

Special Adhesives for Rubber Bonding

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Introduction

This paper deals with the special adhesives and conditions required to produce strong rubber-tearing bonds. Such bonds are termed "maximum performance adhesive bonds" and are characterized by 100% coverage of the substrates with elastomer after failure of the test specimen. Further, the required force to separate the elastomer from the adherend should be a reasonably high value. Nominal values are related to the properties of elastomer being bonded and the method of testing.

A brief review will be given describing the bonding systems for unvulcanized elastomers. The major emphasis, however, will be placed on adhesives and conditions for bonding of vulcanized elastomers.

Discussion

First, let us review the history of the use of organic adhesives for bonding of elastomers to metal. Since early 1900, and until the late 1940's, the brass-plating process was the most widely used system for bonding of elastomers to metals. Now, however, organic adhesives are steadily replacing the brass-plating process throughout the world. Brams¹ estimated that by early 1957, only 20% of the rubber-to-metal bond assemblies produced in the molded goods industry in the United States were made by the brass-plate process. This percentage was decreased to approximately 15% by 1960. The current world picture reflects the same decline. Another authority has estimated that brass plating is employed in the molded goods industry—30 to 40% in England, 15 to 20% in France, and 30 to 40% in Germany. The rate of decline of brass plating abroad has been somewhat slower because their industries were the strongholds of brass plating and, also, they are conditioned to slower production rates and more troublesome processing.

The principal reasons for this decline of brass plating popularity were as follows.

1. Low tolerances both in elastomer compounding and brass compositions. Buchan cited these difficulties in his recent book, *Rubber to Metal Bonding*.² He stated that only certain brass compositions can be employed and to these particular brasses, only specific rubber qualities may be vulcanized if a consistently high level of adhesion is to be maintained."

2. Other limitations included lack of reproducibility due to plating inconsistencies, poor layover characteristics and potential bond failure due to electrolytic and galvanic decay.

3. Finally, the most significant factor in this decline was the introduction of new organic solvent-based adhesives.

The shortcomings and subsequent decline of brass plating have been reviewed. Now, let us discuss the evolution of today's high-strength organic adhesives.

The first adhesives which were developed had certain shortcomings as might be expected with new products. These limiting features included narrow processing limits, relatively poor layover properties, poor corrosion protection, and limited bonding versatility.

This situation was well summarized by Gerstenmaier.³ He stated that "no universal method or no all-purpose cement has been developed, therefore, each combination of materials presents its own problems and resultant bonding procedures." These limiting features prompted research on the fundamentals of adhesion by adhesive suppliers and rubber-bonding companies.

Alstadt⁴ set forth his theories of adhesion and the concept that new and useful adhesives systems could only be produced through creative research and the synthesis of unique polymers and cross-bridging agents especially designed for elastomer-to-metal adhesive use. Out of this research, guided by these theories, emerged a series of com-

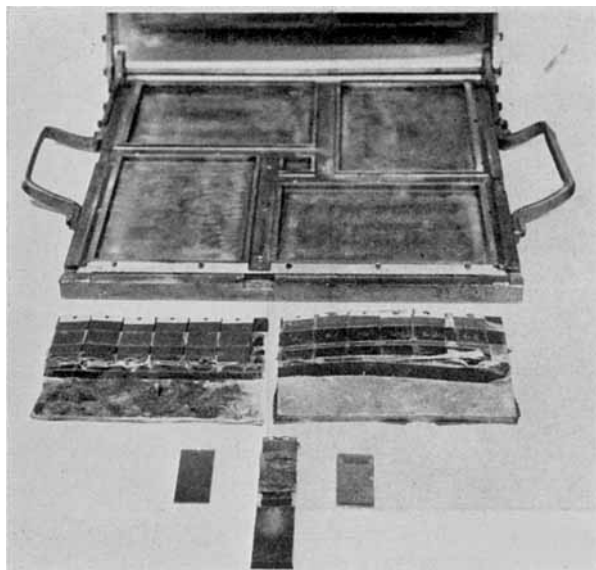


Fig. 1. Mold and flat test specimens.

pletely new adhesives. Other products of this research were unique surface cleaner treatments for metal.

For the first time, a single adhesive system was available which produced rubber-tearing bonds over the entire spectrum of olefinic elastomers. Processing latitudes were enlarged. A prime coat used with this adhesive produced a combination which had an environmental resistance superior to any adhesive system yet developed. These products have contributed greatly to the wide acceptance of organic bonding agents for elastomer-to-metal applications.

