ELASTOMERIC BRIDGE BEARINGS: OZONE PROTECTION, LEACHATE ANALYSIS AND A NATIONAL SURVEY ON MOVEMENT

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This Thesis is dedicated to my parents, sisters and friends
who have helped me believe I could do all I have done.

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ABSTRACT

ELASTOMERIC BRIDGE BEARINGS:
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Elastomeric bearing pads have been used extensively in bridges for the last forty years. Recent problems in the state of Texas with excessive movement of these pads have lead to an investigation of the probable causes. The problem appears to be caused by walking of the pads, a phenomena explained as significant overall bearing pad movement in one direction caused by the accumulation of small movements during shear cycling. One factor found to be conducive to movement was the build up of wax on the bearing surface. The wax, used as ozone protection in vulnerable elastomers, can migrate to the surface of the rubber in large quantities and produce a slick contact surface. Studies not only question the validity of using wax as an antiozonate but also the necessity of the stringent ozone-resistance test required by current codes. This study shows that bearing pad leachate is composed predominately of wax and that use of excessive amounts of wax may be common in bearing pad elastomers. A national survey wasc conducted and indicates that bearing pad movement was experienced by 63% of the states not frequently fixing the movement of their bearing pads. No conclusions could be drawn from the Texas districts survey or the national survey regarding the contribution of natural rubber and tapered bearings to slipping problems.

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CHAPTER 1

INTRODUCTION

1.1 Texas Department of Transportation Project 1304

This study is part of a larger research project at the University of Texas at Austin sponsored by the Texas Department of Transportation (TxDOT), Project No. 1304, "Elastomeric Bearings". The project is intended to study the behavior and performance of elastomeric bridge bearings and to recommend practical design procedures for the TxDOT. The research project was divided into five main phases: field surveys, basic material tests, development of engineering models, development of design procedures, and a study of bearing pad slip. This report focuses on the fifth task, documenting the problem of bearing pad slip around the country and studying the leachate which may be facilitating this movement.

1.2 Problem History

Movement of bridge bearing pads has recently (1992) become a concern in the state of Texas. Slipping – rigid body motion of the bearing pad as opposed to shearing of the elastomer to accommodate bridge movement – has caused some bearing pads to move from their original position. Walking – the phenomena explained as significant bearing pad movement in one direction caused by the accumulation of small movements during shear cycling – has caused some bearing pads to slip completely out from under the girders. An example of the excessive movement caused by walking is shown in Figures 1.1 and 1.2. Because most bearing pads are not physically restrained in the state of Texas, only friction created between the pad and the bridge keeps the pad from moving. It has been the impression of several sources that the cause of slipping may be a film of wax-like material which appears on the surface of the bearing seat and the concrete girders and on the pads that have walked out. The wax layer reduces the coefficient of friction at the contact points between the bridge and the bearing, decreasing the force necessary to induce sliding of the bearing.

TxDOT requires that bearing pads be designed according to the AASHTO specifications which state that no connection is necessary between and bridge and pad if the shear force on the bearing is less than one-fifth the dead load force. The specifications require a physical connection to "secure against horizontal movement" only if the shear force is larger than one-fifth the dead load. Most bridges in Texas are concrete and hence have a large dead load to shear force ratio. So, according to the AASHTO specifications, most pads in use in Texas can be held in place by the friction created by the structure's dead weight. The movement of the bearings indicates that the coefficient of friction assumed by AASHTO was not that which was expected, perhaps due to the wax-like layer observed on the bearing seats and girders.

Many states regularly connect all their pads regardless of the dead load to shear force ratio. Various methods used for connecting the pad are practiced: inserting a dowel which attaches to the girder and/or bearing seat, epoxying the pad to the abutment, vulcanizing the pad to steel shims which are then bolted (or welded) to the girder or bearing seat or steel shims inserted in either the pier cap or the girder.

Figure 1.1 - Bearing Pad Which Has Walked from Under a Texas Bridge

Figure 1.2 - Position of the Same Bearing from Another Angle

Excessive movement caused by walking of the elastomeric bearing pads has required that some bridges be raised while the bearing pads are placed back in their proper locations. This process is costly and inconvenient as it requires the closing of a roadway. Sliding is also undesirable as abrasion caused by sliding will limit the lifetime of the bearing and may require the bearing to be replaced [28].

1.3 Contents of the Study

The first part of this study discusses elastomers, ozone protectants and the migration of protectants to the surface of rubber products. A basic discussion of the polymers of natural rubber and polychloroprene (i.e. Neoprene) and of the compounds used to resist degradation is contained in *Chapter 2*. A more in-depth analysis of the chemical and physical action of antiozonates and protective waxes is contained in *Chapter 3*.

The study then looks at bearing pads from two central Texas bridges that have encountered excessive bearing pad movement and identifies the composition of the leachate on the surface of these bearing pads that could be facilitating slip. The infrared spectrometer analysis of the leachate is found in *Chapter 4*. Third, measurements of the growth of leachate layers on typical bearing pads is discussed in *Chapter 5*. The layer thicknesses are compared to layer thicknesses suggested to provide adequate ozone protection.

Finally, two surveys were conducted documenting bearing pad slip in Texas and around the U.S. A district survey was conducted in Texas to determine the actual extent of the problem in the state. The questionnaire is located in Appendix One. In addition, a nationwide survey was conducted in two phases. First a letter was sent through the mail and later a series of follow up questions were asked over the phone. The questionnaire sent in the mail and the questions used for verbal responses are shown in Appendix Two. *Chapter 6* shows the results of there two surveys. The conclusion of this study are found in *Chapter 7*.

1.4 The Use of Elastomeric Bearings Pads

The oldest known example of bearing pads used in a bridge were 1/2 inch natural rubber pads installed in 1889 under a railway bridge in Melbourne, Australia [10]. These pads, designed to allow rotation and absorb impact in bridges and other structures, have lasted for over 100 years. Made from a natural rubber compound that included no antidegradants, they were found to have experienced only minor degradation when inspected in the mid 1980's.

Elastomeric bearing pads only came into widespread acceptance in the 1950s when the first steel-laminated bearing was used to accommodate the movement of bridge decks. Before then, roller bearings and sliding plates were mainly used, both requiring constant maintenance to continue performing satisfactorily [10]. Today, elastomeric bearing pads are widely used around the world and in most states in the U.S. under concrete superstructures and, thought not as commonly, under steel superstructures. Most pads are designed to allow relative movement between girder and substructure and/or to allow rotation of the bridge superstructure due to concrete shrinkage, prestressing creep and change in camber.

Bridge bearings today are designed to allow movement of the bridge superstructure and supports while generating minimum forces in the structure. Movement is caused by the expansion and contraction due to changes in temperature and the rotation caused by bending under traffic loads. The bearings must also transfer live impact loads to the bridge support in a smooth and controlled manner. Long term movement is caused by concrete shrinkage and prestressing creep. High vertical stiffness of the elastomeric pad, prevents excessive changes in roadway level under traffic loading and low horizontal stiffness of the elastomer minimizes the forces applied to the supports [15].

1.5 The History of Natural Rubber and Neoprene in Bearing Pads

The very first bearing pads that we know of are from the Australian railroad bridge mentioned on the previous page; these pads, still in use today, are made from natural rubber (NR). Vulcanized natural rubber has been available since the late 1800s, decades before the first synthetic rubbers (SR) were introduced in 1910 [17]. These bearing pads and other rubber products have shown that NR possesses the characteristics necessary to perform adequately as a bearing pad and to compete with synthetic rubbers.

Natural rubber has demonstrated the required longevity and durability by providing adequate load-bearing capacity, creep resistance, and environmental and aging resistance. The aging resistance of NR is not as good as that of today's synthetic rubbers but degradation due to heat, ozone and oxygen attack can be prevented by the incorporation of protective compounds [10]. In 1881, wax was first added to natural rubber to retard deterioration in rubber products [2]. While waxes cannot protect against light and heat degradation [17], most bearings are not exposed to either of these. Waxes used in rubber protect against oxygen and ozone attack by forming an impermeable layer on the elastomeric product's surface. Today, chemical antidegradants are available to improve the resistance of rubber to environmental attack.

Polychloroprene (CR) was the world's first commercial synthetic rubber. It was introduced by Dupont in 1932 as an oil resistant rubber called Duprene and was renamed Neoprene in 1936 [30]. Later testing found that in addition to its oil-resistance, Neoprene was also highly resistant to oxidative aging and flex cracking, and was almost completely ozone-resistant.

The first AASHTO specification that addressed bearing pads was the 8th edition in 1961; it specified that only Neoprene could be used in bearing pad construction. Over a decade later, in 1973, the 11th Edition of the AASHTO specifications included natural rubber as an alternative material. It was around this time that many new chemical antidegradants came out from development and began to be used widely. Since then, the AASHTO specifications have allowed "either virgin Neoprene (polychloroprene) or virgin natural rubber (polyisoprene)."

While there are over a dozen types of rubber on the market today to choose from and polychloroprene is certainly not the cheapest rubber available with the necessary characteristics, convention has chosen polychloroprene for use in bearing pad manufacture. Natural rubber has shown the necessary characteristics to perform adequately if compounded properly and at it's current price it is the cheapest rubber available but its price is unstable and varies with the market's demands. Currently it is about half the price per volume of polychloroprene but requires the addition of expensive chemical antidegradants. One manufacturer estimated that currently it costs 25% less to manufacture a laminated bearing with natural rubber instead of Neoprene.

1.6 The Problem of Ozone Attack

Corrosive processes can play a major part in the long term deterioration of rubber; the most common corrosive processes are attack by ozone and oxygen in the atmosphere [18]. In thin walled products, failure can occur as a result of crack growth induced by ozone and oxygen attack. In bulkier products, ozone and oxygen degrades the surface of the product causing unsightly crazing and deterioration of the strength of the surface layer.

Ozone (O_3) composes 90% of the pollutants called oxidants in our atmosphere [24]. Around sea level, ozone is produced by the combustion of fossil fuels and by a number of manufacturing processes [16]. At high pressure and temperature, nitrogen combines with atomic oxygen in internal combustion engines forming NO. Light induces the nitrous oxide to combine with O_2 to form NO_2 and atomic oxygen. Finally NO_2 absorbs 392 nm light to form NO and O. The free oxygen atoms created then combine with O_2 molecules to form ozone (O_3). [24]

Elastomers whose molecular backbone chains contain carbon-carbon double bonds – natural rubber and most synthetics in wide use – are vulnerable to ozone attack [18]. Ozonolysis, the reaction of ozone with these olefinic double bonds, causes the scission of these bonds [31]. Minute concentrations of ozone can cause cracking within a few weeks if rubber is unprotected and a minimum tensile strain occurs [13]. The critical extension in NR for cracking to occur (regardless of ozone concentration) is less than 10% extension. When exposed to weather conditions in an extended mode, vulcanizates with double bonds crack perpendicular to the direction of applied stress. With increased extension, the number of cracks formed per unit area and time increases rapidly.

But rubber products are easily protected from ozone attack. Ozone protection is provided by petroleum waxes, flexible coatings, chemical antiozonants and blending with ozone-inert rubbers [25] and will be discussed further in *Chapter Three*.

CHAPTER 2

ELASTOMER BACKGROUND

2.1 Rubber

The American Society of Testing Materials defines rubber by its characteristic attributes, stating that rubber is a "natural or synthetic material that can be or is already vulcanized to a state in which it has high extensibility and forcible, quick retraction." [12] But a description of rubber chemistry is also essential. Rubber belongs to a class of substances termed “polymers”. Polymers are high molecular weight compounds, usually organic, made from low molecular weight building units called monomers. A rubber polymer chain may contain 1,000 to 20,000 repeating units of the monomer. Natural rubber (polyisoprene) is a homopolymer - meaning it consists of one type of monomer - of the hydrocarbon isoprene, C_5H_8. Neoprene (polychloroprene) is a polymer of chloroprene, a hydrocarbon containing chlorine [4].

In raw natural rubber, the monomers are already connected into polymer chains. The liquid latex derived from the rubber trees is coagulated using a number of processing options, most often acidification, and the solidified rubber is shipped in sheets to the compounding location. Synthetic rubber begins as individual monomer units which require polymerization before compounding. In polymerization, the double or triple bond between two carbon atoms is broken up using a catalyst under appropriate conditions. With the bond broken, the onomeric unit is chemically active and can unite with other units to form the polymer chain [4]. After the polymerized rubber, either natural or synthetic, is received by the rubber manufacturer, it is compounded with other ingredients, processed and then vulcanized (treated with heat) to be transformed into a crosslinked rubber, also known as elastomer.

