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Effect of Silane in the Rubber-Metal Bonding Agent

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Abstract

In this study, the synthesis, characterization and applications of the adhesive for metal vulcanization of NBR rubber (Nitrile Rubber) were investigated. The effect of silane fillers on adhesive was investigated. The adhesive consists of a mixture of polymers, organic compounds and mineral fillers dissolved or dispersed in an organic solvent system. The metal plate is covered with zinc phosphate to provide surface cleanliness and roughness. Adhesive application was made by applying cover-coat. Adhesive was applied by spraying zinc phosphate coated plate. After vulcanization, the adhesive between the rubber and the metal was examined.

Keywords: Nitrile Rubber, organic compounds, mineral fillers dissolved

1) History of Adhesive

Adhesives for broken pottary	~6000 yearsago
Tar like glue (forivory)	~6000 yearsago
Animal glue (tombs-A egypt)	~3500-3000 yearsago
First reference in literature for making animal glue	~2200 yearsback
Animal glue for wood marquetries, fish glues, egg white to glue gold leaf	~2000-1500
Bows (GenghisKhan)	~1000 yearsago
First factory for animal glue in NL	~1000 yearsago
First glue patent GB-Fish Glue	1750
Adhesives Industrialized from NR, fish, bones, starch, milk protein	After 1750yearsago
Phenolic Resin (after invention of Bakalite)	~1910

2) Rubberto Metal Bonding

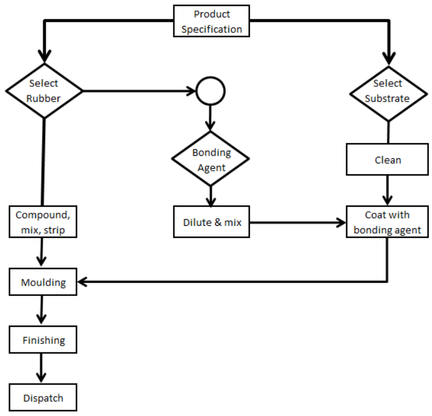
Automotive and industrial manufacturers are increasingly are turning to rubber to metal technology to reduce the raw number of components, eliminate vibration and improve the performance of individual components and subassemblies used in harsh environment applications.

Rubber to metal bonding is a generic phrase that covers several interdependent processes used to manufacture a wide variety of automotive and industrial products used to isolate noise and vibration. Years ago the subject was regarded as a ‘black art’ but today technology allows sophisticated manufacturers to produce high quality, defect-free, uniform rubber to metal components.

The Basic Requirements for a Good Adhesive Bond are;

- Proper choice of adhesive
- Good joint design
- Cleanliness of surfaces
- Wetting of surfaces that are to be bonded together
- Proper adhesive bonding process (solidification and cure)

Application Diagram



3) AdhesiveCharacteristics

General purpose primers and adhesives used for bonding rubber to metal are highly proprietary, specially formulated products. They usually contain a mixture of polymers, resins, curatives, pigments, extenders, and other ingredients, e.g., corrosion inhibitors or viscosity stabilizers. These materials are either dissolved or suspended in a liquid media. Up until the early 1990s, rubbers to metal adhesives were almost exclusively formulated in organic solvents. Due to the need to reduce emissions of volatile organic compounds (VOCs), a growing number of aqueous rubbers to metal adhesives are being commercialized.

Rubber to metal primers contain organic resins which react with most metal (steel, aluminum, stainless steel, copper, brass) surfaces during the vulcanization process to form a chemical bond to the metal. They also contain polymers which allow for better film formation and act as an anchor for the subsequent application of the adhesive.

Rubbers to metal adhesives contain polymeric materials that are compatible with the ingredients in the primer, as well as the rubber compound to be bonded. Many are based on halogenated polymers. Halogenated polymers or resins are known to wet metals efficiently and can be used in both the primer and adhesive formulation. They provide effective barriers to chemicals that can undermine the adhesive bond. The adhesive also contains very powerful curatives that react with both the polymers in the rubber and the polymers in the adhesive. Difunctional and polyfunctional chemicals are capable of making the film forming polymer a thermoset as well as reacting across the interface of the film to link into the rubber.

The rubber to metal bonding mechanism is very complex as there are several reactions occurring simultaneously. All these reactions must take place in a very short period of time (i.e., during the press cure time of the rubber) in order for a strong bond to form.

