p is the polarization resistance

3.2.2 Salt spray test

The bare corrosion protection of silane-treated metals without topcoats was evaluated using this test. In this test, 5% salt solution (NaCl) is atomized in a salt spray chamber at 35°C with the solution pH around 7. The tested panels shall be placed at an angle of 45° in the chamber, exposing to the salt fog for a certain period. The length of the test is varied based on the industry requirement. The standard duration are 336 hrs (as per the ASTM B 117 test procedures) and 1-week test.

4. Results and Discussion

4.1 Formation of silane coupling agent layer on AA5052

As reported by many authors **[44, 73, 74]** water-based silanes have the potential to replace solvent-based adhesives in rubber to metal bonding applications. In this section characterization work has been carried out to understand the mechanism involved in bonding polyacrylate rubbers to AA5052 using the mixture of bis-diamino and vinyl triacetoxy silane.

4.1.1 Hydrolysis of silane mixture of bis-diamino and VTAS

As mentioned earlier, the bis-diamino/VTAS silane mixtures are simply prepared by mixing the individual bis-diamino and VTAS silanes together in a ratio 4/1. When mixing this silanes there is an increase in temperature due to exothermic reaction during the mixing operation as mentioned in the previous work by Zhu et.al [44]. In Figure 4.1, it is suggested that the acidic VTAS reacts with water to release acetic acid and also generating SiOH groups in VTAS. The acetic acid in turn reacts with the basic bis-diamino silane by exchanging the hydrogen of both the secondary amino groups in the bis-diamino silane with the acetoxy group in acetic acid. As a result, amides (-NCOCH₃) are formed in the bis-diamino silane molecule. This reaction may not be immediate, there could be a possible intermediate state before the amide group is formed on the bis-diamino. It is possible that the acetoxy group in acetic acid can react with bis-diamino in



presence of water to form ammonium acetate (\dot{H}), where there is loose hydrogen bond. Then water is released from the ammonium acetate group to form the amide group.

Another important characteristic of a silane system is its stability. The silane solution has to be stable in order to use it in bonding application over a long range of time in industries. One of the criteria to judge the stability of the solution is to see whether the solution is clear. A clear solution is considered stable, while a solution, which is unstable, becomes hazy due to condensation of silanols **[44, 75].** It was seen that the mixture of bis-diamino and VTAS silanes (4/1) were stable for more than 8 weeks [Table 4.1]. The solution stability test was discontinued after 8 weeks for all the silane system, as the silane system was stable and there was no sign of silane condensation. Zhu **[44]** in her work had explained the reason for such stability. Condensation of SiOH groups occurs in a water based silane solution. But such condensation can be inhibited with the addition of a small amount of bis-diamino silane. This happens because the SiOH groups are weakly acidic whilst the secondary amine (–NH–) groups are strongly basic, and therefore the H-bond formed between –NH– and SiOH is more stable than that between SiOH groups. As a result, the VTAS silane solution is stabilized by means of the addition of bis-diamino silane. The hydrolysis reaction mentioned above can also account for the change of color of the solution over a period of time.

4.1.2 Thickness measurement of silane mixture bis-diamino and VTAS

The film thickness of the silane mixture of bis-diamino and VTAS (4/1) was measured on aluminum 5052 substrate using ellipsometry techniques. It was difficult to measure the thickness for 1% concentration, we therefore increased the concentration of the silane system to 3% and 5% to measure thickness. The thickness of silane film on AA5052 using 3% silane solution was around 20 ± 10 nm and for 5% system, it was around 90 ± 10 nm. But it was difficult to reproduce the same thickness in other parts of the substrate, as the film was not uniformly coated. From the results (Table 4.6) obtained in this thesis, we could conclude that the film has to be a monolayer (approximately 1-10 nm) in order to obtain high bond strength. We could also infer that an increase in silane concentration can increase the film thickness [Table 4.2]. So the silane film thickness plays a vital role in obtaining improved bond strength.

4.1.3 Characterization of bis-diamino and VTAS silane mixture by FTIR-RA

To verify the proposed mechanism in Figure 4.1, the silane mixture was investigated using infrared spectroscopy. The infrared spectra of 1% silane mixture of bis-diamino and VTAS (4/1) is shown in Figure 4.2. The peak assignments are shown in Table 4.3. From the figures, a strong peak can be observed at 3471.42 cm^{-1} suggesting the -Si-OH bond is formed due to interaction between VTAS and water. The peak at 678 cm^{-1} is due to CH₂ vibration. We could also see a broad band at 2095 cm⁻¹, which suggests C=C stretching, because of the presence of VTAS in the mixture. The peak at 1636 cm^{-1} is attributed to the RCONR₂ (N, N-disubstituted amide) in the mixture [77]. Thereby the strong peak at 1636 cm^{-1} confirms the reaction mechanism proposed in Figure 4.1.If the silane mixture is condensed, we would generally see a sharp peak at 1145 cm^{-1} which corresponds to Si-O-Si. But from the IR spectrum shown in Figure 4.2 there could be no possible silane condensation in the mixture and the system is very stable.

The broad peaks in Figure 4.2 is formed because the KBr pellet was not dry and since KBr pellet is hydroscopic it absorbs water and this affects the peaks in the spectrum. This could be the reason behind the broad nature of the spectrum.

4.1.4 Characterization of bis-diamino and VTAS silane film on AA5052 by FTIR-RA and TOF-SIMS

To get more information on the nature of chemical structure of the silane layers on AA5052, the silane films were studied using FTIR-RA and TOF-SIMS. Table 4.3 gives the assignment for the observed vibrational modes. The silane mixture of bis-diamino and VTAS (4/1) with different concentrations 1, 0.5, 0.25% and pH 7, 8, 9 were deposited on AA5052. IR spectra for these mixtures are observed in Figure 4.7, 4.8, 4.9. The peak at 1640 cm⁻¹ is due to the amide group in the mixture [**76**]. The peaks at 1145 and 1060 cm⁻¹ are attributed to the SiO asymmetric stretching in SiOSi [**76**].