Today, several companies offer adhesives which will produce high strength bonds to unvulcanized elastomers. These adhesives vary in their processing requirements and bonding latitudes. Adhesive users should contact these suppliers and select an adhesive system which gives them the most satisfactory end product.

Adhesion Testing

Before starting a discussion of adhesives and bonding systems, the testing methods commonly employed to determine the degree of adhesion on bonded test specimens should be reviewed briefly. These tests are all destructive tests. There is no known reliable nondestructive test for evaluating bonded elastomer products.

Adhesion of elastomer to metal bonds is usually determined by a 90° peel test (ASTM D429-58

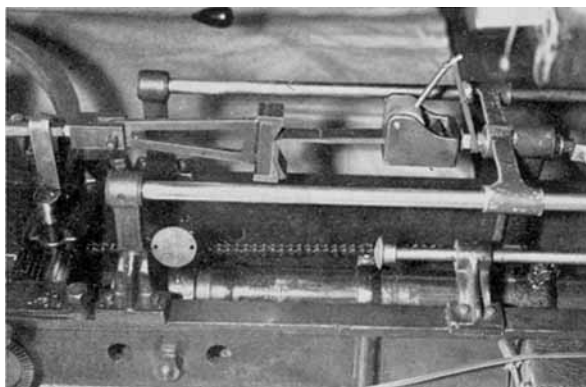


Fig. 2. Ninety degree peel test (ASTM D429-58 method B).

method B). The force required to peel the 1 in. wide x $\frac{1}{4}$ in. thick strip of rubber from the metal is expressed in pounds per inch of width. The per cent elastomer remaining on 1 sq. in. of the metal is an indication of the quality of the bond. A 100% coverage of thick rubber is the maximum obtainable by this test.

The mold and flat test specimens used in this test are illustrated in Figure 1. The bonded specimens are pulled at an angle of 90° (Fig. 2). It has been found that an angle of 45° (Fig. 3) gives more reproducible results and this modification has been proposed to the D-11 Committee of ASTM.

Painter⁵ devised a new conical test to force the failure to occur at the elastomer-metal interface, thus measuring the ultimate or intrinsic adhesion of the bond. This conical test method is far more reproducible than the 90° or 45° peel tests.

The mold and conical test specimens are illustrated in Figure 4. Figure 5 is a cross-sectional view of the test specimen with conical adhesion areas. The stress distribution of conical or wedge-shaped test specimens is shown in Figure 6. As the specimen is loaded, the shear stress is maximum at the points and initiates failure which progresses down along the sides until it is complete. Examples of test specimens after failure are illustrated in Figure 7.

Another common adhesion test is the ASTM button or tensile test (ASTM D429-58, method A) in which unvulcanized elastomer is molded into a cylindrical shape between circular metal discs. The specimen is pulled in tension and the force required to produce bond rupture is recorded in pounds.

Painter used a modification of this button test to compare the effectiveness of his conical

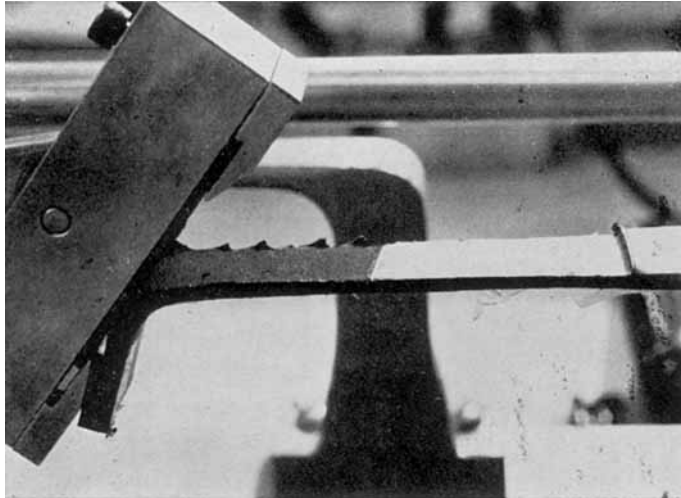


Fig. 3. Forty-five degree peel test.

method. A cross section of this modified test specimen and typical failures are represented in Figures 8 and 9.