An elastomer is a loosely crosslinked network structure that is neither a plastomer (a thermoplastic; a polymer with no crosslinking) nor a duromer (a thermoelast or ebonite; a polymer with a tightly crosslinked network structure). See Figure 2.1. An elastomer is a relatively soft, elastic material exhibiting viscoelastic behavior above a glass transition temperature T_g. As temperature decreases, and the elastomer reaches T_g, the elastomer stiffens. Because the links in the polymer chain can rotate freely, the material is able to flow and distort under stress as much as the crosslinking allows. The three dimensional structure of the elastomer restricts mobility of the molecule, reducing the tendency to crystallize, improving the elasticity, and maintaining a constant modulus and hardness over a wide temperature range.

Figure 2.1 - Plastomer (a), Elastomer (b) and Duromer (c)

NOTE: Hereafter, rubber will only be used to denote elastomer.

2.1.1 Compounding, Processing, and Vulcanization

Rubber is manufactured by taking the polymerized rubber and compounding it with other ingredients, processing (mixing) it and vulcanizing it to achieve a particular form, stiffness and strength.

COMPOUNDING

During compounding, various agents are added to the rubber to improve it's strength, hardness, age resistance, and to aid in crosslinking during vulcanization. Compounding incorporates ingredients to create the desired properties in the final product and to increase processability, all with an eye towards keeping the production price low [30]. The most important agents are listed below along with their use.

Crosslinking Agents: Used to crosslink the long polymer chains. Sulfur, peroxide or urethane are common crosslinking agents.

Accelerators: Used to control crosslinking density. Metal oxides like ZnO are needed to develop the full potential of accelerators. Accelerators are used at around 0.2 to 1.0 phr [parts per hundred of rubber hydrocarbon]. Some accelerator systems require activators like fatty acids, salts of fatty acids (stearic acid), zinc soaps, or amine stearates.

Vulcanization Inhibitors: Used to increase the cure time, delaying the onset of cure to prevent scorching of the elastomer in bulkier products [17].

Plasticizers, Softeners, Processing Aids: Used to decrease rubber viscosity and toughness, to allow greater processability by reducing stickiness and aiding is filler dispersion, and to reduce the cost of compounding. Stearic acid, paraffinic oil, zinc and calcium soaps, and residues of fatty alcohols are some common processing aids [17]. Mineral oils (parrafinic and aromatic) and naphthenic oils of relatively low molecular weight are good softeners. They are easily incorporated in the rubber but are relatively volatile during heat aging, cause bloom at high loadings [17]. Aromatic oils cost less, can be used in high concentrations and reduce the tendency of compounds and vulcanizates to crystallize, but they provide less favorable vulcanizate properties at low loadings. Paraffinic oils serve only as processing aids - to keep compounds from sticking to the mills [17].

Reinforcing Fillers: Used to increase the strength and modulus of the elastomer. Carbon black is the most common reinforcing filler whose small particles impart to the rubber higher modulus and strength, and greater abrasion resistance. Other fillers include fibrous materials like flock, asbestos, and wood flour which harden, toughen, and cheapen the elastomer [30].

Antidegradants: Used to impart resistance against all types of degradation: high heat, dynamic fatigue, oil and liquid ingress, and oxygen and ozone attack. Waxes, when they bloom to the surface, provide protection against light and ozone attack. Aromatic amines, such as p-phenylene diamine derivatives, provide protection against all types of degradation [30].

PROCESSING

Processing the rubber requires first masticating it to the required consistency and then physical mixing the rubber with the compounding ingredients. During mastication, the rubber is worked on a mill by mechanically shearing the material and breaking the polymer chains, reducing the entanglement of the chains. This makes the rubber less tough when mixing begins. Mixing is performed at elevated temperatures on either mixing mills or internal mixers. During mixing, compounding ingredients are added to the elastomer readying it for vulcanization.

VULCANIZATION

Vulcanization produces crosslinking between the long, tangled polymer chains that restrict the chain’s freedom and give the rubber stiffness, strength, and a particular form [30]. By applying pressure and heat to the rubber in a mold, the chemical agents added help the crosslinks to form. The crosslinks created during vulcanization are as strong as the links in the polymer chain

2.1.2 Natural Rubber

Natural rubber is the most widely used type of rubber in the U.S. and in the world. It comprised 24.0% of the 3,658,000 metric tons of rubber used in production in North America in 1990 and is expected to comprise 24.4% of the total rubber used in 1996 [40]. The price of natural rubber fluctuates dramatically as it depends on the world market. One rubber manufacturer estimated that in the past five years, compounded natural rubber (containing antidegradation additives) has been cheaper than special use rubbers like chloroprene by 10% to 50%.

Natural rubber is cis-1,4-polyisoprene, a linear long-chain polymer with repeating isoprenic units (C_5H_8) having a density of 0.93 at 20°C [4]. Because even after vulcanization natural rubber has double bonds in the polymer chain (meaning it is an unsaturated polymer), it is susceptible to ozone attack and cracking when strained past it's threshold strain [17]. Unprotected natural rubber held in simple uninterrupted extension exhibits threshold strains within the 1% to 7% range, depending upon several factors including the vulcanizate stiffness and the surface finish [28]. Unsaturated polymers are protected by the incorporation of paraffin and microcrystalline waxes, and chemical antioxidants and antiozonates, typically p-phenylenediamines [13,17,30].

Natural rubber has the advantage over polychloroprene in that natural rubber has been shown to be less prone to long-term stiffening; some polychloroprenes have been found to stiffen significantly in periods of around ten years. In addition, natural rubber stiffens less at lower winter temperatures [10].

2.1.3 Polychloroprene Rubber

In 1990, polychloroprene comprised 2.1% of the total rubber consumed in North America; in 1996 it is expected to be only 1.9% of the total rubber used [40]. Though polychloroprene (commonly called by its brand name Neoprene) rubber is the oldest synthetic rubber, several general use synthetic rubbers have passed it in world-wide usage, namely solid styrene-butadiene rubber and carboxylated styrene-butadiene rubber [40]. Polychloroprene is more expensive than most synthetic rubbers because it belongs to the class of special use rubbers containing better resistive properties than general use rubbers. It also has a higher density than almost all other elastomers making its cost per volume significantly higher; but the price of polychloroprene is very stable [4, 30].

Neoprene was introduced by the DuPont company as a synthetic rubber with good resistance to oil, ozone and weathering. It is composed mostly of *trans*-1,4-chloro-2-butenylene units and about 10% *cis*-1,4 addition and has a density of 1.24 at room temperature [4].

Polychloroprene has a high tensile strength like NR but is much more ozone resistant [30]. Polychloroprene has superior weatherability, heat resistance, flame resistance, and adhesion to polar substrates (e.g. metals) and is less permeable to air and water vapor than other general-purpose elastomers. Only nitrile rubbers have better oil resistance and only ethylene propylene terpolymer has better ozone resistance [4]. As mentioned on the previous page, at low temperatures and with time, polychloroprene crystallizes and stiffens much more than natural rubber [13].

2.2 Degradation of Rubber

Many agents in the environment cause damage to rubber. In addition, many rubbers are used in applications that require exposure to high heat, abrasion, dynamic fatigue (flexing) and potentially harmful chemicals. Degradation by ozone, oxygen, heat, light and other causes can discolor the rubber and, more importantly, cause cracking. Cracks detract from the appearance, serviceability, and strength of the rubber product and may lead to its early failure [6].

Both natural and synthetic rubber require age resisters for best performance [4]. An 'age resister' or antidegradant is a material added to prolong the life of a rubber product. Because natural rubber and some synthetic rubbers are highly unsaturated and therefore susceptible to attack, they are particularly dependent on protective agents to increase their aging resistance. Protection against oxygen and ozone attack as well as heat and light damage are conferred by antioxidants, antiozonates, ultraviolet light protectors and waxes. Damage to rubber by abrasion is combated by the incorporation of fillers like carbon black. For protection against dynamic fatigue, chemicals classified as anti-flexing, anti-cracking antioxidants can be used.

To protect the rubber, age resisting chemicals in the elastomer often rely on blooming, the migration of compounding ingredients from the bulk of the rubber to its surface, [28]. Coatings and veneers can also be used; they can withstand some flexing and are not temperature sensitive but cannot be repaired if broken [28].

2.3 Ozone Attack of Rubber

2.3.1 Unsaturated Versus Saturated Rubbers

Rubbers with main chain unsaturation, meaning rubbers containing double or triple bonds in the main chain, are susceptible to ozone attack. In fact it is the percentage of vulnerable bonds and the tendency of the polymer to unite with other compounds, also referred to as the "degree of unsaturation" of a polymer, that is the most important factor determining a polymer's susceptibility to attack; the reactivity of the carbon-carbon double bond varies depending upon the chemical structure of particular rubber [25]. Natural rubber, polyisoprene, polybutadiene and the copolymers of butadiene and styrene and all unsaturated rubbers.

Ozone reacts quickly with the carbon-carbon double bonds in unsaturated rubbers causing direct cleavage of the bond, resulting in the scission of the main polymer chain [28]. Ozone concentrations as low as 1 pphm can begin to cause deterioration in the rubber material[4]. Atmospheric ozone levels are usually around a couple parts per hundred million.

Totally saturated elastomers, such as polychloroprene, contain no double or triple bonds in the main chain. They show inherent stability though saturated rubbers sometimes also need the benefit of extra protection. Resistance shown by polychloroprene is attributed to double bond stabilization by the Chlorine atom [21]. Best resistance is found in fully saturated elastomers such as ethylene-propylene copolymers [13].

2.3.2 Stressed Versus Unstressed Rubbers

Ozone attack creates either frosting or cracking in the rubber. In unstretched rubber, ozone degradation is confined to a thin surface layer, typically 0.5 microns thick, creating ***frosting***, a white bloom-like appearance of the rubber [21]. Ozone attack is less apparent in unstretched rubber since frosting is restricted to a very slow uniform erosion of the surface with no visible cracks [13]. Rubber under tensile strain is susceptible to ozone ***cracking***, a phenomena which is much more serious and visible than frosting [25]. Ozone cracks develop at right angles to the tensile strain [30]. Ozone cracks are not simply unsightly; scission of the main chain degrades rubber strength and the cracks may initiate fatigue crack growth which ultimately can lead to failure of the rubber product [13].

2.3.3 Ozonolysis

Initial attack by ozone occurs in both stressed and unstressed rubber [16]. Ozone attacks the carbon-carbon double bonds of unsaturated rubbers. It bridges the double bond with both ends of the ozone molecule [a nucleophilic attack] to form a cyclic ozonide called a molozonide. See Stage 1 of Figure 2.2. This molozonide is unstable and breaks down (dissociating by heterolytic cleavage of the oxygen-oxygen bond) into a zwitterion and a carbonyl group (either an aldehyde or a ketone) [4]. See Stage 2 and Stage 3 of Figure 2.2. In the absence of stress, further combination of the two species occurs in a cage reaction to give a stable iso-ozonide. But in the stressed condition, this reaction cannot occur due to separation of the chain end and the zwitterion must react with another zwitterion or a carbonyl compound located elsewhere in the rubber which leads to a weakening of the rubber structure and initiates crack formation [16].

By recombination, one of four products can be formed [4]. The first possibility is a relatively stable ozonide (usually developed in the unstressed rubber). See Product 1 in Figure 2.2. The second is a polymeric peroxide formed from the carbonyl oxide. See Product 2 in Figure 2.2. The third possibility is a hydroperoxide. See Product 3 in Figure 2.2. The fourth is a readdition of an oxygen molecule. See Product 4 in Figure 2.2.

Unless the rubber is stretched, the ozone is unable to penetrate any appreciable distance into the rubber [13]. In stressed rubber, as the products form, the stretched rubber chains that have broken retreat from the crack and fresh rubber chains become exposed, allowing the ozone to attack the newly exposed unsaturation. Thus ozone penetrates more deeply into stressed rubber causing the rubber under stress to experience more extensive degradation than unstressed rubber[4].

Figure 2.2 - Ozonolysis of unsaturated rubbers

2.3.4 Initiation of Ozone Cracks at Naturally Occurring Flaws

Cracks initiate at naturally occurring flaws or inhomogeneities in the rubber surface when the rubber is in tension [19]. At these flaws, stress concentrations develop in the surface of the rubber which, degraded by ozone scission of the polymer chains, has lost much of its strength. A crack then forms in the weakened rubber perpendicular to the applied tensile strain [18]. As strain increases, cracks will grow from smaller flaws and the size of the individual cracks will decrease due to interference from adjacent cracks [25].

2.3.5 Tearing Energy and Threshold Strain Required for Crack Initiation

In rubber under static or semi-static tensile strain conditions, the most important characteristic parameter governing ozone crack growth is the tearing energy [21]. A minimum tearing energy occurring at a certain "threshold strain" must be introduced. Once this threshold strain is exceeded, many factors effect the rate of crack growth; most important is the ozone concentration [21].