It is known that for industrial application it is important to understand the influence of applying conditions such as the pH, concentration and curing conditions. Hydrolysis of the silanes, condensation of the hydroxyl groups in the silanes and the interaction with the metal substrate depend on the pH. The band of the v(Si-O-Si) shifted to higher frequencies from 1145 cm⁻¹ to 1149 cm⁻¹ and the intensity also increased from 0.175 to 0.275, when we increased the pH from 7 to 9.Similar shifts were observed when the concentration increased from 0.25% to 1 %. The band of the v(Si-O-Si) shifted to higher frequencies from 1137 cm⁻¹ to 1145 cm⁻¹ and the intensity also increased from 1137 cm⁻¹ to 1145 cm⁻¹ and the intensity also increased from 0.175 when the concentration increased. So the variation in pH and concentration affects the adhesion strength, which can be seen from the results in the Table 4.4 to 4.6.

The SIMS spectrum (Figure 4.3) was obtained for the silane film of bis-diamino and VTAS (4/1) at 1% concentration and pH 7 (cured at 150°C and 10 min) coated. The peak at 43 amu arises due to the presence of CH_3CO^+ bond with secondary amine group in bis-diamino silane or could be because of $-Si-CH_3^+$. The peak at 44amu corresponds to Al-OH⁺. The peak at 45 amu and 121 amu corresponds to $-Si-OH^+$ and $-Si-(OCH_3)_3^+$ [3]. Thereby the reaction mechanism between the silanes and water is in agreement with our analytical results mentioned above.

4.2 Bonding results

Initial experiments were carried out using various amino silanes and silanes based on previous work at UC in our group for bonding and corrosion purpose. The silanes mentioned in Table 2.1 and silane mixtures mentioned in Appendix were initially tried for screening purposes. The silane system of amino and sulfur silanes mentioned in the earlier study [3] by this research group was not successful in bonding the rubber compound VAMAC and KO6 used in this study. Also the

silane mixture was highly hydrophobic and was difficult to hydrolyze. Once the silane mixture of bis-diamino / VTAS (4:1) was chosen, various controlled experiments were carried out to optimize the silane system for better bond strength. In the following section I will discuss those conditions. The bond strength obtained in this thesis is based on 3 samples per silane system.

4.2.1 Influence of metal pretreatment method on adhesion strength

Though there are many metal cleaning methods suggested by various authors **[1, 10]**, series of cleaning methods were tried to establish the best process for this project. AA5052 metal substrates were cleaned in 5 different cleaning conditions [Table 4.7] and tested for bond strength with both VAMAC and KO6 rubber. It was clearly seen that when the silane system was alkaline-cleaned, followed by rinsing in DI water, it gave better adhesion strength compared to other cleaning methods.

4.2.2 Effect of curing time on adhesion properties

Before fixing the silane concentration and pH, it was important to fix the curing conditions. In earlier research work done by the group, the silane film were cured at 100°C.So the temperature was fixed at 100°C and the curing time was varied from 5to10 minutes for two different concentration, 3 and 5% of the silane mixture. It could be seen from the bond results [Table 4.5] that the adhesion strength improved for both the concentration when cured longer (10 minutes). So the bond strength was not sufficient to get 100% rubber retention on theAA5052 surface.

4.2.3 Effect of curing conditions on adhesion properties

To improve further the bond strength, various curing conditions were tried. 3% concentration of the silane mixture was used for this experiment at a constant pH of 5. AA5052 treated with the silane mixture were cured at 4 different conditions a) room temperature b) 70 °C,

10 minutes c) 100 °C, 10 minutes and d) 150°C, 10 minutes. It was seen that the bond strength increased with the increasing curing temperature. The bond strength between VAMAC and AA 5052 increased from 109 N to 182 N [Table 4.8]. But that was not sufficient to give the 100% rubber retention. We would also observe from the IR spectra [Figure 4.4] of these conditions that the intensity of (-NCOCH₃) group increased with increasing temperature [0.02-0.05] and that could be the reason for the better bond strength. The curing temperature was fixed at 150°C for forthcoming experiments based on the results obtained [Table 4.8].

4.2.4 Effect of silane concentration on adhesion properties

As mentioned in the previous work by Jayaseelan et .al [9] the silane concentration plays an important role in the film thickness and also the adhesion strength. So the silane mixture of bis-diamino / VTAS (4:1) was mixed in water at varying concentration from 5% to 0.25%. The silane mixture is immediately hydrolyzed, irrespective of the concentration. It can also be used with in the first hour of hydrolysis. We could see a trend with the varying concentration. As the concentration was decreased from 5-1%, there was a considerable increase in bond strength from 183 N to 233 N. But the trend reversed [Table 4.6] when we decreased the concentration further to 0.25%. The adhesion strength dropped drastically to 168 N. So we could conclude that an optimum film thickness is required for better adhesion strength. If the thickness increased or decreased from that optimum thickness, there is a considerable difference in bond strength.

4.2.5 Effect of pH of silane mixture on the adhesion strength

As mentioned by various authors **[44, 78] the** pH plays a vital role on the amount of silane adsorbed and the orientation of the silane on the metal surface. To optimize the pH for the silane mixture, the other parameters i.e. curing time, temperature and concentration were fixed at 10 minutes, 150 C and 1 %. The pH was varied from 5 to 10. The bond strength for these conditions

showed 2 different trends. The bond strength [Table 4.4] increased when increased the pH from 5 to 7, but decreased when the pH was increased from 7- 10.Also at higher pH, the silane mixture wasn't stable, the silane condensation takes place in the solution and the system becomes hazy. This explains the poor bond strength at higher pH.

4.2.6 SEM analysis of AA5052 substrate after bond test

To establish that the bond failure was cohesive; the failed metal substrate was studied by SEM. It could be seen clearly from the SEM images [Figure 4.5] that a rubber layer is covering the AA5052 metal substrate and EDX [Figure 4.6] of the failed surface showed there was considerable amount of carbon content to prove that the metal substrate is covered with rubber and the failure was cohesive.