One test for vulcanized and unvulcanized elastomer-to-elastomer adhesion is a modification of the elastomer-metal peel test (ASTM D429-58, method B modified). In this test, 1 in. wide strips $\frac{1}{8}$ in. thick are peeled apart at a 180° angle, usually at 2 ipm. (Fig. 10). Bond strength is recorded in pounds per inch of width.

The dead load wraparound peel test (ASTM D413-19) is used to determine adhesion or friction strength of vulcanized elastomer to fabric, elastomer, and metal. This test is also useful in determining ply adhesion or adhesion between layers.

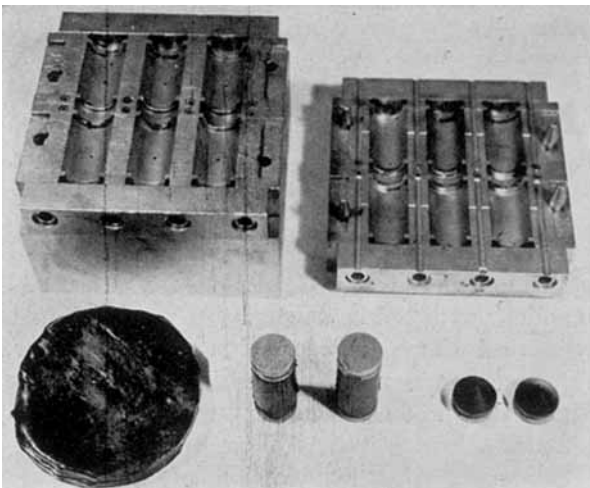


Fig. 4. Mold and conical test specimens.

Unvulcanized Elastomer-to-Metal Bonding

With proper use of present-day high-strength organic adhesives, it is possible to produce strong rubber-tearing bonds between a variety of olefinic elastomers and a wide variety of metals and other rigid adherends.

The more common elastomers include nitrile, neoprene, natural, styrene butadiene rubber (SBR), and butyl. They constitute the major part of the elastomers used today in the molded goods industry. The largest volume used is SBR or SBR-natural blends.

There are three important links in the chain of a maximum performance adhesive bond. These three links are surface treatment, adhesive, and elastomer. Improper processing or selection of any of these three links will weaken the chain. Failure will always occur at the weakest link or interface.

Your adhesive supplier will suggest the best combination of links for building the strongest bond. He will suggest mechanical or chemical surface preparations for the adherends to be

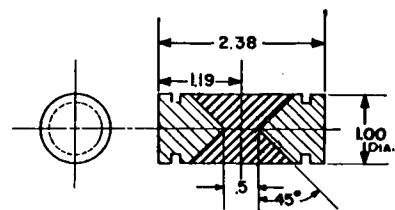


Fig. 5. Test specimen with conical adhesion areas (type III)

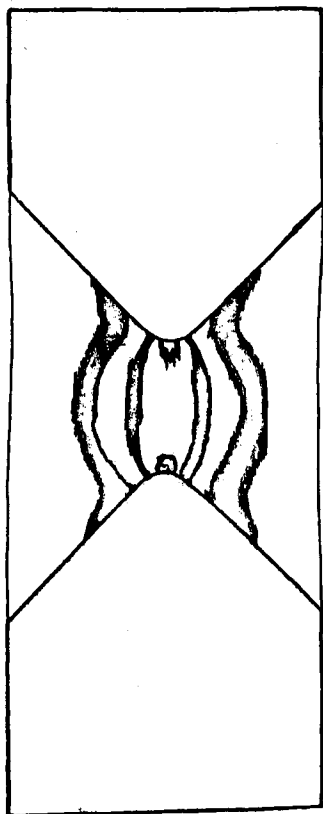


Fig. 6. Lines of constant shear stress obtained on photo-elastic specimen.

bonded. Mechanical abrasion (blasting) and degreasing are most universally used on metals though chemical treatments are becoming more popular.

Though some of today's adhesives have exceptional bonding latitude, certain compounding ingredients have been found to cause weak bonds. These include certain ester-type low-temperature plasticizers, highly paraffinic or highly aromatic

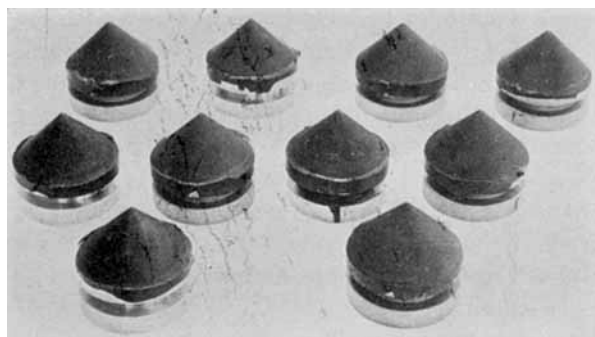


Fig. 7. Photograph of type III test specimens after failure.