The onset of the growth of an ozone crack is characterized by a small but finite energy requirement. This "tearing energy" is usually characterized as a surface energy requirement, though some believe it may quite simply be a measure of the strength of the ozone-degraded material [25]. This tearing energy is produced when the rubber is subjected to a strain higher than a rubber's "threshold" strain. Threshold strain is the highest strain at which a vulcanizate can be exposed to ozone for a relatively indefinite periods of time without ozone cracks developing [19].

In natural rubber and other unprotected unsaturated vulcanizates in simple extension, the threshold strain is 3%-5% [10,18,25,28]. In saturated rubbers such as ethylene-propylene copolymers and terpolymers, polyurethanes and chlorobutyl rubber, breaking strains are much higher, between 120% and 190% [28]. Polychloroprene, like other saturated rubbers, is inherently resistant to ozone attack though some tests have found that it can crack at elongations as low as 18% [10]. Though it possess a carbon-carbon double bond, polychloroprene has an electron-withdrawing chlorine atom on the 1,4-*trans* double bond which decreases the nucleophilic tendency of the olefin (C=C bond), deactivating the double bond toward attack by oxygen and ozone [4,13].

The tearing energy required is believed to be the energy required to separate the chain ends after ozone has caused direct cleavage of the carbon-carbon double bonds in the main polymer chains [13]. After tensile forces separate the main chains of the damaged rubber, the ozone is free to attack underlying polymer layers. Cracks, once formed, leave a preferential site at their tips for attack and propagation of the crack continues [18]. An open crack allows a much more direct route for the ozone to reach the interior rubber as compared to diffusion through the rubber. As crack length increases, growth decreases because the ozone must travel farther from the exterior surface of the rubber product to the crack tip [25].

2.3.6 Factors Influencing Crack Growth

The type of strain being applied to the rubber product is very important. Because cracks will only occur in regions where tensile stresses are induced, they are unable to penetrate very far into objects under compression where tensile forces only occur at the surface of the product. In objects mainly under compression or shear, growth ceases close to the surface because the cracks quickly encounter compressive rather than tensile stresses [13].

Studies disagree as to whether the amount of strain influences the rate of crack growth on a surface, although the majority of researchers seem to agree that crack growth increases at higher strains [13,21,25]. It is certain, however, that with an increase in strain, crack density increases [13]. The increase in crack density can be understood in terms of a distribution of surface flaws, with the threshold energy being attained at progressively smaller flaws as the strain increases [13].

Crack growth is time-dependent and, most importantly, occurs at a rate proportional to the ozone concentration. The speed of ozone crack formation also depends on temperature and humidity of the air [17]. The degree of crosslinking influences the rate of crack growth: growth varies inversely with crosslink density [8,18]. Above the rubber's threshold strain, ozone cracking is limited primarily by the ozone concentration and presence of an antiozonate [13].

2.3.7 Mitigating Ozone Attack and Crack Growth Rate

Ozone degradation and cracking can be combated in numerous ways. First, restricting the tensile strain on the product's exposed surface can prevent or limit ozone attack. Second, improving the surface finish so that severe flaws or other stress raisers are not present can reduce the energy available for crack growth [8].

Third, the rate of crack growth can be reduced by increasing the degree of crosslinking [8]. But since the stiffness of the vulcanizate determines the amount of stored energy at a particular strain, stiffer vulcanizates will have lower critical strains [14]. Finally, the incorporation of antiozonates and wax will raise the threshold strain significantly, as shown in *Chapter Three*.

CHAPTER 3

WAX AND OZONE DEGRADATION RESEARCH

3.1 The Protective Action of Chemical Antiozonates

Cracking occurs when rubber is stressed in the presence of ozone. The cracks, oriented perpendicular to the applied tensile stress, form quickly and may cause loss of strength, excessive permeability, tearing, general degradation or even failure of the rubber product [14]. Chemical antiozonates greatly reduce the damage produced by ozone by both decreasing the rate of crack growth and increasing the critical strain necessary for cracking to occur [22]. To be successful, ozone protection systems must raise the threshold strain above the highest extension experienced by the product during its service lifetime [28]. The exact mechanisms by which these chemicals prevent cracking is not exactly known though it is believed that antiozonates may prevent chain scission even while allowing ozone to interact with the double bonds.

Chemical antiozonates improve ozone resistance by either raising the threshold strain (the characteristic elongation that must be exceeded before cracks can be initiated) or by reducing the rate at which individual cracks grow thereby extending the time needed to reach a given severity of cracking [18,22,28]. When a chemical antiozonate is present, a second threshold strain may be exhibited above which no cracking occurs [19]. It has been found that chemical antiozonates can effectively raise the threshold tearing energy by factors of ten or more [13].

3.1.1 Proposed Protection Mechanisms

It has been proposed that antiozonates react in four possible ways to protect rubber from ozone attack:

1) A scavenging mechanism occurs wherein the antiozonate reacts directly with ozone, "scavenging" the ozone before it attacks the rubber [21]. The reaction yields an inactive product [8].
2) The antiozonate reacts with the ozone to form a stress-free protective film of ozonized antiozonate which prevents the ozone from reaching the rubber surface [21,23]. Formation of a stable layer will confer protection subsequently if the layer is not disturbed [8].
3) The antiozonate reacts with the zwitterion or the ozonized rubber to form a stress-free, low molecular mass film capable of repair upon rupture [21].
4) The antiozonate reacts with the ozonized rubber in such a way as to prevent chain scission or to couple broken chains terminated by active groups such as aldehydes to create polymeric compounds [21]. Severed chains are relinked in this way when the antiozonate becomes attached to the rubber network [23]. This protective action is restricted to amines such as *p*-phenylenediamines.

The first theory, a simple ozone-scavenging mechanism, does not appear to be an important mechanism according to the results of experiments [8,22]. More reactive chemicals were used in place of antiozonates and were found to have no protective action; therefore the antiozonates must not consume a significant enough quantity of ozone to deplete the ozone and confer protection to the rubber [8]. In addition, scavenging cannot account for the enhancement in thresholds strain since protection remains as the flux of unreacted antiozonate to the surface decreases [28]. The three other theories proposed have not been disproved and thus are considered possible mechanisms [21].

3.1.2 *p*-Phenylenediamine Derivatives

The best antiozonates today are *N*,*N'*-disubstituted *p*-phenylenediamines (PPDAs), most commonly *N*,*N'*-dialkyl, *N*-alkyl-*N'*-phenyl and *N*,*N'*-diaryl substituted *p*-phenylenediamines [4,28]. One strong antiozonate provided by several suppliers is *N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine [4]. These aromatic amines protect against oxidative degradation, ozone and heat degradation and dynamic fatigue. The *p*-phenylenediamine derivatives slightly reduce the rate of growth of ozone cracks and greatly increase the critical strain (increasing the critical energy necessary to form ozone cracks). By causing crack formation to start at higher extension, they confer a high level of protection to natural rubber and other vulcanizates [14,17].

Three reactions characteristic of *p*-phenylenediamines contribute to antiozonate action. First, research shows that *p*-phenylenediamines form a protective film. Recent spectroscopic analyses have confirmed that the surface film on rubber consists of the ozonation reaction products of the *p*-phenylenediamine [28]. Second, they react directly with the ozone. Diamines are particularly successful at this because they show a higher rate of reaction with ozone than that shown by rubber [22]. Finally, diamines react directly with ozonization products of the rubber hydrocarbon causing the diamine to become attached to the rubber network [22]. Most importantly, *p*-phenylenediamines in rubber show sufficient diffusion to the exposed surface once a concentration gradient has been established to keep the surface supplied with fresh antiozonate.

3.1.3 Conditions Affecting Necessary Loading of Chemical Antiozonates

The effectiveness of the *p*-phenylenediamine derivates and other antiozonates depends upon the strain conditions to which the rubber is subjected. The rubber product may be used in either static or dynamic strain; in the former, the strain may be present intermittently (semi-static) or constantly (pure static) [14]. The dependence on strain conditions is due to the fact that the protective layer formed by reacted antiozonate is brittle and easily damaged [28]. Consumption increases if the piece is flexed or if it is strained and then restrained because the layer is broken and needs fresh antiozonate to be repaired [28]. Environmental exposure conditions are also essential in determining the long-term effectiveness of antidegradants. Protective additives are lost due to abrasion and to surface leaching by water and other fluids, increasing consumption over the rubber product's lifetime [21,28].

Antidegradants are also lost by oxidation, volatilization and reaction with ozone. If environmental exposure is not considered, the primary loss of antidegradants is due to reaction with ozone or ozonolysis products of the rubber [22]. Reaction with ozone gradually consumes the antiozonate for as long as the antidegradants can diffuse across the layer already formed to react with ozone at the surface [28]. Lake calculated that the minimum antiozonate level needed for protection will be related to the reciprocal of the reaction rate constant at the surface which is directly proportional to the ozone concentration [28]. Thus high ozone concentrations require the use of excessive quantities of antiozonates [28]. Deficiency in free antiozonate will lead to loss of resistance. Damage to the product will then occur if the critical strain is lowered to a strain level that is exceeded during the product's lifetime [28].

The relation of antiozonate quantity to protection conferred is shown in Table 3.1 below. The rubber strips used were 1.5 cm (0.59 in.) wide and 7 cm (2.76 in.) long with thicknesses ranging from 0.02 cm to 0.2 cm (0.00787 to 0.0787 in.) [7]. The antiozonate used is *N*,*N'*-dioctyl-*p*-phenylenediamine (DOPPD) [8]. Exposure was to outdoor levels of ozone in Herts, England [7].

TABLE 3.1 DOPPD Concentrations and critical strains of natural rubber specimens on exposure to outdoor atmosphere [8].

DOPPD Concentration %	Critical Extension %
0	6 to 8
0.5	7 to 15
1.0	7 to 15
1.5	10 to 15
2.0	30 to 80
2.5	>200

The antidegradants are usually used at loading levels of 0.5 phr to 5 phr with most formulas calling for loadings of 1 to 3 phr [4]. It is generally agreed that the loading should not exceed 5 phr of antiozonate in the elastomer [21]. The compounder must ensure that sufficient antidegradants are added so that a certain level of protection is maintained throughout the economic life of the product [28].

Chemical antiozonates can provide even better long term protection when used in conjunction with a wax which blooms at the temperatures reached by the rubber product [28].

3.2 Wax Used as an Antiozonate

In 1881, wax was first added to rubber products to retard deterioration [27]. At the time it was not known if the wax protected the rubber through a physical or chemical mechanism. It is now known that waxes bloom to the rubber surface to create a physical barrier protecting the product from oxygen and ozone attack. The wax migrates to the surface as a consequence of a concentration gradient and elastic forces working on the dissolved wax in the rubber [28]. Blooming of the wax to the rubber surface continues until the level of wax remaining is completely soluble in the rubber compound. The type of wax and the rubber composition determine the ability of the wax to bloom and the rate of bloom. The solubility and mobility of a specific wax are influenced by the type of wax, the rubber composition and the temperature[25].

3.2.1 Paraffin and Microcrystalline Waxes

Two types of petroleum waxes, paraffinic and microcrystalline, are commonly used in non-specialty rubber products to protect against ozone and oxygen degradation. These waxes migrate to the rubber surface, or "bloom," to form a protective impervious layer [17]. A wax bloom develops rapidly in 8 to 10 days at room temperature [25]. A comparison of the basic properties of paraffin and microcrystalline waxes is shown in Table 3.2.

TABLE 3.2 Comparing Paraffin and Microcrystalline Waxes [11]

	Paraffinic	**Microcrystalline**
Average molecular weight	350-420	490-800
% Normal paraffin	High	Low
% and napthenes	Low	High
Melting point range, °C	38 - 75	57 - 100
Typical carbon chain length	C-26	C-60

Paraffin wax is a high molecular weight hydrocarbon mostly composed of straight chains (alkanes). Because its chain length is insufficiently long for entanglement, it is not a polymer [33]. Paraffins, in general, have a lower molecular weight, a lower melting point, a higher concentration of straight chain or linear hydrocarbons and greater crystallinity compared to microcrystalline waxes [11,25]. Microcrystalline wax is mostly composed of amorphous chains which are highly branched and do not crystallize easily [4] Because microcrystalline waxes contain fewer straight chains (normal paraffin alkanes), they are less mobile in rubber [11].