4.2.7 Bonding results of AA5052 with polyacrylate rubber KO6

Though the primary focus of the project was VAMAC rubber, the bonding results of the polyacrylate rubber, KO6 with AA5052, did follow the trend of VAMAC rubber at various experimental conditions mentioned above. But the bond strength [Table 4.4, 4.5, 4.6, 4.8] was low compared to VAMAC rubber and furthermore silane systems have to be screened to optimize the results for KO6.

4.3 Mechanism of rubber silane interaction

Based on the above results a possible mechanism for reaction between the silane mixture and the VAMAC rubber is depicted as shown in Figure 4.7 - 4.8. The formation of (-NCOCH₃) in bis-diamino silanes has been demonstrated by infrared analysis and TOF-SIMS spectrum. The presence of basic amine groups in the bis-diamino silane catalyses the formation of Si-O-Si linkages and Al-O-Si linkages that are formed at the metal surfaces.

The silane mixture can react with VAMAC rubber during curing in one more possible mechanism [Figure 4.8]. But the most possible way is the reaction between the –OH group in the cure site of VAMAC and the (-NCOCH₃) group on the backbone of the silane film. This reaction [Figure 4.7] helps in forming an amide crosslink [-CONH-]. This reaction is put forth based on the curing mechanism of hexamethylene diamine with VAMAC [72].

The other possible reaction between the polymer and silane film is the unreacted –OH group from hydrolyzed VTAS can react with –OR group of the cure site to form a penetrating network as mentioned in Figure 4.4

The above reaction mechanisms explain the fact why the silane film mentioned in this thesis provides good adhesion between AA5052 and VAMAC. Also the importance of the silane film thickness is established as we have seen that the thickness increases with concentration and only thickness lower than 20 nm gives good adhesion strength.

4.4 Corrosion resistance of AA5052 using silane mixture of bis-diamino and VTAS

4.4.1 DC Corrosion and Tafel plots

The DC polarization tests were conducted on the bis-diamino/VTAS treated AA5052 panels in a 0.6 M NaCl solution (pH 6.5). The results are represented as the Tafel curve in figure 4.19.It was seen that the current densities for AA5052 has been largely reduced after the silane deposition compared to bare AA 5052.It was also observed that with decreasing pH from 10 to 7,

the current densities was still reduced. Furthermore the I_{corr} values for the silane coated AA5052 differed by two decades over the bare AA5052 and corrosion rate [Table 4.9] was also reduced by a factor of 3.28 in the presence of the bis-diamino /VTAS silane layer.

As seen from Figure 4.9, 4.10, 4.11 & Table 4.9, the pH of the coating solution has a strong effect on the corrosion protection offered by the silane film. For all the film formed from solution with pH greater than 7, the corrosion rates were higher and for pH 9 the corrosion rates were comparable to the blank AA5052 sample. Silane films formed from solutions with pH greater than 7 are unstable in corrosive medium.

So for this particular silane mixture, only at pH 7 is the ratio of the rate of hydrolysis to the rate of condensation higher. Though in most cases, this system is inferior with respect to hydrophobic silane films such as bis-sulfur and bis-sulfur/bis-amino silane mixture. But in present industrial conditions in which we need water based silane adhesive system to comply with the EPA regulation, these results are acceptable. There is also a scope for further improvement by adding corrosion inhibitors to the system.

To further establish these results, polarization measurement was performed over a narrow range of voltage of ± 12 mV with respect to E_{oc}. Here, too, the silane coated substrate show very large polarization resistance at pH 7 compared to other higher pH and various other curing conditions. A silane film allowed to dry at room temperature showed lower corrosion rate and higher polarization resistance. Considering the bonding results, we could conclude that 1% bis-diamino /VTAS silane at pH7 is the best possible system for bonding polyacrylate rubber.

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4.4.2 Salt spray test

It was important in automotive industry that the metal substrate coated with silane has to pass the 1-week salt spray test. Even though the metal substrate coated with the silane mixture of bis-diamino /VTAS silane (4:1) did not have severe rust compared to the blank substrate, it had slight discoloration and slight white rust [Figure 4.12] on the surface, but the chromated surface was superior and did pass the 1-week salt spray test.

4.5 Surface analysis after metal pretreatment

To further approve of the cleaning method used in this project, the surface energies of the various cleaning method were calculated using the contact angle equipment. These results [Table 4.10] showed that with alkaline cleaning method, the highest surface energy was obtained. Surfaces with higher surface energies wet the substrate easily.

Figure 4.13 shows the electron microscope pictures of the AA5052 surface cleaned by various pretreatment methods. Alkaline cleaning method was once again best compared to the acid cleaning method as the later made the surface really rough and a porous surface was obtained.

Further more the XPS results (Table 4.12) for acid cleaned surface showed a lot of contamination, as the atomic concentration of carbon was 53% in acid cleaned surface compared to 12% in alkaline cleaned surface.

4.6 Advantages of our silane system over current phenolic adhesives

The silane mixture (1% bis-diamino / VTAS (4:1), pH 7) proposed in this thesis has more advantages compared to the current phenolic adhesive. The silane system has very low concentration (1%) compared to the phenolic adhesive used at Federal Mogul, thereby making the silane system inexpensive compared to the current phenolic adhesive.

The silane system has bond strength of 233 N, which is comparable with the bond strength of phenolic adhesive (241 N). Also the silane system has comparable corrosion performance, which is proved by the DC corrosion and polarization resistance measurement [Table 4.9].

Though the silane system has many advantages, the system has to be optimized to replicate the bond strength and corrosion performance obtained in this thesis. Also the silane system could get only 80% rubber retention with VAMAC rubber after edge pull test, but phenolic adhesives had 100% rubber retention. So more research work has to be carried out to make a robust system.