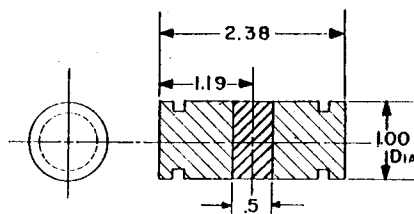


Fig. 8. Test specimen with flat adhesion areas (type III).

oils, copper-bearing accelerators, etc. These compounding ingredients which affect adhesion have recently been summarized by DeCrease.⁶ DeCrease also determined that certain polymer ratios affect the bondability of elastomers. He has rated this degree or ease of bondability in terms of a "bondability index" (Fig. 11). Nitrile rubber, the most polar, is readily bonded and is given an index of 10. At the opposite end of the scale we find butyl, which is a low polarity compound, is difficult to bond, and has an index of 1. In some instances, controlled levels of adhesion are desired, for example, in the wire and cable industry. According to Stout,⁷ the adhesion level can be controlled and varied from rubber tearing to "free stripping" by dilution and other modifications to the bonding sequence.

A detailed discussion of elastomer-to-metal bonding, using these modern adhesive systems, has recently been prepared by Gallagher.⁸ Gallagher's article includes a history of bonding, a description of bonding sequence, and a multitude of typical adhesion data. Another recent review of rubber bonding systems appeared in Buchan's book, *Rubber to Metal Bonding*.²

The less common unvulcanized elastomers, such as silicones, fluorocarbons (Viton and Fluorel), chlorosulfonated polyethylene (Hypalon), polyurethanes (castable and millable), and poly-

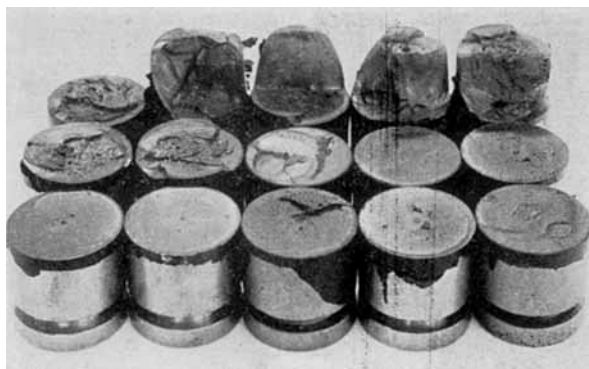


Fig. 9. Photograph of type II test specimens after failure.

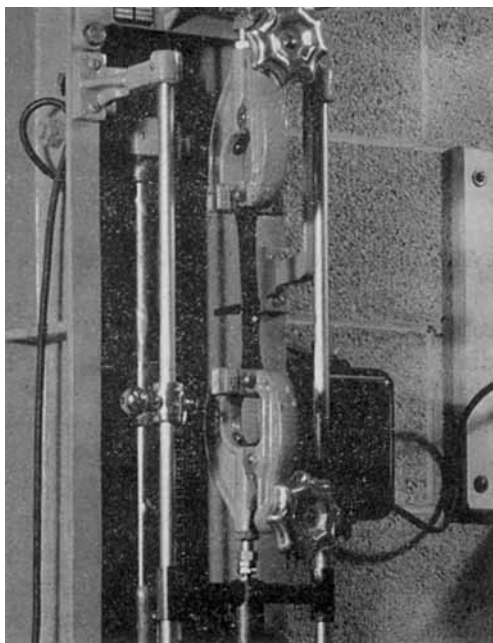


Fig. 10. One-hundred eighty degree peel test.

acrylate present a slightly more difficult task for adhesives. Unlike the olefinic members of the unvulcanized elastomer clan, no single adhesive system will produce rubber-tearing bonds to this entire group of polymers. There are adhesives which will bond most of these; however, each elastomer usually requires slightly different bonding adhesives and processing. Your adhesive supplier can suggest the best bonding system for your individual application.