3.2.2 Wax Blooms

The wax bloom on the rubber surface is not a flat sheet; it is composed of crystals of up to some tens of microns in size [26]. Low melting point waxes, mostly paraffins, have large crystals in the blooms. These crystals have little adhesion to the rubber surface and are easily flaked off. Higher melting point waxes, which include most microcrystalline waxes, have closely-packed fine crystals producing blooms. These blooms have considerably more plasticity, adhering better to the rubber surface [27]. It is the cyclic and branched paraffins which impart to microcrystalline wax a flexibility superior to that of the straight chained waxes.

Adding a microcrystalline wax to a paraffin modifies the protective action of the paraffin in several ways. The high crystallinity and low intercrystalline forces in paraffin wax are modified. The microcrystalline wax controls the crystal size, limiting it significantly. Finally, increasing the amount of amorphous intercrystalline material makes the brittle paraffin waxes tough, better able to resist fracture [27]. Manufactur-ers blend microcrystalline waxes with paraffines for the purpose of seeding the development of small, closely packed crystals which produce more flexible blooms [21].

3.2.3 Blooming

Above its melting point, wax is highly soluble in rubber, dissolving easily at mixing and vulcanization temperatures. At ambient temperatures, its solubility is reduced so blooming commences immediately after vulcanization as the rubber begins to cool [28]. Migration should occur continuously until the level of wax in the rubber falls to its solubility limit and equilibrium is reached between wax on the surface and wax in the bulk of the rubber [28]. Solubility of wax in natural rubber at room temperature can be up to 2 phr though it is seldom greater than 0.5 phr. [27,28]. The extent of migration is sensitive to exposure temperature, exposure time, wax concentration and rubber composition [11].

After it cools, the solubility of wax quickly decreases and the wax becomes supersaturated in the rubber. The wax in excess of equilibrium begins to crystallize out of the rubber matrix to the surface and into voids in the rubber. In the rubber, wax precipitates out as spheres around voids created by flaws or impurities in the rubber [28]. As these wax crystals grow, they exert pressure on the rubber, trying to deform it to allow room for growth. The wax in the interior of the rubber is then in equilibrium with the rubber in its immediate vicinity, but the wax on the surface is completely unstressed. This pressure gradient creates a force favoring the redissolving of the wax in the interior into the rubber and its migration to the free surface where it can recrystallize in an unstressed state [26].

Blooming, migration of waxes to the rubber surface, is diffusion controlled [28]. The kinetics of the blooming process, however, do not follow a simple saturation model. The blooming process is driven by the elastic forces acting on the wax which precipitates out of the rubber due to supersaturation [28]. Because the elastic forces surrounding the wax precipitates are believed to be the driving force for the blooming process, the modulus of the rubber will affect the blooming rate [28]. Blooming rate is seen to increase with the amount of crosslinking (hardness) in the rubber [26,28]. Elastic forces and thus blooming rate are also known to increase as the size of the precipitates increases; this occurs when the wax concentration increases [28]. Thus the extent of bloom increases when wax concentration is increased, provided the solubility limit of rubber is exceeded [11]. The rate of bloom thickness growth decreases with time, like all diffusion processes [28]. Rates of bloom growth will increase only slowly as the level of wax approaches the solubility limit [27].

The most important climatic variable is temperature because it affects the diffusion coefficient and solubility of the wax [28]. An increase in the temperature causes an increase in the diffusion coefficient and the solubility of the wax. The increased diffusion coefficient results in a faster rate of blooming while the increased solubility will result in a lower blooming rate [28]. The graph in Figure 3.1 demonstrates the sensitivity of the wax to temperature, showing wax bloom as a function of mobility and solubility. Temperature is elemental in determining the rate and extent of wax bloom.

Figure 3.1 - Wax bloom as a function of mobility and solubility [25]

Figure 3.1 shows why waxes with melting points above 65°C (149°F) are unsuitable for low temperature uses [28]. Even if a sufficient bloom is formed prior to exposure, thermal contraction or handling, shock and weathering can break the bloom. The bloom will be repaired too slowly to afford adequate protection even if a high level of supersaturation exists [28].

The graphs in Figure 3.2 show that a typical paraffin wax blooms more rapidly and to a greater extent at 20°C (68°F) and a typical microcrystalline at 50°C

(122°F) [25]. The diffusion coefficient of wax decreases as its molecular weight increases. And as waxes become lighter, they are more soluble in rubber [28]. Proprietary waxes are almost always blends of waxes with different melting points so that protection is assured over a wide temperature range [28].

Figure 3.2 - Bloom versus temperature for a typical paraffin wax, a typical microcrystalline wax and a typical wax blend [25]

3.2.4 Determining a Proper Wax Loading

Wax alone, if used in high concentrations, is capable of conferring protection to a black sidewall vulcanizate up to 25% strain at normal ozone levels [14]. Studies have found wax blends to raise the threshold strain to around 40% strain in some specimens [28]. The type of wax that is used and the level of protection desired determine the wax loading needed. For thin rubber products, the typical loading range is 1 to 3.5 phr [17].

Protection depends on the quality and thickness of the bloom formed. A critical thickness must be achieved to prevent cracking. In ozone concentration of 25 pphm and less, thicknesses required are 0.5mm or less. The critical thicknesses are averages over an area of surface - the true minimum being smaller since in can be seen under a microscope that the blooms are not uniform, especially after prolonged growth [27]. Further discussion of protective layer thicknesses and wax loading is given in Section 5.5.

3.2.5 Protecting With Wax

As with chemical antiozonates, sufficient wax must be added to provide protection throughout the life of the elastomer [27]. The manufacturer must properly determine the level of wax required to ensure that the solubility is exceeded throughout the life of a product. At the same time, the manufacturer must be careful not to overload the product creating a loading so high that other properties are adversely affected. A good protective wax must provide protection at the thinnest possible bloom thickness. The rate of diffusion of the wax should be sufficient to repair the bloom when this is required but should not become so great that the wax in the rubber becomes exhausted.

3.3 Combined Action of Wax and Chemical Antiozonates

The best protection is created when wax and chemical antiozonates like *p*-phenylenediamine are used in conjunction [14]. Wax film is brittle and may not provide protection under dynamic conditions. A microcrystalline wax bloom can break if the rubber is extended above about 25% extension [28]. Wax blooms are able to withstand much more flexing when used with chemical antiozonates. These chemicals confer significant flexibility to the wax layer [27]. Wax blooms also enhance the protective action of chemical antiozonates. They function as carriers for the chemical antidegradant from the interior to the surface where it is most needed [25]. The synergistic action of wax and other protectors is dramatic as shown in Table 3.3 below.

TABLE 3.3 Effect of Varying the Antiozonate Concentration Upon the Critical Strain of a Black Natural Rubber Sidewall Vulcanizate in a Static Exposure Test [14]

Antiozonate	**IPPD**		**DMHPD**	
(phr)	**no wax**	**1.5 phr wax**	**no wax**	**1.5 phr wax**
0	4 - 6	10 - 15	4 - 6	10 - 15
0.5	—	—	—	c. 25
1	6 -10	50 - 75	10 - 15	50
2	8 - 12	c. 100	40 - 50	c. 150
3	c. 25	—	100 - 150	—

IPPD : *N*-isopropyl-*N'*-phenyl-paraphenylenediamine

DMHPD : *N*,*N'*-di(methyl-heptyl)-paraphenylenediamine

3.4 Ozone Attack of Bearing Pads

3.4.1 Longevity Without Resisters

In 1889, natural rubber pads were installed in a rail viaduct in Melbourne, Victoria, Australia to absorb impact and noise [35]. The pads were 1/2" thick and composed of natural rubber, clay, sulfur and iron oxide, none of which are antidegradants [35]. The bridge bearings were examined in the mid-1980s after 95 years of service; though not protected by antiozonates and antioxidants, they were found to be in perfect condition except for 1.5 mm of surface degradation due to oxygen and ozone attack [10 & 28].

Modern engineering elastomers with chemical antioxidants (and antiozonates) should and do show even greater longevity [35]. A 20 year old elastomeric bearing pad was removed in 1982 from a bridge in Kent, UK. There was absolutely no evidence of any ozone cracks or oxidation [35].

The evidence seems to indicate that unprotected natural rubber bearings can be expected to function efficiently for at least a century while incurring only minor damage due to environmental attack. The amount of damage done by 1.5 mm of ozone attack is insignificant and will not affect the serviceability of the product. But since the state of strain in the bearings studied is not known, the evidence may be inconclusive and it can not be stated definitively that oxidation and ozone attack are not a concern in bulkier products under compression such as bridge bearings [28].

3.4.2 Experimental Surface Strains in Representative Bearing Pads

Analytical studies of typical bearing pads were studied by Osama Hamzeh in his doctoral dissertation "Analysis of Elastomeric Bridge Bearings" [38]. Tensile strains from these finite element computer models show typical strain conditions on the exterior rubber layers of typical rubber bearing pads. To determine the necessary level of protection against ozone attack, the tensile strains developed in the computer models on the vulnerable outer elastomer layer were found.

Hamzeh modeled typical Texas steel-reinforced bearing pads. He studied 3 shim and 6 shim pads with gage 12 steel plate (thickness = 0.2657 cm or 0.1046 in.). The elastomeric material was given a shear modulus of either 689 kPa or 1.379 kPa (100 psi or 200 psi). A compressive stress of either 3.447 kPa or 6.895 kPa (500 psi or 1000 psi) and shear strains of 0% to 50%, the maximum allowable, were applied. The bearing pads had a width of 22.9 cm (9.00 in.) and a total elastomer thickness of 4.45 cm (1.75 in.).

To find the worst case strains on the outer rubber layer, the 3 shim bearings with the less stiff rubber were studied. The 6 shim bearing experiences lower stresses and strains (due to the shape factor). Stiffer elastomers have lower shear moduli and hence experience lower strains. So the pad of interest is the 3 shim bearing with a 689 kPa (100 psi) shear modulus under a compressive load of 3.447 kPa or 6.895 kPa (500 psi or 1000 psi) and at 0% and 50% shear strain.

Figures 3.3 through 3.6 show the tensile strains of the 3 shim bearings. The graphs show that the tensile strain on the exposed surface, meaning the vertical edges, is seldom larger than 30%. In addition, the area experiencing stresses over 30% is a very small portion of the entire exposed area. Actual tensile strains were found to reach 70% to 90% at localized points but they were present on less than 5% of the exposed surface area. Horizontal surfaces were not considered vulnerable because of the reduced availability of ozone on contact surfaces.

To determine the loading of antiozonates and/or wax necessary to protect the rubber, Table 3.3 may be used as a reference. Actual necessary loadings in a product such as a bearing will be less as explained in the next section, Section 3.4.3.

Contour lines = 10% 20% 30% tensile strain

Figure 3.3 - Compression of 3.447 kPa (500 psi) at 0% shear

Contour lines = 10% 20% 30% tensile strain

Figure 3.4 - Compression of 3.447 kPa (500 psi) at 50% shear

Contour lines = 10% 20% 30% tensile strain

Figure 3.5 - Compression of 6.895 kPa (1000 psi) at 0% shear

Contour lines = 10% 20% 30% tensile strain

Figure 3.6 - Compression of 6.895 kPa (1000 psi) at 50% shear

3.4.3 AASHTO Ozone Tests: Comments on Accuracy and Relevance

Ozone tests recommended by AASHTO (the American Association of State Highway and Transportation Officials) for the elastomeric material used in bridge bearings pad construction are shown in Table 3.4. Serious discussion has questioned whether these ozone tests should be used for bulky products such as bridge bearing pads because these tests were designed to evaluate the adequacy of elastomeric material used in thin-walled applications. All sources that evaluated the ozone test agreed that the ozone tests required by AASHTO are overly stringent for large, bulky rubber products, specifically bearing pads. Five researchers (A. Gent, G. J. Lake, P. M. Lewis, A. D. Roberts, and A. Stevenson) contend that ozone damage is a serious concern in thin-walled products but not in those rubber products with a large volume of rubber and a relatively small surface area [6 & 13, 19 & 20, 21, 28, 35].

TABLE 3.4 AASHTO Ozone Test for Elastomeric Bearings

Neoprene Rubber	100 pphm ozone in air by volume for 100 hours	No Cracks
Natural Rubber	25 pphm ozone in air by volume for 48 hours	No Cracks

Ozone test is ASTM D1149:
Using Test Specimens 25 by 150 mm (1 by 6 in.)
with a thickness between 1.9 and 2.5 mm (0.075 to 0.10 in.)
Tensile Strain is 20% at 37.8°C ±1°C (100°F ±2°F)
using ASTM mounting procedure D518, Procedure A.