5. Conclusions and scope for further research

5.1 Conclusions

Among the hundreds of silanes that were screened and investigated for the rubber to metal bonding, a mixture of bis-diamino /VTAS silanes proved to be the best candidate for this particular application. The analytical results and bond results suggest that the concentration and pH of this silane mixture play a vital role in the bond strength. In summary the following conclusions can be drawn based on the above mentioned results

- 1) A mixture of two silanes bis-[trimethoxysilylpropyl] ethylenediamine and vinyl triacetoxy silane in the ratio of 4:1 was found to give bond strength of 218 ± 15 N with VAMAC rubber and AA5052 combination, which is comparable with the bond strength (241 N) obtained using phenolic adhesive.
- 2) Further improvements in bond strength $(233 \pm 8 \text{ N})$ are obtained if 1% silane mixture of above combination at pH 7 is treated on metal substrate and is cured at 150 °C for 10 minutes.
- 3) Increasing the bis-diamino silane content in the mixture, the bond strength is improved which further proves that the presence of amino group helps in crosslinking reaction with the rubber molecule.
- 4) Increase in silane mixture concentration improves the silane film thickness, but an optimum film thickness (less than 20 nm) is required to obtain the maximum adhesion strength of 233 N.
- 5) This system can potentially eliminate the organic solvents in the manufacture of silane adhesive as it uses only water as the dissolving medium.
- 6) The silane system at pH 7 gave comparable corrosion performance as supported by the DC corrosion and polarization resistance measurements. The corrosion rate at pH 7 was

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5.3 mpy and the polarization resistance was 2.26E+03 ohms, which is comparable with the chromated sample.

Metal substrate cleaning method is important in obtaining better adhesion strength (112
N) as mentioned in Table 4.7. Also it was proved that the alkaline cleaning method proposed in this project was better than the acid cleaning for AA5052 by means of surface characterization studies.

So with modifications to current adhesive system proposed in this thesis, there is a high possibility to eliminate environmentally hazardous solvent based adhesive.

5.2 Scope for further research

The optimized silane system from this project can further be modified and turned into a robust process that can stand upto the requirement of industrial environment. Following are some of the suggested areas, which can be extensively investigated to give a universal silane adhesive for bonding rubber to metal.

- Addition of nanoparticles to the silane films to improve the strength of the film and also the bond strength
- 2) Since it was difficult to obtain a uniform silane film by dipping, surfactant can be added to improve the uniformity of the silane film. A few surfactant have been tried, but none were successful in giving better uniformity and also improved bond strength
- Aqueous suspension of silanes not soluble in water can broaden our scope in developing a universal adhesive.
- Catalysts that can improve the crosslinking of the film can be used in the silane mixture.

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b

Fig 2.1 (a, b) Mold used in the research to bond rubber to metal.



a

b

Fig 2.2 (a, b) Solvent filled tanks used in the project for cleaning metal substrates



b

Figure 2.3 a) diagrammatic representation of adhesion testing sample b)Original sample after molding









Figure 4.1 Reaction of bis-diamino with vinyl triacetoxy silane in water (after prolonged hydrolysis)



Figure 4.2 IR Spectra of solution (bis- diamino silane / vinyltriacetoxy silane = 4:1, 1% in 99ml water, pH 7)



Figure 4.3



Figure 4.4 IR Spectra of varying cure conditions {S1, S9, S10 = 150 C, 10 min; 100 C, 10 min; room temp)



Fig 4.5 SEM pictures a) Y9400/VTAS mixture, pH7, Conc. 1% b) AA5052 covered with Vamac Rubber after bond test



Figure 4.6 EDS of AA5052 after bond test





+



2 CH₃COOH

Figure 4.7 Reaction of VAMAC rubber with silane mixture







Cure site

Methyl Acrylate

(VAMAC)



ROH

Figure 4.8 Other possible reaction mechanism between Vamac rubber (L75) and hydrolysed VTAS



Figure 4.9 Polarization resistance, R_p of various silane systems

Corrosion Rate, CR(mpy)



Figure 4.10 Corrosion rate, CR of various silane systems



Figure 4.12 Tafel plot of silane coating on AA5052 at increasing pH


Figure 4.12 1 week salt spray tested samples a) Silane treated b) Chromated c) blank-untreated AA5052







Figure 4.13 SEM Image of the various cleaning method



Figure 4.14 IR Spectra of varying pH {S 1, S 2, S 3 = pH 7, 8, 9} at 1% concentration and cured at 150 °C for 10 min



Figure 4.15 IR Spectra of varying concentration {S 1, S 7, S 8 =1, 0.5 & 0.25% conc.} at pH 7 and cured at 150 C for 10 min

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Suppliers	Primer	Cover	Elastomers
Lord Corporation	Chemlok W8003	Chemlok 8282	NR, IIR SBR, BR, CR
Henkel	Chemosil XW 1190-23	ChemosilXW7500-21	NR, SBR,
	Chemosil W1200	Chemosil W 7600	NBR, CR, IIR, EPDM
C.I.L.	Cilbond R6130	Cilbond 60 WMV	NBR, SBR, ACM, ECO,
			Vamac
Morton	Thixon AP20	Thixon 5100	NR, SBR, IIR, CR, NBR,
			EPDM
	Thixon 3010(a)		FKM, Vamac
Chemetall	Megum W 23500	Megum W 23800	Non polar rubbers: NR,
			SBR, EPDM
	Megum W 2502 (a)		Polar rubbers: BR, CR,
			ACM, ECO
		Megum W 3295(b)	Special Elastomers: FKM

a) One component system which can be used as primer and cover

b) One component system with organosilane which can be used as primer and cover

Table 1.1 Examples of some [72] of the commercially available water borne agents(1995-2001)

Number	Trade Names	Chemical Names
1	A1170	Bis-[trimethoxysilylpropyl]amine
2	VTAS	Vinyl triacetoxy silane
3	Y9400	Bis-[trimethoxysilylpropyl]ethylenediamine
4	Bis-UPS	Bis-[trimethoxysilylpropyl]urea
5	γ-UPS	γ-ureidopropyltriethoxy silane
6	GPS	Gamma-glycidoxypropyl trimethoxysilane
7	SIS6994.0, SIT 8415	Quaternary amine functional silanes
8	SIC 2295.5,SIC2298.4	Chlorofunctional silanes
9	A1289	Bis-[3-triethoxysilylpropyl] tetrasulfide
10	A1589	Bis-[3-triethoxysilylpropyl] disulfide
11	APS	Aminopropylsilane
12	BTSE	Bis- [triethoxysilyl] ethane
13	TEOS	Tetraethoxy silane

Table 2.1 Partial list of silanes used in this project

Name	PHR
VAMAC	100
Antioxidant: Naugard 445	2
Stearic acid	1.5
Release agent: Alkyl phosphate	1
Release agent: Octadecylamine	0.5
Co accelerator: DOTG	4
Curative DIAK No1	1.5
Carbon Black: FEF Black	60
Plasticizer: TP759	10

 Table 2.2 Typical formulation [7] used in an O-ring using VAMAC

Compound	Time & Temperature
L75 (VAMAC)	3 min @ 360 F + post cure @ 350 F for 6 hrs
KO6 (Polyacrylate)	4min @ 365 F + post cure @ 350 F for 6 hrs

 Table 2.3 Curing time and temperature for various rubber compounds.