The polyacrylate polymers and very low durometer (usually oil extended) elastomers are not easy to bond with existing adhesives. It is anticipated that recently developed new adhesives will improve the bonding of these elastomers.

Vulcanized Elastomers

Bonding of vulcanized elastomers to produce rubber-tearing maximum performance bonds is a difficult task. No adhesive system has yet been devised which will consistently produce a bond to vulcanized elastomer equivalent to that produced to unvulcanized elastomer.

There are several good reasons why this is true. Consider the nature of a vulcanized elastomer and the effects upon adhesion.

1. The elastomer is a crosslinked polymer which is sometimes compounded to give solvent

and other environmental resistance. Polymers of this nature are difficult to solvate and obtain any degree of a "sorbed" bond. It is also more difficult to obtain any degree of chemical crosslinking to a reacted polymer.

2. The surface is relatively smooth and non-mobile. These are difficult to bond since they display difficulty in wettability and conformity. The nonmobility or low plasticity also limits diffusion.

3. The surface may be contaminated with mold release agents or plasticizers and compounding ingredients which may have migrated, bled, or bloomed. These contaminants make wetting with the adhesive unpredictable and provide slippery, weak boundary layers.

How do we attack these problems—usually by brute force tactics. As in all good adhesion practices, removal of oily, dusty materials from the surfaces is the first step. A solvent wipe and/or rubbing with a clean dry applicator is standard practice. Next, the nonmobile, chemically cross-linked surface must be modified to permit wetting and some sort of mechanical and chemical foothold for the adhesive to function. Four methods have been used with varying degrees of success. These include mechanical abrasion or buffing, cyclizing, isocyanate treatment, and chlorination. The chemical treatments, it is thought, actually cause a reversion, depolymerization, or oxidation of the surface of the elastomer. In addition, they increase the surface roughness slightly (possibly with the exception of cyclizing, which actually hardens the surface if excessive treatment is encountered).

Cyclizing is probably the oldest technique for modifying the surface of vulcanized elastomers. Various concentrated acids have been used, with sulfuric being used most frequently. As mentioned above, care must be taken not to overtreat the elastomer as the surface actually hardens and becomes quite brittle. Cyclizing was used with the old Redux system in England and produced excellent bonds. The Redux system uses a liquid phenolic in conjunction with powdered polyvinyl formal. Cyclizing plus a neoprene or nitrile-phenolic adhesive is the basis of the cycle-weld process. Cyclized rubber cements are produced in the Vulcalock process. This system never attained very good bonds and was never used to much extent.

Isocyanates used alone as a pretreatment for bonding and in conjunction with chlorinated

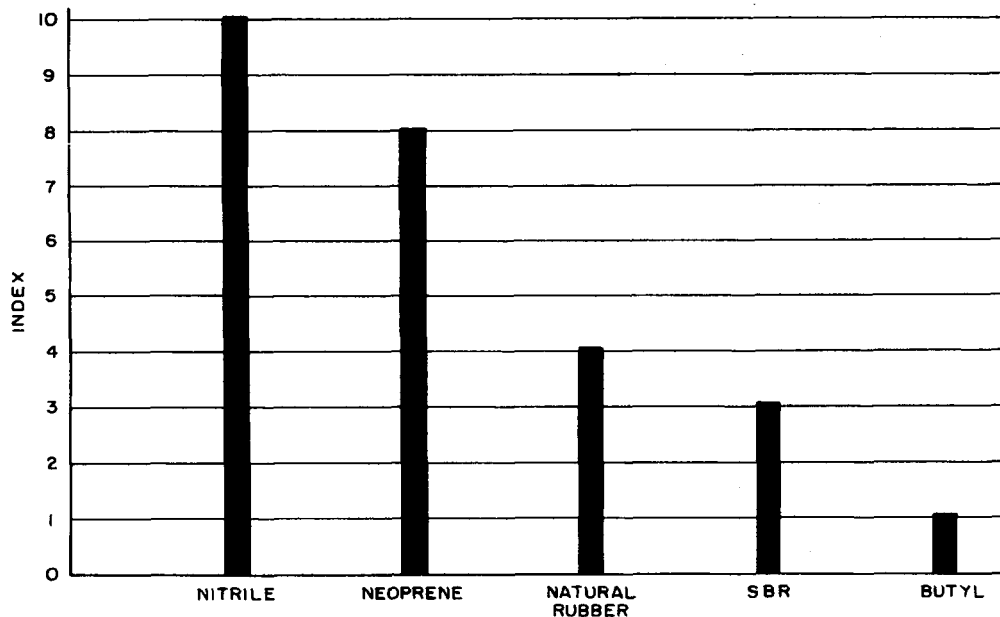


Fig. 11. Bondability index of common elastomers.