Degradation manifested as surface cracking can shorten the service life of a "thin-walled" product by initiating premature tensile or fatigue failure, or by increasing relaxation and creep [21]. In addition to leading to early failure, cracks detract from the appearance, serviceability, and strength [6]. But, Lake points out, “under primarily constant loading, ozone cracking is mainly of concern for relatively thin articles used in tension [20].” For large rubber components such as bridge bearings which are used in compression, Gent notes that ozone cracking is not a "big problem" [13]. Lewis agrees, saying that in bulkier products ozone cracking is no more than superficial, creating no adverse effect on the properties of the product [21].

In addition to finding that ozone degradation does not significantly effect the performance of a bulky product, the authors also contend that the ozone tests required by AASHTO cannot correctly evaluate an elastomer for use in a bearing pad. The ASTM ozone test does not accurately model the elastomer response to ozone attack because the test uses thin rubber test specimens in tension to evaluate bulky products in compression and shear, using elevated test temperatures and high ozone concentrations. Stevenson states, "accelerated tests exposing thin rubber sheets to elevated temperatures can give a misleadingly pessimistic view of the longevity of rubber pads for civil engineering applications [35]."

Laboratory tests carried out in tension do not reflect the crack growth rate of articles in compression. In compression or shear, the growth rate has been found to be up to several hundred times slower than in tension. A test piece under 10% compression subjected to 105 pphm ozone for 20 hours, a test equivalent to 100 years at normal service at average atmospheric ozone concentrations, was cracked only in a 1 mm deep region. The same test pieces failed in 2 hours when subjected to a 10% tensile strain [20]. The compression specimens resisted ozone attack much better than the tension specimens for two reasons. First, the crack openings are restricted in compression, reducing the diffusion of ozone into the rubber bulk. Second, tensile stresses high enough to induce ozone cracking are localized at the surface of a compression piece and so cracks stop growing altogether after penetrating a small distance [20]. Obviously ozone attack of rubber subjected to compression and shear cannot be estimated by tensile tests.

The ASTM tests which are performed on a specimen 1.9 to 2.5 mm (0.075 to 0.10 in.) thick cannot model the behavior of the rubber in a bearing pad having a total elastomer thickness around 20 times larger than that. The test does not indicate if the rubber manufacturer has met the objective: to ensure that the antiozonate additive has a flux high enough to form or repair a protective surface but low enough to ensure a reservoir of unused antiozonate exists throughout the service life of the product. The effect of the huge discrepancy between the surface to volume ratio of the test specimen and that of the final product is to make the test invalid in modeling the flux of the additive in the actual product. The thin test specimen cannot model the "reservoir effect" of a bulky product whose volume contains excess antiozonate, giving it more available free antiozonate per unit surface of exposed area [21].

Several researchers fault the elevated test temperatures and ozone concentrations for leading to inaccuracy in the test results. Lake found that the high ozone concentrations used in the ASTM test combined with the high temperatures may cause cracking in rubbers that are completely protected at normal temperatures by their antiozonates and wax [20]. Lake notes “a wax that is effective in a short term test at elevated temperature may be quite ineffective under service conditions and vice versa [20].” This is due to the fact that blooming of wax is a temperature dependent phenomenon [See Section 3.2.3]. "The view is sometimes expressed that a higher temperature [Ozone tests are carried out at 38°C (100°F)] makes testing more severe...it is not [true] with respect to ozone attack [19]." Because of the fact that wax bloom is temperature dependent, Lake points out that testing at temperatures other than those expected during service will not necessarily lead to more severe tests, but simply to less accurate tests.

Lewis has found that the high ozone concentrations used in testing may require a higher level of protection and force the rubber manufacturer to overload the rubber with either chemical antiozonates or wax to pass the ozone test. "The dependence of *p*-phenylenediamine antiozonate activity upon ozone concentration means that an accelerated test requires the use of an antiozonate level that the product may not need. Because of its bulk, that product (a bearing) may have the benefit of an antiozonate reservoir not available to thin (2 mm) test pieces. The higher antiozonate level merely increases costs and the risk of adverse side effects [21]." Thus high temperatures and high ozone concentrations lead to inaccurate models and unnecessarily high levels of antiozonate loading.

Stevenson has found that oxidized rubber which forms as a result of aging can act as a protective layer to inhibit further ingress of degradants [35]. Roberts has reached the same conclusion, noting that ozone attack will only affect "a relatively thin outer layer of rubber so may remain only a surface effect for structural bearings." He found that the presence of a "skin" of degraded rubber results in the standard aging test on thin strips of rubber being misleading [28]. Lake concludes that if the exposed surface is small in relation to the bulk of the rubber, degraded rubber, and even dirt or grease can create a layer restricting ozone access [20].

In conclusion, all five researches concluded that the ASTM ozone tests required by AASHTO for bridge bearing pads produces test results that are not relevant for bulky rubber products. Lake found that “ozone cracking in service is generally found to be slower, often much slower, than would be expected from straightforward extrapolation from laboratory tests [20]." The researchers also agree that ozone attack does not effect the performance of a bridge bearing and other bulky rubber products. Finally, Roberts concludes that because damage is restricted to surfaces only, large components such as bearings are "virtually immune to aging and have a proven longevity [28]." It is important to note that the researchers are not suggesting ozone protection is not necessary; some form of antiozonate is certainly necessary for protection. Another concern with the conclusions reached by the researchers is that they did not study the problem of the exterior elastomer cover falling outside typical bearing pad specifications and lacking adequate thickness. If the bearing had a thinner exterior layer than those studied in the finite element analysis, the stresses could be much larger. The failure mechanism could be an ozone crack exposing the steel shim and causing corrosion.

CHAPTER 4

BEARING LEACHATE ANALYSIS:

DETERMINING THE COMPOSITION OF LEACHATE FROM NATURAL RUBBER BRIDGE BEARINGS OF TWO TEXAS BRIDGES

4.1 Source of Bearing Leachate Samples

In order to verify the composition of the leachate that had migrated to the surface of bridge bearings in service, an infrared spectroanalysis was performed on scrapings taken from the surface of natural rubber bearings recently taken out of service. The bearings were removed from two bridges in central Texas that had experienced problems with bearing pad movement. The first bridge is the Slaughter Creek IH35 frontage road bridge in South Austin of Texas District 14 (Travis County). The second bridge is the Valley Ridge Blvd. Bridge over IH35E outside of Dallas of Texas District 18 (Dallas County).

Two bearings from each bridge were scraped for leachate samples. The two samples from Slaughter Creek (SC4 and SC6) were taken from the bearings formerly under girders 4 and 6. The two samples from the Dallas Bridge (D3 and D6) were taken from the bearings formerly under girders 3 and 6. Markings on the bearings indicated that both sets of bearings were produced by the same manufacturer, which happened to be one of the three suppliers of bearings to this research project, Manufacturer C in the experiments conducted by Joseph Muscarella [39]. The four samples were analyzed using infrared spectroscopy.

4.2 Infrared Spectroscopy

Infrared Spectroscopy is an analysis technique used to identify the compounds or elements that compose an unknown sample. If it is a solid, the sample must first be dissolved in a solvent (or melted onto a base composed of crystals of known composition). If the sample is a liquid or gas, it can be analyzed without dissolving or melting it. IR Spectroscopy classifies (identifies) these compounds by interacting with the sample using electromagnetic radiation. The infrared region of the electromagnetic spectrum lies between the visible and radio wave regions (10^{-6} and 10^{-4} m). When a molecule is irradiated with infrared radiation of various wavelengths, some of the radiation is absorbed by the molecule. The energy of the absorbed radiation is stored in the molecule as molecular vibrations (vibrations of the various nuclei in the molecule). The spectrum produced is a plot of the amount of radiation absorbed versus the frequency or wavelength of the radiation [24].

The IR spectrum of an organic molecule shows a great deal of information about the structure of the molecule. The various vibrational motions of the groups of atoms in molecules lead to characteristic absorption of infrared radiation and can be used to verify the presence of certain bonds. Some bonds stretch back and forth with a characteristic frequency and some bonds vibrate at angles. The spectra reveal the type and arrangement of the bonds in the molecules, giving a "fingerprint" of the molecule [24]. Comparison of the sample's spectrum to known spectra reveal the compound.

4.3 The Infrared Spectroanalysis

The samples were analyzed at the University of Texas Chemical Engineering Laboratories by chemical engineering doctoral student David Sullivan. The analyses were performed on the Mattson Research Series 1 FTIR Spectrometer using a MCT (Mercury Cadmium Telluride) Detector which saves the average of 64 scans and has a resolution of 4 cm^{-1}. Both liquid cell solution (dissolving the sample in a solvent) and KBr optics (melting the sample onto a KBr crystal base) were employed. Solvent used included acetone, chloroform, benzene, fomblin, and trichloroethylene. In the final analyses, in addition to KBr optics only chloroform (CCl_3H) and trichloroethylene ($HClC{=}CCl_2$) were used.

After determining that chloroform provided one of the best view of the leachate samples in the desired ranges, the four samples were dissolved, analyzed and their spectra compared to determine if they were identical compounds. Figure 4.1 is the spectra of the four samples (SC4, SC6, D3, and D6) dissolved in the solvent chloroform and also the spectrum of the chloroform itself. We will ignore the first peak because it is just one of the characteristic peaks of chloroform and not of the samples themselves as spectra of the samples in other solvents has shown. The second two peaks are, respectively, the characteristic peaks of the CH_3 and CH_2 bonds found in hydrocarbons. The peaks of all four samples are at the same frequency exactly. The location of the peaks shows that these bonds are present, identifying the compounds in the substance. The height of a peak should only be viewed in relation to other peaks in the same sample's spectrum; these relative heights indicate the number of bonds of one type in relation to the number of bonds of another type. The absolute height of the peaks should not be compared because they simply indicate different masses or amounts of sample and are a result of dissolving unequal amounts of leachate in the solvent.

Figure 4.1 - Comparing Bearing Scraping Samples

The exact coincidence of these peaks indicate that the four samples are identical substances. Peaks from 600 cm^{-1} to 4000 cm^{-1} were also monitored to see if they contained additional information. These peaks were also checked for coincidence and were found to be equal in all four samples. Finding that the samples were identical allowed the rest of the analysis to continue by analyzing just one sample. The sample SC4 was chosen. The full IR spectrum of SC4 in chloroform is shown in Figure 4.2. A plot of the sample SC4 in the solvent trichloroethylene is plotted versus the solvent in Figure 4.3. By examining both Figure 4.2 and Figure 4.3, it was determined that the peaks other than the two near 3000 cm^{-1} were of minor importance. Therefore the IR analysis focused on the two peaks between 3000 and 2800 cm^{-1} though all peaks were considered when the sample spectra was compared to known spectra.

It was necessary to determine what compounds were likely to compose the leachate so that the spectra of these substances could be gathered to compare to the spectra of the leachate. Several rubber manufacturers were contacted and asked to suggest what substances were expected to migrate to the surface of a natural rubber elastomer. The manufacturers all agreed that wax and perhaps antioxidants and antiozonates should be in the leachate. One source suggested that plasticizer might be present. Another manufacturer suggested that processing aids like mineral oil and plasticizer might be present. It was necessary to gather the spectra for the wax used by the manufacturer, for the antiozonates and antioxidants, for the plasticizers, and for the mineral oil.

Samples of the wax and plasticizer used in the bearings were obtained from the rubber manufacturer. The wax is Sunproof Extra, a proprietary mix of paraffin and microcrystalline waxes produced by Uniroyal Chemical. The wax came in white flakes and is said by the manufacturer to bloom "moderately from cured and uncured stocks when used in excess of 0.5 part per 100 RHC (rubber hydrocarbon)." The wax spectrum was produced by melting the wax onto a KBr crystal base. The plasticizer is Supramix 2016 by C. P. Hall and came as a brown slippery powder. The plasticizer spectra were produced by dissolving in several solvents: Nujol, benzene, etc. The IR Spectrum of mineral oil was obtained from a computer database. IR Spectra of typical antioxidants and antiozonates were obtained from *The Aldrich Library of FT-IR* [1]. The 1,4-Pheylenediamine and *N*-Dimethyl-*p*-phenylenediamine were of particular interest as these are compounds commonly used by manufacturers because they are both antioxidants and antiozonates.

Figure 4.2 - IR Spectrum of Sample from Slaughter Creek Bearing No. 4 in Chloroform

Figure 4.3 - IR Spectrum of Sample from Slaughter Creek Bearing No. 4 in Trichloroethylene

The plasticizer was the first substance determined not to be present in the leachate; several key peaks of the plasticizer were not found in the sample's spectrum. Then the antioxidants/antiozonates were studied. Some spectra used for comparison are shown in Appendix 1. None of the key peaks of the 1,4-Phenylenediamine and *N*-Dimethyl-*p*-phenylenediamine were present in the sample. Even if these substances had at one time been present in the leachate, and considering their function they most probably were, they would not have been expected to have survived in their original state after their prolonged exposure to the atmosphere. The antioxidants/antiozonates would have reacted and changed their chemical structure after contact with the atmosphere in a relatively short amount of time. Thus it was not surprising they were not found in the leachate sample.