Silane Composition	рН	Stability (weeks)
5 ml of (Y9400/VTAS = 4:1)	7.0	4 weeks (hazy)
3 ml of (Y9400/VTAS = 4:1)	7.0	More than 8 weeks
2 ml of (Y9400/VTAS = 4:1)	7.0	More than 8 weeks
1 ml of (Y9400/VTAS = 4:1)	7.0	More than 8 weeks
0.5 ml of (Y9400 /VTAS = 4:1)	7.0	More than 8 weeks
0.25 ml of (Y9400 /VTAS = 4:1)	7.0	More than 8 weeks
1 ml of (Y9400/VTAS = 4:1)	5.0	More than 8 weeks
1 ml of (Y9400/VTAS = 4:1)	8.0	5(hazy)
1 ml of (Y9400/VTAS = 4:1)	9.0	1 day (hazy)
1 ml of (Y9400/VTAS = 4:1)	10.0	1 day (hazy)
3 ml of (Y9400/VTAS = 5:1)	5.0	5 weeks (hazy)
3 ml of (Y9400/VTAS = 5:1)	5.0	5 weeks(hazy)
3 ml of (Y9400/VTAS = 5:1)	5.0	5 weeks (hazy)
3 ml of (Y9400/VTAS = 5:1)	5.0	5 weeks (hazy)

Table 4.1Solution stability of silane system used in this project

No.	Silane mixture	Thickness from Ellipsometer
1	Y9400/VTAS mixture, pH7, Conc. 3%	10-30 nm
2	Y9400/VTAS mixture, pH7, Conc. 5%	80-100 nm

 Table 4.2 Thickness of silane mixture from ellipsometer (Thickness based on 2 readings per sample)

Peak position (cm ⁻¹)	Peak assignment
3471	Si-O-H, -O-H stretching vibration
2940	CH ₃ asymmetric stretch from Si-O-CH ₃
2095	C=C stretching vibration
1636,1640,1653	-RCONR ₂ in the mixture
1410	Mainly CH ₃ rock in Si-O-CH ₃
1276	C-H deformation vibration
1145	Si-O-Si
1060	Si-O-Si
916,924	Broad diffuse band; out-of-plane deformation vibration
768	CH ₂ rocking vibration
678	CH ₂ deformation vibration

Table 4.3Infrared peak assignments [77] for 1% Y9400/VTAS Solution (4:1) & 1% Y9400/VTAS (4:1) on AA5052

Silane formulation	pН	Curing Conditions	Conc., %	Bond strength KO6 (N)	Bond strength L75 (N)
1 ml of (Y9400/VTAS = 4:1)	5.0	150,10 min	1	100 ± 10	199 ± 8
1 ml of (Y9400/VTAS = 4:1)	7.0	150,10 min	1	159 ± 8	233 ± 8
1 ml of (Y9400/VTAS = 4:1)	8.0	150,10 min	1	146 ± 5	225 ± 5
1 ml of (Y9400/VTAS = 4:1)	9.0	150,10 min	1	148 ± 12	207 ± 5
1 ml of (Y9400/VTAS = 4:1)	10.0	150,10 min	1	75 ± 6	164 ± 12

Table 4.4Bond strength of various rubbers at varying pH

Silane formulation	pН	Curing Conditions	Conc., %	Bond strength KO6 (N)	Bond strength L75 (N)
3 ml of (Y9400/VTAS = 4:1)	6.0	100, 5 min	3	130 ± 4	135 ± 4
3 ml of (Y9400/VTAS = 4:1)	6.0	100, 10 min	3	117 ± 5	169 ± 9
5ml of (Y9400/VTAS = 4:1)	6.0	100, 5 min	5	116 ± 4	134 ± 9
5ml of (Y9400/VTAS = 4:1)	6.0	100, 10 min	5	119 ± 6	146 ± 8

Table 4.5Bond strength of various rubbers at varying cure time

Silane formulation	рН	Curing Conditions	Conc., %	Bond strength KO6 (N)	Bond strength L75 (N)
5 ml of (Y9400/VTAS = 4:1)	7.0	150,10 min	5	127 ± 12	182 ± 7
3 ml of (Y9400/VTAS = 4:1)	7.0	150,10 min	3	121 ± 8	203 ± 6
2 ml of (Y9400/VTAS = 4:1)	7.0	150,10 min	2	152 ± 7	222 ± 6
1 ml of (Y9400/VTAS = 4:1)	7.0	150,10 min	1	159 ± 8	233 ± 8
0.5 ml of (Y9400 /VTAS = 4:1)	7.0	150,10 min	0.5	119 ± 10	183 ± 4
0.25 ml of (Y9400 /VTAS = 4:1)	7.0	150,10 min	0.25	93 ± 5	168 ± 4

Table 4.6Bond strength of various rubbers at varying silane concentration

Cleaning method	Bond strength(N)	Bond strength(N)	Bond strength(N)
	J (Y9400/BIS-UPS)	F (Y9400/BIS-UPS/VTAS)	Z (gamma-APS)
Ultrasonic cleaning	96	91	40
Acid etching	80	74	43
Alkaline cleaning	96	112	78
Deoxidizer	80	78	48
Alkaline Cleaning + Deoxidizer	98	69	90