elastomers have been used particularly in Germany and England. The two more common systems are known as Desmodur R and Vulcabond TX. Cyclizing, Redux, and Isocyanate bonding systems have been adequately described in several places in the literature.^{2,9}

Chlorination of vulcanized elastomer surfaces to promote adhesion to coatings was reported by du Pont.¹⁰ We have found that this chlorination treatment markedly improves the bondability of vulcanized olefinic elastomers. The solution is freshly mixed before treatment. The formulation is as follows:

Materials	Parts by volume
Water	100
5.25% sodium hypochlorite (Clorox)	3.0
37% hydrochloric acid	0.5

All of the Clorox is added to the water and the acid is added slowly to this mixture with stirring. Chlorine gas may be bubbled into water to give an equivalent treatment solution. Care should be taken to use these systems in a ventilated area as free chlorine is evolved. The standard treatment sequence includes immersion of the vulcanized elastomer in the above solution for 1 to 3 min. This is followed by a rinse in running cold or hot water. Hot water will facilitate drying and speed up processing. This is followed by drying in forced air. Treatment time may be varied to suit the elastomer. High durometer stocks, 80 to

90 Shore A hardness, may require more than 3 min., while softer stocks in the 30 to 40 Shore A range are adequately treated in 1 min. or less. Highly filled neoprene elastomers may require a more concentrated treatment solution, i.e., 6 parts or volumes of Clorox per hundred parts of water. Treatment time of up to 6 min. may also be required for such stocks.

Several adhesive systems were previously mentioned which have or can be used in conjunction with these surface modification systems. Many of the adhesives normally employed to bond unvulcanized elastomers can be used with the modified surface of the vulcanized elastomer. Usually, however, a change in the coating weight, and/or use of a tie cement is required to adequately bridge the gap of hard elastomer to hard adherend. The adhesive now must play the major role in stress relieving the bonded assembly during cure.

Newer polymer-based adhesives are now on the market. They are continuously being evaluated in an effort to produce a high-strength permanent bond to vulcanized elastomers.

Some fabricators are successfully using epoxy-based adhesives for this application. These bonds can be cured at room temperature over a period of several days or for shorter times at elevated temperature, i.e., 1 to 2 hr. at 160°F., 1 hr. at 300°F.

It is of particular interest that the epoxy system which is cured with a polyamide is well suited for this task. This is undoubtedly due to the fact

that the polyamides are good adhesives and wetting agents in their own right. As a matter of fact, they are probably the main contributors to adhesion in this application. The epoxy in this case is probably functioning as the thermosetting agent or hardener. Further, the polyamides offer the unique advantage of providing variable modulus adhesives simply by changing the mixing ratio with the epoxy. In other words, the modulus of the elastomer can be matched, if desired, by the bonding agent. The main disadvantage of this system is that it is two-part and requires premixing. However, recent advances in technology indicate that one-part low-temperature-curing epoxy polyamide adhesives will probably be available in the near future.

Vulcanized silicones have not yet been mentioned. There are several systems which produce adequate bonds. Proprietary adhesives, tie cements, and combinations of primers and RTV silicones perform quite well.

In some instances, cements derived from the elastomer to be bonded, combined with heat-activating accelerators, have performed well for bonding a variety of vulcanized elastomers. At best, however, the bonds are only fair.

Several experimental adhesives have produced high strength bonds to vulcanized elastomers without resorting to brute force tactics. These unique adhesives will pave the way for future bonding agents which will perform equal to those for unvulcanized elastomers.

Future Bonding Agents for Elastomers

Production of maximum performance bonds to all of the present-day unvulcanized elastomers is nearly a reality. We would like to say they are a 100% reality, easy to process, and foolproof with minimal scrap losses—we cannot. Certain elastomers under certain environmental conditions pose a problem for the fabricators and adhesive supplier. We are confident, however, that through the cooperative efforts of compounders, processing personnel, and adhesive suppliers we can consummate the marriage of these elastomers with all types of adherends.