Finally, the wax and mineral oil spectra were compared to the sample's spectra. Both had peaks in the location of interest and no significant peaks elsewhere. A close up of the spectra in this region are shown in Figure 4.4. First note that peak 5 in the sample is caused by the solvent. Peaks 1,2 and 4 are all in the same locations if we allow for the resolution error of up to 4 cm^{-1} of the IR Spectrometer. Peak 2 and 4 are of the same relative height in the sample, the wax and the mineral oil. But peak 1 in the mineral oil has an inconsistent height relative to it's other peaks. Also peak 3 exists only in the mineral oil. It is therefore certain that no mineral oil is present. The leachate is thus shown to be almost entirely composed of the wax supplied by the rubber manufacturer.

4.4 Results of the Analysis

The IR spectroanalysis showed that the leachate samples taken from the two bridges are composed mainly of the wax used by the rubber manufacturer. Other substances suggested by the manufacturers to have possibly migrated to the surface were eliminated as possibilities by the analysis. Some other trace substances present but not identified due to their minute amount are most likely products of the completed reaction of antiozonates/antioxidants and also dirt.

Figure 4.4 - Leachate Sample versus Wax, Mineral Oil and Solvent

CHAPTER 5

BEARING LEACHATE THICKNESS MEASUREMENT: MEASURING THE LAYER THICKNESS OF A BRIDGE BEARING FROM A TYPICAL TEXAS BRIDGE

5.1 Bloom Rates and Layer Thicknesses

After it was determined that the leachate of a typical Texas bearing was composed mainly of wax, it was of interest to see at what rate the wax was migrating and to determine the layer thickness of the leachate. Since the bearings used in Project 1304 were made from typical Texas bridge bearing compounds, eight of these bearings from one manufacturer were selected to measure wax leachate layer thicknesses.

The work of other researchers was examined to find typical rates of wax migration in natural rubber as well as layer thicknesses required for adequate protection. Experiments by researchers using lightly loaded unstressed natural rubber specimens suggests layer thicknesses reach an equilibrium value in a certain amount of time [11]. The final layer thickness and the time to reach this thickness depend on several variables: the concentration of the wax, the boiling point of the wax, the elastomer stiffness and storage temperature. The wax layer thicknesses found by the researchers were used to compare to the leachate layer thicknesses measured on the eight bearings. The wax layer thicknesses suggested for adequate ozone protection are also compared to the layer thicknesses measured on the eight bearings.

5.2 Bloom Rates and Layer Thicknesses Reported by Other Researchers

All wax loading in excess of the solubility level in the elastomer should eventually migrate to the surface. Migration rates begin rapidly but quickly slow as the surface layer becomes thicker. Some research done by Dimauro, Paris and Fath on wax bloom development suggests that once the layer reaches a certain thickness, the bloom will only grow at very slow speeds or to replenish itself if wax is lost through abrasion or erosion [11]. The speed of the wax migration (initially and as it slows) and the equilibrium layer thickness are dependent on the stiffness of the elastomer, the concentration of wax in the rubber, the stress the product is subjected to, the temperature at which the rubber is stored, and the boiling point of the wax (which affects its solubility and mobility in rubber).

Dimauro *et al* tested 14 natural rubber specimens loaded with fourteen different waxes, the eleven of interest being six paraffinic and five microcrystalline, at 1.6 phr (parts per hundred parts of rubber by weight). They assumed the solubility level in the rubber to be a generous 0.8 phr at room temperature; usually natural rubber is expected to be at equilibrium in rubber with slightly over 0.5 phr of wax at 20°C [28]. If all the wax in excess of the solubility level were to have migrated to the surface of their specimens during the study period of 49 days, the leachate layer thickness would have been around 7.7 μm. Instead, typical layer thickness were from 0.08 to 3.56 μm [11]. The bloom development of four waxes is shown in Figure 5.1. Longer studies showed continued layer growth for the waxes which were more mobile at room temperature.

Note that the 52ºC paraffin plateaus after the first week indicating that it is highly soluble and hence less mobile in the elastomer. It appears that the other three waxes had not reached equilibrium at the end of the experiment and were not finished blooming. Though both microcrystalline waxes were beginning to level out, the 68ºC paraffin does not appear to be plateauing.

Figure 5.1 - Effect of Wax Melting Point on Rate of Bloom in Natural Rubber [25]

5.3 Bearings used for Leachate Layer Thickness Measurements

Eight bearings were used in the layer measurement. They were from the company labeled Manufacturer B in the experiments by Joseph Muscarella [39]. Both plain and steel laminated bearings were used. The laminated pads had three or six steel shims and had varying slopes and exterior elastomer layer thicknesses.

Two elastomer compounds were tested, one having a Shore A durometer of 55 the second having a Shore A durometer of 70. The leachate layer thicknesses were measured at a migration time of six and nine months for the 55 durometer bearings and at three and six months for the 70 durometer bearings.

The layer thickness was determined by scraping the top and bottom surfaces of the bearing clean with a steel blade and weighing the scrapings on an electronic scale accurate to the 100th of a gram. See Figure 5.3. Layer thicknesses were determined using a wax specific gravity of 0.92 as suggested by Dimauro *et al*. This seemed to be a reasonable value as typical waxes range from specific gravity of 0.90 to 0.94 [26]. During the time between scrapings, the bearings were stored in a temperature controlled room between 20ºC and 25ºC (68 and 77 degrees Fahrenheit). The bearings were stored on their sides to ensure the leachate was not transferred from the bearing surface during storage.

Figure 5.2 - Scraping the Bearings with a Steel Blade and Collecting the Leachate

The bearings of 55 durometer were manufactured around 5/5/94 and were scraped 11/5/94 and 2/5/95. The bearings of 70 durometer were manufactured around 8/20/94 and were scraped 11/22/94 and 2/20/95. On bearing number 6, leachate was only found on one surface. The results are shown in Table 5.1.

Table 5.1 Wax Leachate Layer Thickness
at 6 and 9 Month Migration Times for 55 Durometer Bearings
and at 3 and 6 Month Migration Times for 70 Durometer Bearings

	Number of Shims	**Hardness in Shore A Durometer**	**Slope**	**Elastomer Thickness (cm)**	**Migration Time**	**Weight of Wax (g)**	**Layer Thickness (micrometers)**	**Migration in micrometers/cm**
1	3	55	6%	2.022	6 months	1.14	**7.46**	**3.69**
2	3	55	6%	2.022	"	0.93	**6.09**	**3.01**
3	Plain	55	0%	2.540	"	1.40	**9.16**	**3.61**
4	6	55	4%	0.919	"	1.19	**7.79**	**8.47**
5	6	55	6%	1.179	"	1.11	**7.26**	**6.16**
6	Plain	70	0%	2.540	3 months	0.22	**2.88**	**1.13**
7	6	70	4%	0.919	"	0.31	**2.03**	**2.21**
8	6	70	6%	1.179	"	0.43	**2.81**	**2.39**

	Number of Shims	**Hardness in Shore A Durometer**	**Slope**	**Elastomer Thickness (cm)**	**Migration Time**	**Weight of Wax (g)**	**Layer Thickness (micrometers)**	**Migration in micrometers/cm**
1	3	55	6%	2.022	9 months	1.82	**11.91**	**5.89**
2	3	55	6%	2.022	"	1.40	**9.16**	**4.53**
3	Plain	55	0%	2.540	"	1.84	**12.04**	**4.74**
4	6	55	4%	0.919	"	1.68	**10.99**	**11.96**
5	6	55	6%	1.179	"	1.38	**9.03**	**7.66**
6	Plain	70	0%	2.540	6 months	0.33	**4.32**	**1.70**
7	6	70	4%	0.919	"	0.52	**3.40**	**3.70**
8	6	70	6%	1.179	"	0.55	**3.60**	**3.05**

5.4 Results of Analysis

The bearings exhibited bloom thicknesses of **2.03 to 12.04μm**, much higher than those of Dimauro *et al* which ranged from **0.08 to 3.56 μm** at 48 days. This is explained by three facts. First, the elastomer layer thicknesses from which the wax migrated were 5 to 14 times greater, 0.92 cm to 2.54 cm compared to 0.18 cm in the experiments of Dimauro *et al*. Second, the thicknesses were measured at much longer migration times, at 90, 180 and 270 days instead of 50 days as in the Dimauro *et al* study. Third, the wax concentration was probably higher in the bearings; wax loadings of 2 to 3 phr were probably present in the bearings as compared to the 1.6 phr loading of the specimens of Dimauro *et al*. In addition, the study by Dimauro *et al* did not mention the elastomer stiffness which also influences wax migration.

Table 5.2 compares the actual layer thicknesses to the expected layer thicknesses if all the wax above the solubility limit were to come to the surface of the bearings. After 6 to 9 months, only 6 to 28 percent of the wax capable of migrating has bloomed. In the experiments of Dimauro *et al*, after 50 days 1 to 46 percent of the wax has bloomed with 28% being an average for paraffins and 7% being an average for microcrystallines. The wax blend used by the manufacturer is most certainly a blend of paraffins and microcrystalline waxes.

Table 5.2 The Actual Wax Layer Thickness at 6 Months of Migration Compared to the Layer Thickness Expected for Migration of All Wax Above the Solubility Limit

	Shore A Durometer	**Exterior Elastomer Thickness (cm)**	**Migration Time A & B**	**A - Actual Layer Thickness (micrometers)**	**B - Actual Layer Thickness (micrometers)**	**Expected Layer Thickness (micrometers)**	**Real Thickness at 6 months as a percentage of Expected**
1	55	2.022	6 & 9 months	**7.5**	**11.9**	62	**12**
2	55	2.022	"	**6.1**	**9.2**	62	**10**
3	55	2.540	"	**9.2**	**12.0**	78	**12**
4	55	0.919	"	**7.8**	**11.0**	28	**28**
5	55	1.179	"	**7.3**	**9.0**	36	**20**
6	70	2.540	3 & 6 months	**2.9**	**4.3**	78	**6**
7	70	0.919	"	**2.0**	**3.4**	28	**12**
8	70	1.179	"	**2.8**	**3.6**	36	**10**

For straight line growth, a 50% growth would be expected for the blooms measured first at 6 then again at 9 months and 100% growth for the blooms measured first at 3 then again at 6 months. The actual bloom growth is shown in Table 5.3. With the 55 durometer specimens, average growth was 41% with a range of

24% to 60% growth, close to the 50% expected for a linear increase in bloom. Obviously the limiting layer thickness has not yet been reached by the 55 durometer bearings because the growth of the blooms is not slowing significantly in any of the five specimens. With the 70 durometer specimens, average growth was 49% with a range of 28% to 68% growth, less than the 100% expected for linearly increasing bloom. Thus the 70 durometer bearings must be reaching the equilibrium layer thickness. This demonstrates the strong influence the stiffness of the elastomer has on the limiting layer thickness, assuming the same type of wax and level of wax loading was used in the two elastomer compounds.

Table 5.3 Percent Increase in Wax Layer Thickness from 6 to 9 Months for 55 Durometer Bearings and from 3 to 6 Months for 70 Durometer Bearings

	Shims	**Durometer**	**Elastomer Thickness (cm)**	**Migration Time Allowed**	**Percent Increase in Thickness**
1	3	55	2.022	6-9 months	**160**
2	3	55	2.022	"	**151**
3	Plain	55	2.540	"	**131**
4	6	55	0.919	"	**141**
5	6	55	1.179	"	**124**
6	Plain	70	2.540	3-6 months	**150**
7	6	70	0.919	"	**168**
8	6	70	1.179	"	**128**

5.5 Comparing Bearing Bloom Thicknesses to Layer Thicknesses Suggested for Ozone Protection

Several authorities have put forward bloom thickness required for adequate ozone protection. One source concludes that bloom thicknesses as small as 0.5 micrometers can attain suitable protection against ozone attack if undisturbed [28]. Another source states that for a concentration of 1000 pphm, a wax layer on the order of 1 micrometer is sufficient protection [25]. Considering that average ground level ozone concentrations are between 0 and 5 pphm with slightly higher values in the spring and early summer and in areas with heavy air pollution, 1 micrometer is probably an upper limit on the thickness required to protect a bearing.

In thin rubber products, a wax loading of 1 to 3.5 phr and more is common [17]. This is understandable because in these thinner elastomer products, this loading creates blooms between 0.5 and 3 micrometers which provide sufficient but not excessive bloom which ensures proper protection. But for articles like bearings with larger volume to surface area ratios, these wax loading levels appear to be too high. In these products, the supply of wax to the surface area is too great and loadings of around 2 phr appear to be leading to excessively high wax blooms of 2 to 12 micrometers.