 Table 4.7 Bond strength of KO6 rubber with silane treated AA5052

Silane formulation	рН	Curing Conditions	Conc., %	Bond strength KO6 (N)	Bond strength L75 (N)
3 ml of (Y9400/VTAS = 5:1)	5.0	20 min	3	62 ± 5	159± 7
3 ml of (Y9400/VTAS = 5:1)	5.0	70° C, 10 min	3	87± 15	108± 18
3 ml of (Y9400/VTAS = 5:1)	5.0	100 ° C, 10min	3	112± 14	165± 20
3 ml of (Y9400/VTAS = 5:1)	5.0	150 ° C, 10 min	3	120± 8	182± 7

Table 4.8Bond strength of various rubbers at varying curing conditions

No.	Sample	Curing conditions	I _{CORR} (A/cm²)	E _{CORR} (mv)	К	D (gm/cm)	EW (gm/equiv)	R _p , ohm	CR, mpy
1	Chromate		6.72E-06	-777.25	1.29E+05	7.87	27.92	3.88E+03	3.1
2	BLANK		3.81E-05	-796.7	1.29E+05	7.87	27.92	6.86E+02	17.4
3	NEW21	7,1,150C	1.15E-05	-788.35	1.29E+05	7.87	27.92	2.26E+03	5.3
4	NEW22	7,1,100C	1.36E-05	-787	1.29E+05	7.87	27.92	1.92E+03	6.2
5	NEW23	7,1,ROOM	5.22E-06	-789.3	1.29E+05	7.87	27.92	5.00E+03	2.4
6	NEW61	7,0.25,150C	2.22E-05	-788.2	1.29E+05	7.87	27.92	1.18E+03	10.1
7	NEW41	7,0.5,150C	1.48E-05	-800.9	1.29E+05	7.87	27.92	1.77E+03	6.7
8	NEW21	7,1,150C	1.15E-05	-788.35	1.29E+05	7.87	27.92	2.26E+03	5.3
9	OLD31	9,1,150C	2.95E-05	-821.8	1.29E+05	7.87	27.92	8.86E+02	13.5
10	OLD2	8,1,150C	1.35E-05	-803.1	1.29E+05	7.87	27.92	1.93E+03	6.2
11	NEW21	7,1,150C	1.15E-05	-788.35	1.29E+05	7.87	27.92	2.26E+03	5.3

Table 4.9Polarization resistanc, R_p and Corrosion rate, CR of AA5052 coated with silane mixture

No	Surface treatment	Contact angle Water (1)	Contact Angle Water (2)	Contact angle Methylene iodide (1)	Contact Angle Methylene iodide (2)	Surface Energy (mJ/m ²)
1	Uncleaned	95.7	95.4	19.7	19.9	42.4
2	Alkaline cleaned	46.8	47.3	30.5	31.0	49.9
3	Acid cleaned	64.1	64.5	8.8	9.0	43.7
4	Alkaline+ acid	66.4	66.3	45.6	45.7	48.4
5	Alkaline + deoxidizer	67	66.9	45.5	45.4	48.0

Table 4.10Contact angle and surface energies of various pretreatment methods

Adhesive composition	pН	Curing Conditions	Conc., %	Bond strength KO6 (N)	Bond strength L75 (N)
1 ml of (Y9400/VTAS = 4:1)	7.0	150 C, 10 min	1	159 ± 8	232 ± 8 (80% rubber retension)
Phenolic adhesive with chromate coating	-	100C, 10min		216 ± 7	241± 12 (100% rubber retension)
Oxilane coating only	-	100 C, 10 min		125 ± 7	201 ± 10 (80% rubber retension)

Table 4.11Bond strength when compared to existing phenolic adhesive

Elements	Atomic concentration of Alkaline cleaned AA 5052 (%)	Atomic concentration of Acid cleaned AA 5052 (%)				
AI 2 _p	22	9.3				
C 1 _s	12.1	53.6				
0 1 _s	60.2	33.3				
F 1 _s	3.3	1.4				
P 2 _P	2.1	0				
Ca 2 _p	0.2	0				
Na 1 _s	0	0.3				
N 1 _s	0	1.7				
CI 2 _p	0	0.4				

Table 4.12Atomic concentration of alkaline and acid cleaned AA5052

Appendix: A

Various silane system tried in this project are listed below along with the bond strength obtained

Sets	No.	Sys	Composition	рН	Conc.%	Bond strength KO6 (N)	Bond strength L75 (N)
	1	A4	AEAPS, 2%	5.0	2	49	
	2	A3	APS / AEAPS (1:1), 3%	5.0	3	59	
	3	A2	A1170/Y9400 (1:1) @ 70 ° C / 6 Min	5.0	3	57	
	4	ΒΤΑΡ	BTSE (5%) / APS (2%) (1:1)	5.0	3	36	
	5	BTAE	BTSE (5%) / AEAPS (2%) (1:1)	5.0	3	61	
	6	A1	Y9400/APS/A1170 (1:1:1), 3 %	5.0	3	108	
	7	A11	A1 cured at room temp	5.0	3	80	
1	8	A12	A1 cured at 70 C	5.0	3	88	Not tested
	9	A13	A1 cured at 100 C	5.0	3	69	
	10	JQ1	(Varying the amount of onium in system J	5.0	3	117	
	11	JQ11	1 gm onium	5.0	3	53	
	12	JQ15	0.5 gm onium in J	5.0	3	47	
	13	JCN1	1gm Cerium Nitrate + 0.5gm onium	5.0	3	48	
	14	JCN2	1gm Cerium Nitrate + 1gm onium	5.0	3	57	