One further challenge is presented to the adhesive supplier—to provide adhesive systems which will not only process at higher and lower temperatures in shorter times but also have increased environmental resistance at ever-broadening service temperatures. New polymers are being engineered

to meet these new requirements and they will require special adhesives to bond them and match their performance.

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Synopsis

Special adhesives for bonding of unvulcanized and vulcanized elastomers are discussed. Major emphasis is placed on adhesives and conditions for bonding of vulcanized elastomers. The decline of brass plating is reviewed. Various methods of adhesion testing are discussed and illustrated. Available organic polymer based adhesives will produce high strength bonds to a wide variety of unvulcanized olefinic elastomers. A single coat adhesive has been developed which provides "maximum performance adhesive bonds" to a variety of unvulcanized elastomers. Factors affecting bonding and "bondability index" for the common elastomers are described. The bonding of vulcanized elastomers is a more difficult task. Present adhesives require mechanical or chemical modification of the surface of the elastomer. Brute force tactics used in conjunction with epoxy-polyamide, phenolic-polyvinyl formal, or nitrile-phenolic systems have performed well in some applications. The quality of these bonds, however, does not equal those produced to unvulcanized elastomers. With cooperation of the users, the adhesive suppliers are developing newer, more effective products to meet the challenge of the advanced polymers and increasingly severe environments in which they are used.

Résumé

On discute les propriétés d'adhésifs spéciaux pour la fixation d'élastomères vulcanisés. On insiste surtout sur les adhésifs et les conditions de fixation d'élastomères vulcanisés. Différentes méthodes d'essais d'adhésion sont discutées et illustrées. Des adhésifs basés sur les polymères organiques existants donneront lieu à une adhésion très forte sur une large variété d'élastomères oléfiniques non-vulcanisés. On a développé un adhésif à une couche, qui donne une fixation maximum pour une large variété d'élastomères; les facteurs influençant la fixation et l'index de "fixabilité" pour les élastomères communs sont décrits. La fixation d'élastomères vulcanisés constitue une tâche plus difficile. Les adhésifs actuels nécessitent une transformation mécanique ou chimique de la surface de l'élastomère. Les méthodes de "force brutale" employées avec les systèmes époxy-polyamides, phénoliques-formol polyvinyliques ou nitrile-phénoliques se sont comportés de façon satisfaisante pour

certaines applications. La qualité de cette fixation n'égalé toutefois pas celle produite dans le cas des élastomères non-vulcanisés. En coopération avec les usagers, les fournisseurs d'adhésifs développent des produits neufs et plus effectifs pour répondre à la concurrence des nouveaux types de polymères et aux exigences de plus en plus sévères.

Zusammenfassung

Spezialklebstoffe für die Verklebung unvulkanisierter und vulkanisierter Elastomere werden besprochen. Das Hauptgewicht wird auf Klebstoffe und Verklebungsbedingungen für vulkanisierte Elastomere gelegt. Der Rückgang der Messingplattierung wird erörtert. Verschiedene Methoden zur Adhäsionstestung werden diskutiert und erläutert. Klebstoffe auf Basis bekannter organischer Polymerer erzeugen Verbindungen hoher Festigkeit mit einer Vielzahl unvulkanisierter Olefinelastomere. Ein Einschichten-

Klebstoff wurde entwickelt, der "Klebeverbindungen maximaler Wirksamkeit" mit einer Vielfalt unvulkanisierter Elastomere liefert. Faktoren, welche die Klebefähigkeit beeinflussen, sowie ein "Klebefähigkeits-Index" für die üblichen Elastomere werden beschrieben. Die Verklebung vulkanisierter Elastomere ist schwieriger durchzuführen. Gegenwärtig verfügbare Klebstoffe erfordern mechanische oder chemische Modifizierung der Oberfläche des Elastomere. "Gewalt"-Methoden haben sich mit Epoxyd-Polyamid-, Phenolharz-Polyvinylformal- oder Nitril-Phenolharzsystemen bei einigen Anwendungen bewährt. Die Güte dieser Verbindungen kommt aber der bei unvulkanisierten Elastomeren erzielten nicht gleich. Unter Mitarbeit der Verbraucher entwickeln die Klebstoffhersteller neue, wirksame Produkte, die den Anforderungen der weiter entwickelten Polymeren und zunehmend schwierigeren Anwendungsbedingungen besser entsprechen können.