It is important to note that these bearings were not stressed during storage. Studies suggest that compressive stresses will increase the rate of wax bloom [28]. Thus the layers developed in the unstressed bearings are not as thick as the bloom expected to develop in the same amount of time in normally stressed bearings. On the other hand, these bearing samples were not exposed to the elements or abrasion. Both of these would decrease the layer thickness by eroding away the wax bloom. Studies suggest that when eroded or scraped off, the wax bloom will repair itself with the same initial rate of growth if sufficient wax remains inside the elastomer

[11]. Sufficient has not been defined but probably refers to a quantity of wax available in the elastomer capable of producing a bloom in excess of two times the limiting layer thickness. If this definition is correct, all the eight specimens had more than the necessary amount of wax available.

5.6 Conclusions on Wax Bloom Rate and Layer Thickness

The wax seemed to migrate from the "typical Texas" bearings at a reasonable rate as compared to migration rates found by other researchers. After 6 months, it appeared that the 70 durometer bearings were beginning to reach their limiting layer thickness. After 9 months of observation, the 55 durometer bearings had not yet reached their limiting thickness. The 55 durometer were, however, seeing more total migration at 6 months. All this is as expected since it has been shown by researchers that a stiffer elastomer reaches the limiting layer thickness more quickly but sees less overall migration [See *Chapter 3*].

The loading of the elastomers created blooms of 2 to 12 micrometers, more than enough to protect against ozone attack. It seems that a loading of around 2 phr is too high for rubber items such as bearing pads which have such a large reservoir of wax from which to draw.

CHAPTER 6

SURVEYS ON THE PROBLEM OF BEARING PAD SLIP

6.1 Nationwide Survey

Between April 1994 and April 1995, a nationwide survey was conducted, attempting to document the extent of the problem of bearing pad slip in the nation. The information was gathered from the transportation departments of the fifty states and the District of Columbia. The survey was conducted in two phases. In April 1994 a letter was sent to the Department of Transportation (DOT) maintenance divisions along with a questionnaire regarding bearing pad slipping. A photo of bearing pad slippage in Texas (Figure 6.1) was enclosed to assist the engineer in recognizing the phenomenon. The letter and questionnaire are reprinted in Appendix B. After most (44) responses were received, a second survey with additional questions was conducted over the phone. During the phone interviews, the DOT maintenance and design departments were contacted. In addition, answers were elicited from states not responding to the earlier questionnaire. The questions asked in the phone interviews are also found in Appendix B. The results of the two part survey are shown in table format in Appendix C.

Figure 6.1 Photo of Bearing Pad Slip in Texas

As shown in Figure 6.2, 28 states (55%) reported having problems with bearing pad slippage. Because many states regularly fix the bearing pads to the bridge or pier cap regardless of dead load to shear ratio, this number may be mis-leading. The frequency with which states connect the bearing to the bridge or pier cap is shown in Figure 6.3. The survey unearthed various methods for connecting the pad. Many states insert a dowel through the pad which attaches to the girder and/or bearing seat. Some states epoxy the pad to the abutment. Several vulcanize the pad to steel shims which are then bolted (or welded) to the girder or bearing seat or to steel shims inserted in either the pier cap or the girder. When the states which frequently connect their bearings to the bridges are removed from the data, the percentage of states experiencing slipping is much higher. If the thirteen states frequently connecting their bearings are excluded, 63% of the respondents (24 states) report having slipping. See Figure 6.4.

Figure 6.2 - States Reporting Bearing Pad Slipping

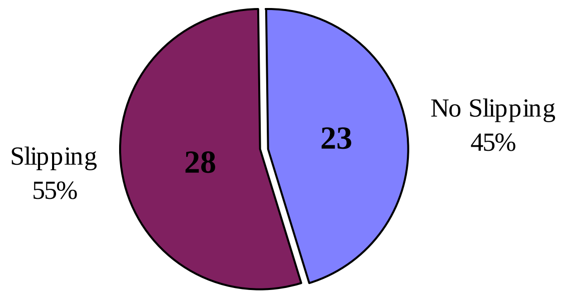


Figure 6.3 - States' Use of Connection between Bearing and Bridge

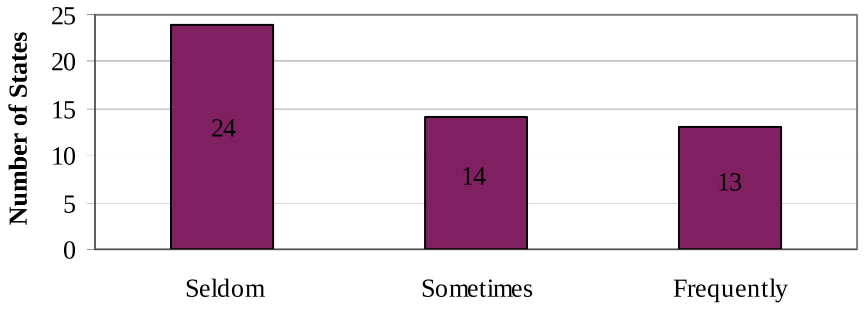
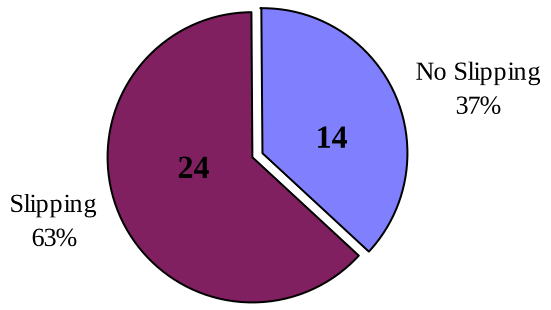
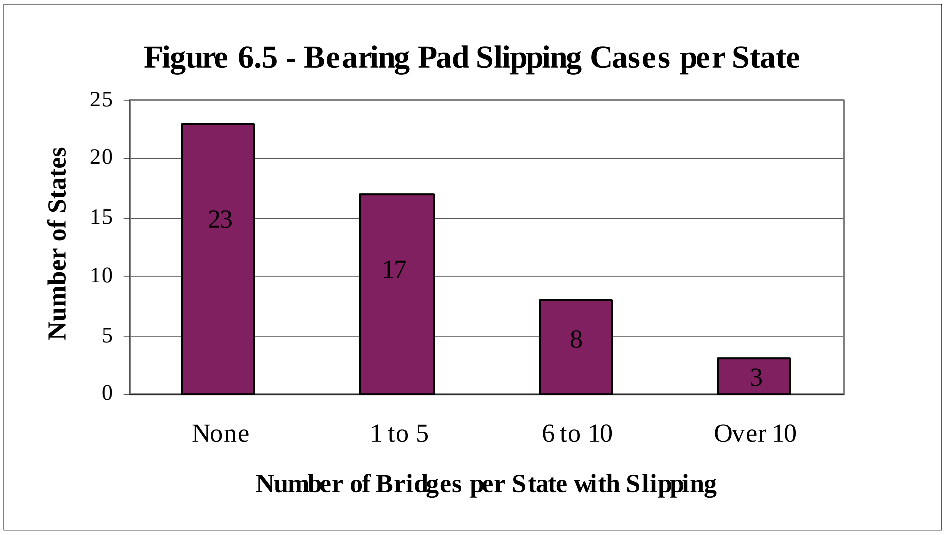


Figure 6.4 - States with Slipping Excluding States Which Frequently Connect Bearings to Bridges



Of the 28 states that experienced slipping, 22 states felt that the slip was structurally significant. While most did not experience more than 3" to 6" of movement, some states had bearing pads that experienced excessive movement caused by walking out of the elastomeric bearing pads. These states had to raise the bridges to place the bearing pads back in their proper locations.

The number of reported or known bearing pad slipping cases in each state is shown in Figure 6.5. Only three states, Texas, Florida and Idaho, were aware of more than 10 cases of slip. The vast majority of state reporting slipping were only aware of one to three cases.

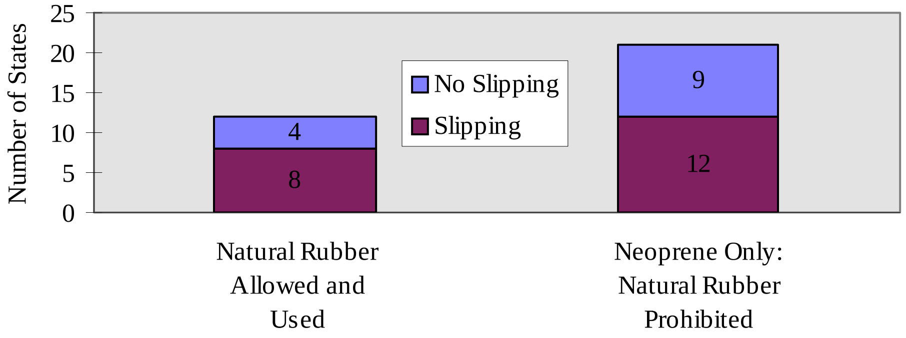


States were asked if they allowed the use of natural rubber in their bearing pads. Most were unsure and so responses were verified during the phone interview. To cross-check the responses, several nationwide bearing manufacturers were asked to list the states that used natural rubber. The final responses are shown in Figure 6.6. Oddly enough, many states with low temperature concerns such as Michigan and Minnesota prohibited the use of natural rubber.

Figure 6.6 - Use of Natural Rubber in Bearing Pads

Finally, an attempt was made to see if a correlation could be found between states with slipping problems and states which used tapered bearings or natural rubber. Of the 11 states which currently use tapered bearings, 7 states (64%) experienced slipping. Because this was so close to the percentage of all states experiencing slip (63%), it was inconclusive. The results of the effort to relate natural rubber to slipping are shown in Figure 6.7. All states which allowed natural rubber bearings but seldom used them were excluded from the graph. This analysis was also inconclusive. A significant percentage of the states that prohibited natural rubber still experienced slipping. Many states attributed the bearing pad movement to improper design, incorrect placement, large roadway skews or long bridge spans. Because of the number of other factors causing slippage, the survey could not conclude that natural rubber pads were more susceptible to slipping.

Figure 6.7 - Comparing Natural Rubber and Neoprene



6.2 Texas Survey

Since 1985, movement of bridge bearing pads has become a concern in the state of Texas. A district by district survey was conducted in the Spring of 1994 by TxDOT to study the problem. The letter and the questionnaire sent to the districts are reprinted in Appendix D. Information obtained during an earlier study also conducted for TxDOT Project 1304 was incorporated into the data obtained from the survey. The study was TxDOT Research Report 1304-1 entitled “Elastomeric Bearings: Background Information and Field Study” written by Bruce A. English, Richard E. Klingner and Joseph A. Yura at the Center for Transportation Research at the University of Texas at Austin, published June 1994. The combined results of the field study and survey are presented in Table 6.1 on the next page.

Of the 25 districts in Texas, 14 districts experienced slipping, 6 experienced none and 5 did not respond to the questionnaire. The 14 districts that reported slipping discovered movement in a total of 38 bridges. These bridges were constructed between 1955 and 1993.

Project 1304 targeted 13 of these 38 bridges for closer study and discovered several things. The bearing pad failures of the older bridges were predominately due to inadequate design. In the late 1960’s and early 70’s, TxDOT designed some bearings to lower standards which allowed higher compressive strains than current AASHTO provisions allow. In addition, elastomer layer thicknesses were inadequate for the movements of the bridge. Commonly, movements were larger than those designed for due to an increase in the span length caused by deck overlay or debris filling expansion joints or fixing ends. Of the newer bridges specifically studied by Project 1304, only one was found to have used Neoprene bearings. The bridge with Neoprene bearings, found in Amarillo, had used a 2.54 cm (1”) pad for a 98.9 m (300’) bridge, an obvious case of inadequate design. The rest of the newer bridges all used natural rubber bearing pads.

Thus slipping failures of older bearings were associated with inadequate design, maintenance or alteration of the bridges’ character and newer failures were linked to use of natural rubber. No connection was found between slipping and taper.