Sets	No.	Sys	Composition	рН	Conc.%	Bond strength KO6 (N)	Bond strength L75 (N)
	15	AQ1	SR610 / Silane J (3:2)	5	5	95	
	16	AQ2	AMPS 2045 / J (3:2)	5	5	89	
	17	AQ3	AMPS 2404 /J (3:2)	5	5	96	
	18	AQ4	Anquamine 401(0.4 gram) / J (2ML)	5	2	94	
	19	AQ5	Y9400/Y9669 (2/1)	3	3	103	
	20	AQ6	Y9669, 1ml	3	1	74	
2	21	AQ7	Aliquat 175 / J (3:2)	5	5	78	
	22	AQ8	Aliquat HTA / Silane J (3:2)	5	5	83	
	23	AQ9	QAFS 1/ silane J (3:2)	5	5	85	
	24	AQ9a	QAFS 2/ silane J (2:3)	5	5	87	
	25	AQ10	QAFS 2 /silane J (3:2)	5	5	83	
	26	AQ11	WBSO 1/ Silane J (3:2)	5	5	95	
	27	AQ12	WBSO 2 / Silane J (3:2)	5	5	84	Not Tested
	28	AY1	AMPS 2405 / Y9969 (2 / 1.5)	3	3.5	56	31
	29	AY2	3 ml (A1170/VTAS = 3:1) + 1ml Bis-UPS +1ml Y9669	5	5	117	240
	30	AY3	Y9969 (2ml)	5	2	110	73
	31	AY4	Aliquat 175 /Y9669 (2:1)	5	3	34	0
	32	AY5	Aliquat HTA1 /Y9669 (2:1)	3	3	62	0
3	33	AY6	Bis-UPS (0.4gm) + 1ml Y9669	3		122	198
5	34	AY7	2 ml (A1170/VTAS = 3:1) +1ml Y9669	5	3	117	222
	35	AY8	4ml (A1170/VTAS = 3:1) +1ml Y9669	5	5	111	212
	36	AY9	SR610 /Y9669 (2:1)	3	3	54	0
	37	AY10	Y9969 (3ml)	5	3	106	0
	38	AY11	Bis-UPS (2ml) + 1ml Y9669	3	3	93	174
	39	AY12	QAFS / Y9669/Surfynol 2502(4:1:0.25)	5	5	89	45

Sets	No	Sys	Composition	рН	Conc.%	Bond Strength KO6 (N)	Bond Strength L75 (N)
	40	5	3 ml of (A1170/VTAS = 2:1) + 2 ml of Bis -UPS	5.0	5	91	182
	41	6	3 ml of (A1170/VTAS = 2:1)	5.0	3	69	74
	42	7	2 ml of (A1170/VTAS = 2:1) + 1 ml of Bis -UPS	5.0	3	92	183
	43	8	2 ml of (A1170/VTAS = 2:1) + 3 ml of Bis -UPS	5.0	5	92	195
	44	9	3 ml of (A1170/VTAS = 2.5:1) + 2 ml of Bis -UPS	5.0	5	66	211
	45	10	3 ml of (A1170/VTAS = 2.5:1)	5.0	3	61	95
	46	11	2 ml of (A1170/VTAS = 2.5:1) + 1 ml of Bis -UPS	5.0	3	83	192
	47	12	2 ml of (A1170/VTAS = 2.5:1) + 3 ml of Bis -UPS	5.0	5	87	225
	48	1	3 ml of (A1170/VTAS = 3:1) + 2 ml of Bis -UPS	5.0	5	72	117
	49	2	3 ml of (A1170/VTAS = 3:1)	5.0	3	93	121
4	50	3	2 ml of (A1170/VTAS = 3:1) + 1 ml of Bis -UPS	5.0	3	75	144
•	51	4	2 ml of (A1170/VTAS = 3:1) + 3 ml of Bis -UPS	5.0	5	78	132
	52	13	3ml of (Y9400/VTAS = 4:1) +2ml of Bis -UPS	5.0	5	83	216
	53	15	3 ml of (Y9400/VTAS = 4:1)	5.0	3	91	185
	54	16	2 ml of (Y9400/VTAS = 4:1) + 1 ml of Bis -UPS	5.0	3	87	226
	55	17	3 ml of (Y9400/VTAS = 5:1)	5.0	3	84	237
		18	2.5 ml of (Y9400/VTAS = 4:1)+ 0.5ml of Bis-UPS	5.0	3		
	56		+ 10 ml silica water			87	225
		20	2.5 ml of (A1170/VTAS = 2.5:1) + 0.5 ml of Bis –	5.0	3		
	57		UPS + 10 ml silica water			83	204
		21	3ml of (Y9400/VTAS = 4:1)+ 1ml of Bis-UPS + 1	5.0	5		
	58		ml of Y9669+ 10 ml silica water			80	234

Sets	Νο	Sys	Composition	рН	Conc.%	Bond Strength KO6 (N)	Bond Strength L75 (N)
	59	1	3 ml of (Y9400/VTAS = 5:1) + 5 ml silica water	5.0	3	130	158
	60	2	3 ml of (Y9400/VTAS = 5:1) + 10 ml silica water	5.0	3	116	117
	61	3	3 ml of (Y9400/VTAS = 5:1) + 15 ml silica water	5.0	3	123	155
	62	4	3 ml of (Y9400/VTAS = 5:1) + 20 ml silica water	5.0	3	122	146
	63	5	3 ml of (Y9400/VTAS = 5:1) + Onium (1.0 gm)	5.0	3	91	157
	64	6	3 ml of (Y9400/VTAS = 5:1) + Onium (1.5 gm)	5.0	3	73	112
	65	7	3 ml of (Y9400/VTAS = 5:1) + Onium (0.5 gm)	5.0	3	108	151
		8	3 ml of (Y9400/VTAS = 5:1) + 1gm Cerium		3		
	66		nitrate	5.0		56	70
		9	3 ml of (Y9400/VTAS = 5:1) + 2gm Cerium		3		
	67		Nitrate	5.0		58	49
5		10	3 ml of (Y9400/VTAS = 5:1) + 10 ml silica		3		
	68		water+1 gram Cerium Nitrate+ 0.5gm Onium	5.0		84	60
	69	11	3 ml of (Y9400/VTAS = 5:1)	8.0	3	129	220
	70	12	3 ml of (Y9400/VTAS = 5:1)	6.0	3	108	146
	71	13	3 ml of (Y9400/VTAS = 5:1)	5.0	3	120	165
	72	14	3 ml of (Y9400/VTAS = 5:1)	4.0	3	110	120
	73	15	3 ml of (Y9400/VTAS = 5:1)	7.0	3	137	198
		16	3 ml of (Y9400/VTAS = 5:1) - Room temperature		3		
	74		curing	5.0		63	160
		17	3 ml of (Y9400/VTAS = 5:1) - 70 C curing for 10		3		
	75		min	5.0		88	109
		13	3 ml of (Y9400/VTAS = 5:1) - 100 C Curing for		3		
	76		10 min	5.0		120	165