	Bond length [nm]	**Bond energy [kj/mol]**
Chemical Bond		
Covalent	0,1 – 0,2	150 – 950
Metallic	0,3 – 0,4	100 – 400
Ionic	0,2 – 0,3	400 – 800
Molecularinteractions		
Van der waals forces	0,4 – 0,5	2 – 15
Hydrogen bridges	0,2	20 – 30

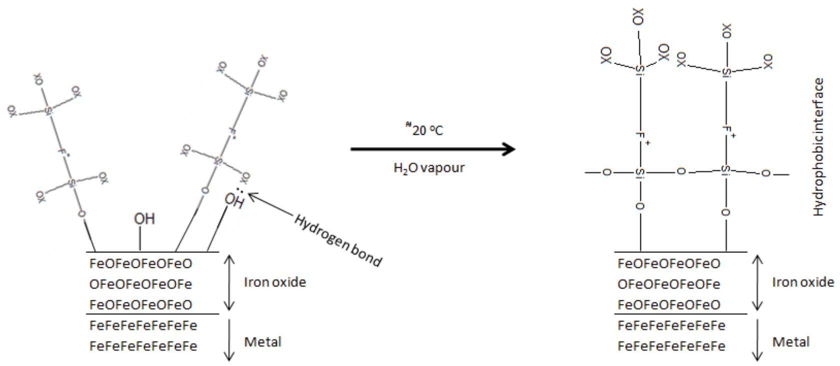
4) Organo functional Silanes in Rubber–Metal Bonding

A new development in rubber-brass bonding appears to be in organo functional silanes. Such molecules are commonly of the type Y-$CH_2CH_2CH_2$-$Si(OX)_3$where Y is an organo functional group and OX is an ethoxy or methoxy group. Such silanes are all stable, colourless liquids. They can be hydrolysed in water or water/alcohol mixtures toyield Y-$CH_2CH_2CH_2$-$Si(OH)_3$.

The silanol groups are active to hydroxyl groups on glass,silica and metal oxides and can form MeOSi bonds of the type:

Me-O-Si-$CH_2CH_2CH_2$Y

The remaining silanol groups in the film can react with each other and form siloxane units:



Since the Me-O-Si bonds are relatively stable, and because the Si-O-Si bonds are highly hydrophobic, the interphase polymer-silane-substrate has become highly resistant to moisture, or in other words, to corrosive attack. The functional group X can be selected from a wide range of available molecules, so that it interacts with functional groups in the polymer. In this way, an extremely stable interface can be obtained that is completely covalently bonded and resistant to water. Such silane technology has been very successful and is widely used in polymer, paint, adhesives and other industries. Van Ooij and others have recently demonstrated that silanes, in addition to acting as coupling agents, can also be used very effectively as corrosion inhibiting metal treatments. In their work the use of so-called bis-silanes of the following types were particularly featured:

$(XO)_3Si\text{-}CH_2CH_2\text{-}Si\text{-}(OX)_3$

$(XO)_3Si\text{-}CH_2CH_2CH_2\text{-}S_X\text{-}CH_2CH_2CH_2\text{-}Si\text{-}(OX)_3$

$(XO)_3Si\text{-}CH_2CH_2CH_2\text{-}NH\text{-}CH_2CH_2CH_2\text{-}Si\text{-}(OX)_3$

OX= methoxyorethoxy

S_X = tetrasulphide (average x = 3.8)

It was demonstrated that such silanes, alone or in combination with the standard single silanes, can prevent corrosion of the metals of stainless steel, carbon steel, zinc, aluminium, brass, aluminium alloys and magnesium alloys from various forms of corrosion, even without paint coating. Adhesion to paint systems and adhesives was also improved. Several silane-based metal pre-treatment systems are now commercially used successfully in metal finishing processes where they replace chromate metal pre-treatments.

5) Bonding-Agent Preparation

Adhesive Formulation-1	
Ingredients	**weight (%)**
Polymer	13,38
Activator	0,53
Accelerator	0,4
Filler (Silane)	2,68
Resin	2,68
Antioxidant	0,13
Sulphur	0,2
Solvent	80

Adhesive Formulation-2	
Ingredients	**weight (%)**
Polymer	13,38
Activator	0,53
Accelerator	0,4
Filler (Carbon Black)	2,68
Resin	2,68
Antioxidant	0,13
Sulphur	0,2
Solvent	80

Method of Manufacture of Adhesive

The traditional method of preparing adhesive solutions is with milled or masticated polymer. This is dissolved in a suitable solvent such as trichloroethylene or hexane, as the case may be, and the resin is added as a separate solution. High-speed shear mixers are used for churning and homogenizing. The main purpose of milling is to break down the gels in the case of synthetics or to reduce the nerve in the case of natural rubber, thereby increasing the smoothness and consistency of the cement. Mill mixing gives improved dispersion leading to resistance to sedimentation in the finished adhesive. During mixing the temperature should be maintained as low as possible, say at 50°C, to avoid scorching.

The milled sheet is cut into pieces and then dissolved in solvent in the mixer. With all the equipment used for preparing the cements, care should be taken while using flammable solvents and the problems of static electrical discharge. With the advent of high-speed and high-shear rate cement mixers such as the Zigma-type solution mixers with a series of rotating paddles, production of adhesives by direct dissolving techniques has become very popular.