TABLE 6.1 Texas Districts’ Responses to Bearing Pad Slipping Questionnaire

DISTRICT	**Slipping**			**No. of Bridges**	**No. of Pads**	**Pad Movement**	**Taper**	**Natural Rubber**	**Year of Construction**
	Yes	**No**	**?**						
Amarillo	1			1	5	9"	0	0	1982
Atlanta	1			4	many	1" - out	1	?	'76,'80(2),'87
Austin	1			4	14	3" - out	0	1	'89(2),'90
Beaumont	1			3	many	4" - out	0,1	1,?	'76,'89(2)
Dallas	1			1	some	?	?	?	?
El Paso	1			1	some	out	?	1	1989
Fort Worth	1			4	many	.75" - 4"	0,1	0,1	'81,'82,'85,'90
Houston	1			8	many	1" - out	0,1	?	'56,'86,'88,'90, '91(2),'92,'93
Lubbock	1			1	some	0" - out	0	1	1988
Odessa	1			2	some	1.5" - 3"	0	0	'55,'65
Paris	1			1	some	4" - 6"	0	0	1977
Pharr	1			3	many	.5" - 2.25"	0	0	'68(2),'69
San Angelo	1			1	some	?	?	?	?
Yoakum	1			4	some	?	?	?	?
Abilene		1							
Brownwood		1							
Bryan		1							
Tyler		1							
Waco		1							
Wichita		1							
Childress			1						
Corpus Christi			1						
Larado			1						
Lufkin			1						
San Antonio			1						

CHAPTER 7

CONCLUSION: SUMMARY, RESULTS, RECOMMENDATIONS

7.1 Study Summary

This study accomplished four main tasks. First, the relevance of AASHTO ozone tests for bearing pad materials was determined. Second, the leachate which was believed to be facilitating bearing pad movement was analyzed; in addition, the layer thicknesses developed in typical bearings were measured and compared to required bloom thicknesses for adequate ozone protection. Third, the results of the surveys documenting the extent of the problem of bearing pad slip in Texas and around the country were presented. Fourth, an attempt was made to determine if natural rubber or tapered bearings were more susceptible to slipping.

7.2 Study Results

Results of the research of five other experimenters on ozone tests and bearing pad resistance to ozone attack is presented in Chapter 3, Section 4. Researchers conclude that the ASTM tests required by AASHTO for bridge bearing pad materials are neither accurate in assessing true behavior in the final product nor relevant to the product's performance. In addition to being inaccurate, the requirements of AASHTO are excessively stringent. The researchers agree that ozone attack is much slower and less damaging than indicated by tensile tests. They also found that the performance of a bulky product like a bridge bearing is not affected by ozone attack. The researchers conclude that ozone attack is not a serious concern for large, bulky products such as bearing pads and that bearing pads are "virtually immune to aging [28]."

The IR spectroanalysis in Chapter 4 showed that the leachate samples taken from the bearings of two Texas bridges were composed mainly of wax. The analysis also determined that the leachate did not contain any of the other substances suggested by the rubber manufacturers. In Chapter 5 it was found that the wax migrates at an expected rate from the "typical Texas" bearing, creating bloom thicknesses of 3 to 9 micrometers of leachate after 6 months. Researchers suggest that only 1 μm is necessary to protect rubber and that over 3 μm is excessive bloom. Thus, the loading of around 2 phr (parts per hundred of rubber hydrocarbon) used by the rubber manufacturers appears to be excessive when used in a bulky item such as a bearing pad.

In Chapter 6, we found 55% of the states (or 28 states) were aware of problems with bearing pad movement in their state. If the states who frequently connect their bearings against movement are excluded, we find 63% of the states (or 24 states) were aware they had experienced problems. Only Texas, Florida and Idaho knew of more than 10 slipping cases in their state. A total of 22 states felt the bearing pad movement they had experienced was structurally significant. An attempt to correlate the use of natural rubber or the use of tapered bearing pads with slippage were inconclusive. Because many states attributed the bearing pad movement to improper design, incorrect placement, large roadway skews or long bridge spans, the survey could not conclude that natural rubber or tapered bearings were more susceptible to slipping. The Texas district survey was more conclusive showing older bearing pad slipping was caused by problems with design, alteration and maintenance and newer bridge bearing movement was related to the use of natural rubber.

7.3 Recommendations to TxDOT

The results of this study indicate that for the long-term economic benefit of the state of Texas, the following recommendations arising from the study should be adopted. The ASTM ozone test requirement for the elastomeric material should be considered inaccurate and a less stringent test adopted. The test could simply be a modification of the ASTM test using atmospheric instead of elevated temperatures and perhaps using lower ozone concentrations. Although the researchers suggest ozone degradation of bearing pads will not affect performance and is not a major concern, the warning should be given that if the exterior elastomer layer is thin, there is the possibility of ozone-induced cracking exposing the shim. Once the steel is exposed, corrosion may degrade the integrity of the bearing. Thus adequate protection against ozone cracking is absolutely essential.

The use of natural rubber in bridge bearings should be continued if certain stipulations are met, namely prohibiting the use of wax in the rubber. Because it is not known what wax layer thickness could be allowed that would not induce walking, it would not be safe to allow the use of *any* wax loading, no matter how small. Further experimentation is needed to assess the influence of the different variables in producing wax bloom. The most important variables seem to be the amount of wax loading as a percentage of elastomer layer thickness producing bloom, applied compressive and shear strain, elastomer modulus or durometer, and temperature. Natural rubber should not be banned since it performs better at low temperatures, is periodically significantly cheaper than Neoprene due to fluctuations in the rubber market, and appears to have no greater chance of slipping if a proper wax loading is used by the rubber manufacturer.

APPENDIX A

Infrared Spectra of Antiozonates

A.1 IR Spectrum of *p*-Phenylenediamine

A.2 IR Spectrum of *N*-Dimethyl-*p*-phenylenediamine

(Wavelength in microns and Wavenumber in cm^{-1} vs. % Transmittance)

APPENDIX B

B.1 Nationwide Mail Survey Letter and Form

Survey Sent in the Mail to the DOTs of 49 States (excluding Texas)

B.2 Nationwide Phone Survey Form

Survey Conducted over the Phone of the DOTs of the 49 States

B.1 Nationwide Mail Survey Letter and Form

April 26, 1994

Dear Sir or Madam,

The Texas DOT and the Federal Highway Administration are sponsoring a research project at the University of Texas at Austin to study the problem of excessive movement of elastomeric bearing pads under bridge girders. Recently in Texas, natural rubber bearing pads (especially those with a taper) have been "walking out" from under their girders. In our research to date, it appears that wax used for ozone protection in the elastomer is the major contributor to bearing pad movement.

Our research project consists of lab experiments and field tests. But at this point, we would also like to examine if this phenomenon is occurring in other states and to document to what extent bearing pad movement is a nationwide problem.

If you would please answer the following questions, it would be a great help to our research project and the solution of this problem. [If you would rather have individual districts within your state fill out the questionnaire, please copy this survey and send it to them. If you would like to gather the data from the districts yourself to study the problem within your own state, please mail us copies of the results.] It would be helpful to the overall solution and greatly appreciated if we could receive your reply in the next two months.

If you have any questions or would prefer to call rather than answer the survey by mail, please contact Dr. Joseph Yura at (512) 471-4586. Also, if your state has already investigated the problem of bearing pad movement, we would be interested in hearing from you and would encourage your call. Since it is the objective of this research to resolve the problem of bearing pad movement, we would also be happy to send you the result of our research which will be completed in a year and a half.

Thank you for your help.

Sincerely,

Rose Chen,
Graduate Research Assistant

c.c. Enclosed is a photo showing typical movement of a bridge bearing pad in Texas.

BEARING PAD QUESTIONNAIRE:

Circle Yes or No.

Yes No 1. Have any bearing pads in your state slipped from their original position? [Usually when slipping has occurred, black skid marks can be seen on the girder or abutment as shown in the photo.]

Yes No 2. Are the bearing pads used in your concrete bridges designed with **positive connections** between the bearing pad and the concrete surface? [Positive connections may consists of dowels, vulcanized plates, steel bracing, etc. connecting the pad to the abutment or girder.]

Yes No. 3. Do you restrain the movement of your pads by placing a steel or concrete frame around the bearing pad?

Yes No 4. Does your state use tapered bearings?

Yes No 5. Does your state use natural rubber pads? [To differentiate between natural rubber and neoprene, take a sliver of the pad and attempt to light it with a match. Neoprene will extinguish when the flame is removed. Natural rubber will stay lit even when the flame is removed until you extinguish it.]

Yes No 6. Do you normally check for slipping of bearing pads during routine inspections?

If you answered **No** to questions 1 **and** 2, please fill out your name and address on the next page and thank you for helping us with the survey. If you answered **Yes** to questions 1 **or** 2, please continue.

7. Does your state use mostly natural rubber or neoprene (polychloroprene) rubber in your bearing pads? Does your state allow the use of natural rubber in your bearing pads?

8. How many of the bridges in your state (or district) have encountered slipping of the bearing pads (given also as a percentage of total if possible)? How far did the pads move on each bridge?

9. Were the pads that slipped tapered? To what degree (slope) were they tapered?

10. Were the pads that slipped natural or neoprene rubber?

11. Do you know the type of ozone protection used in the manufacture of the elastomer of the bearings that slipped: Paraffin wax, microcrystalline wax, a blend? Other antiozonates?

12. What measures has your Department of Transportation taken to prevent further slip?

If possible, please attach the plans for a typical bridge that has slipping bearing pads.

Please attach any further comments.

Check here if you would like a copy of the results of our research ________

Name, address and phone number of the person who can be contacted
if further information is necessary:

Name: ____
Position: ____
Address: ____
____
____
Telephone Number: ___________________________________

<u>Please Mail to:</u>
Rose Chen, Dept. of Structural Engineering, University of Texas at Austin, 10100 Burnet Rd.,
Bldg. 24 (Ferguson Structural Eng. Laboratory), Austin, TX 78758
THANK YOU

B.2 Nationwide Phone Survey Form

STATE: ____

PERSON CONTACTED: ____

____

NOT SLIPPING AND SLIPPING

1. Does you state allow or specifically prohibit the use of natural rubber in bearing in the specifications?

2. Why do you use positive moment connections or restraining devices?

3. Does you design procedure check for a slipping load?

4. Do you know the name and phone number of the bearing manufacturer you use most frequently?

SLIPPING ONLY

1. Of the bearings that you said moved, would you say they slipped out of position due to excessive shear deformation or that they walked, moving more than an inch or 2 or 3?

2. Was there any structural significance to the slip?

3. Did you replace the bearings that were moving? If so, did you keep some of the bearings that walked out? Could we have these bearings?

4. Did the bearings move because the slip load was exceeded, possibly due to unforeseen excessive expansion due to debris filling expansion joints, etc.?

APPENDIX C

Results of the Nationwide Survey

APPENDIX D

D.1 Texas Districts Survey Letter

Survey Letter Mailed to the 25 Districts of the Texas DOT

D.2 Texas Districts Survey Form

Survey Form Mailed to the 25 Districts of the Texas DOT

D1. Texas Districts Survey Letter

April 20, 1994

Dear Sir or Madam,

The Texas DOT and the Federal Highway Administration are sponsoring a research project at the University of Texas at Austin to study the problem of excessive movement of elastomeric bearing pads under bridge girders. As you know, natural rubber bearing pads (especially those with a taper) have been "walking out" from under their girders. In our research to date, it appears that wax used for ozone protection in the elastomer is the major contributor to bearing pad movement.

We realize that you may have already alerted the department as to the specific bridges that have encountered problems. We would, however, ask you to list all the bridges in your district **again**, in order to make sure that the current list is completely thorough. The questionnaire will ask you to report on each bridge that is encountering bearing slipping, including such things as:

1. Bridge Number
2. Bridge's State Contract Number
3. Date of Contract Letting (month and year)
4. Name of Prestressing Supplier

These will help us track down some variables we are interested in studying.

Thank you for your help.

Sincerely,

Rose Chen

D2. Texas Districts Survey Form

BEARING PAD QUESTIONNAIRE:

1. Have any bearing pads in your district slipped from their original position? [Usually when slipping has occurred, black skid marks can be seen on the girder or abutment.]

If so, please list them on a separate sheet including:

1. Bridge Number
2. Bridge's State Contract Number
3. Date of Contract Letting (month and year)
4. Name of Prestressing Supplier

Also, please try to answer for each bridge:

5. How far the pads moved.
6. If the pads that slipped were tapered and if so to what degree (slope).
7. If the pads that slipped were natural or neoprene rubber. [To differentiate between natural rubber and neoprene, take a sliver of the pad and attempt to light it with a match. Neoprene will extinguish when the flame is removed. Natural rubber will catch the flame and hold it even when the flame is removed.]
8. What measures has your district taken to prevent further slip?

2. Describe any positive connections between the bearing pad and the concrete surface used in your district. [Positive connections may consists of dowels, vulcanized plates, steel bracing, etc. connecting the pad to the abutment or girder.] Do you use these connections because of slipping of the bearing pads?

Please attach additional comments.

Name, address and phone number of the person who can be contacted if further information is necessary:

Name: ____

Position: ____

Address: ____

____

____

____

Telephone Number: ____

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