Sets	No	Sys	Composition	рН	Conc.%	Bond Strength KO6 (N)	Bond Strength L75 (N)
	77	1	2 ml of (Y9400/A1170 = 1:1) / 1 ml of VTAS	5.0	3	79	214
	78	2	2 ml of (Y9400/A1170 = 2:1) / 1 ml of VTAS	5.0	3	155	125
	79	3	2 ml of (Y9400/A1170/APS = 1:1:1) / 1 ml of VTAS	5.0	3	106	233
	80	5	5 ml of (Y9400/ VTAS=4:1)	5.0	5	131	236
c	81	6	2 ml of (A1170/Bis-UPS = 1:3) / 1 ml of VTAS	5.0	3	101	178
0	82	7	5 ml of (Y9400/Y15626 = 4:1)	5.0	5	128	238
	83	8	2 ml of (Y9400/A1170 = 1:1) / 1 ml of Y15626	5.0	3	95	202
	84	9	2 ml of (Y9400/A1170 = 2:1) / 1 ml of Y15626	5.0	3	78	150
	85	10	2 ml of (Y9400/A1170/APS = 1:1:1) / 1 ml of Y15626	5.0	3	129	102
	86	11	2 ml of (Y9400/Bis-UPS = 1:4) / 1 ml of Y15626	5.0	3	141	221

Sets	No	Sys	Composition	рН	Conc.%	Bond Strength KO6 (N)	Bond Strength L75 (N)
	87	4	2 ml of (Y9400/A1170 = 3:1) / 1 ml of VTAS	5.5	3	125	175
	88	5	5ml of (Y9400/VTAS = 4:1) + Onium (10ml)	5.5	5	88	171
	89	6	3ml of (Y9400/VTAS = 4:1) + Onium (10ml)	5.5	3	65	144
	90	71	5 ml of (Y9400/VTAS = 4:1)	4.0	5	98	157
	91	72	5 ml of (Y9400/VTAS = 4:1)	4.0	5	113	182
	92	8	5 ml of (Y9400/VTAS = 4:1)	5.0	5	83	171
	93	91	5ml of (Y9400/VTAS = 4:1)	6.0	5	116	135
	94	92	5ml of (Y9400/VTAS = 4:1)	6.0	5	104	151
	95	93	5ml of (Y9400/VTAS = 4:1)	6.0	5	119	146
	96	94	5ml of (Y9400/VTAS = 4:1)	6.0	5	105	125
	97	101	5 ml of (Y9400/VTAS = 4:1)	7.0	5	124	181
7	98	102	5 ml of (Y9400/VTAS = 4:1)	7.0	5	127	203
	99	111	3 ml of (Y9400/VTAS = 4:1)	4.0	3	95	166
	100	112	3ml of (Y9400/VTAS = 4:1)	4.0	3	118	138
	101	12	3 ml of (Y9400/VTAS = 4:1)	5.0	3	102	146
	102	131	3 ml of (Y9400/VTAS = 4:1)	6.0	3	130	134
	103	132	3ml of (Y9400/VTAS = 4:1)	6.0	3	78	178
	104	133	3 ml of (Y9400/VTAS = 4:1)	6.0	3	117	169
	105	134	3 ml of (Y9400/VTAS = 4:1)	6.0	3	86	181
	106	141	3 ml of (Y9400/VTAS = 4:1)	7.0	3	117	196
	107	142	3 ml of (Y9400/VTAS = 4:1)	7.0	3	122	183
			(0.5 gm of CN in 50 ml of water) take from this 10		3		
	108	15	ml +3 ml (Y9400/VTAS = 4:1) +87 ml water	6.0		108	178

8	Νο	Sys	Composition	рН	Conc.%	Bond Strength KO6 (N)	Bond Strength L75 (N)
	109	41	2 ml of (Y9400/A1170 = 3:1) / 1 ml of VTAS	5.5	3	90	172
	110	42	2 ml of (Y9400/A1170 = 3:1) / 1 ml of VTAS	5.5	3	81	127
	111	94	5ml of (Y9400/VTAS = 4:1)	6.0	5	95	117
	112	91	5ml of (Y9400/VTAS = 4:1)	6.0	5	87	164
	113	93	5ml of (Y9400/VTAS = 4:1)	6.0	5	98	167
	114	92	5ml of (Y9400/VTAS = 4:1)	6.0	5	70	172
•	115	101	5 ml of (Y9400/VTAS = 4:1)	7.0	5	60	134
	116	102	5 ml of (Y9400/VTAS = 4:1)	7.0	5	95	205
	117	131	3 ml of (Y9400/VTAS = 4:1)	6.0	3	39	130
	118	133	3 ml of (Y9400/VTAS = 4:1)	6.0	3	108	161
	119	134	3 ml of (Y9400/VTAS = 4:1)	6.0	3	69	182
	120	141	3 ml of (Y9400/VTAS = 4:1)	7.0	3	57	125
	121	142	3 ml of (Y9400/VTAS = 4:1)	7.0	3	107	163
	122	Y66	PHENOLIC ADHESIVE			216	242





IR of pure bis-diamino silane (Y9400)



IR of vinyl triacetoxy silane (VTAS)



IR of mixture of bis-diamino & vinyl triacetoxy silane (4:1) before hydrolysis

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LIST OF ABBREVIATIONS

- CRS **Cold-Rolled Steel** CR **Corrosion Rate** di-o-tolyl-guanidine DOTG Energy Dispersive X-ray Analysis EDX Fourier Transform Infrared Spectroscopy FTIR Polyacrylate rubber KO6 L75 VAMAC rubber Reflection Absorption Infrared Spectroscopy RAIR SEM Scanning Electron Microscope Time-of-Flight Secondary Ion Mass Spectrometry TOFSIMS Ethylene acrylic rubber VAMAC
- XPS X-ray Photoelectron Spectroscopy

Aluminum 5052

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