Adhesives made from milled rubber versus unmilled rubber will show the following properties:

Much lower viscosity

Less tendency to sediment

Better brushability

Better penetration of the adhesive into the substrate

6) Metal SurfacePreparation

Surface Treatment Purpose

- Increase adhesive adhesion
- To increase corrosion resistance

Surface Finishing

- Cleaning and activating the metal surface
- Layer formation on metal surface

- Final passivation

Zinc Phosphate Process

1. Degreasing
2. Rinse
3. Activation
4. Zincphosphating
5. Rinse
6. Passivation
7. DI Rinse

Surface Reactions:

Etching Reaction : $Fe^0 + 2H^+ \rightarrow Fe^{2+} + 2[H^0]$

Depolarization: $2[H^0] + [O] \rightarrow H_2O$

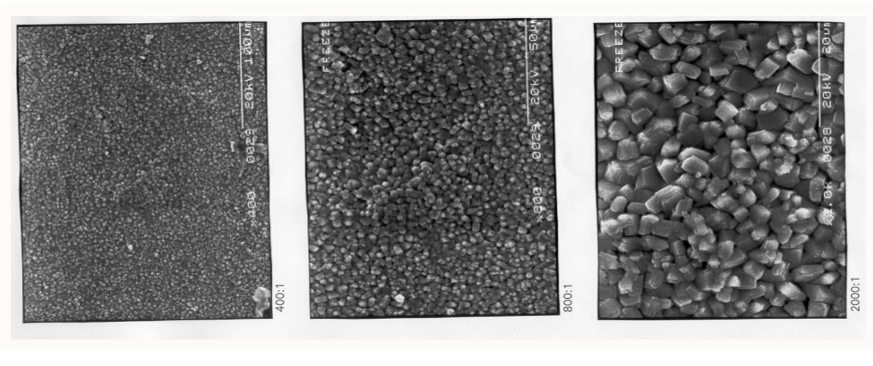
Coating Occurrence:

$3Zn^{2+} + 6H_2PO_4^- + 4H_2O \rightarrow \underline{Zn_3(PO_4)_2 x\ 4H_2O} + 4H_3PO_4$

Hopeite

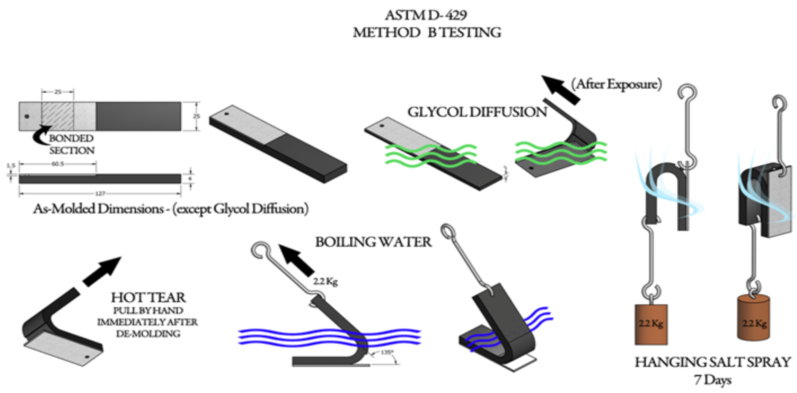
$2Zn^{2+} + Fe^{2+} + 6H_2PO_4^- + 4H_2O \rightarrow \underline{Zn_2Fe(PO_4)_2 x\ 4H_2O} + 4H_3PO_4$

Phosphophyllite



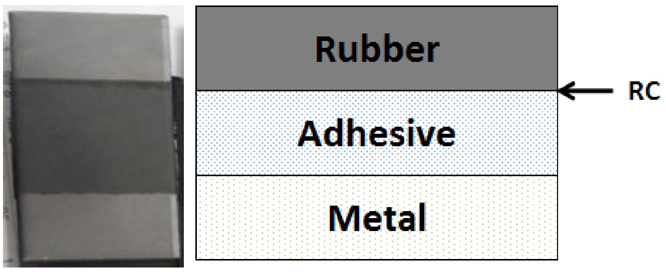
ZincPhosphateCoatingCrystalStructure(ScanningElectronMicroscope)

Test MethodsForAdhesion



Rubber-to-Cement (RC) Failure

- Designated as RC, cement = adhesive
- Failure occurs between rubber and adhesive
- Look for evidence of adhesive adhering to substrate, but not to rubber surface
- 50+% occurrence in industry



7) Results

The rubber-metal bonding material prepared with Silane Filler provided better adhesion than Carbon Black.

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Ingredients	**weight (%)**
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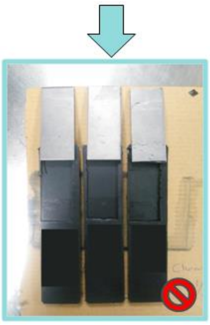

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