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RUBBERY ACRYLIC POLYMER ADHESIVES

BY

STEVEN WALTER

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN ENGINEERING SCIENCE

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey
1973

ABSTRACT

This study shows how rubbery acrylic polymer adhesives can be used to adhere rubber substrates to each other. Two substrate rubber compounds were used. A styrene-butadiene copolymer and a styrene-acrylonitrile copolymer. The adhesives were homopolymers based on polybutyl acrylate and poly2-ethyl hexyl acrylate.

Two reference standards were used. The first was commercial rubber based, solvent cements. The second was commercial acrylic solution polymers. All experimental work was compared to these standards. An attempt was made to optimize the adhesive components, as well as the adhesive application procedures and curing conditions.

A primer coating consisting of polymer, monomer, and catalyst was applied to the rubber prior to the application of the adhesive. This primer coating had to be cured at 375°F for twenty minutes. It was also found to be advantageous to swell the rubber with the monomer to a slight degree before the application of the primer coating and the subsequent bonding of the rubber.

The optimal adhesive was applied to the primed surfaces and cured at 375°F for three hours. The bonding strengths generated were 15 lbs./sq. in. for a lap shear sample and 41 oz./in. for a peel strength sample. These

values were $1/3$ the strength of the commercial rubber solvent cements and twice the strength of the commercial solution acrylic polymers.

APPROVAL OF THESIS
RUBBERY ACRYLIC POLYMER ADHESIVES
BY
STEVEN WALTER
FOR
DEPARTMENT OF CHEMISTRY
NEWARK COLLEGE OF ENGINEERING
BY
FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

SEPT. 1973

ACKNOWLEDGMENTS

I would like to acknowledge the kind assistance of Professor William Snyder, who contributed his time and knowledge to the completion of this project. I would also like to acknowledge the very kind assistance of Mr. Robert Bernarth and Mr. John Phelps of B.F. Goodrich Chemical Co., who kept me supplied with the substrate rubber that was needed for my experimental work. Last, but not least, I wish to thank my wife, who gave me the moral support that I needed to complete the degree for which I am writing this thesis.

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INTRODUCTION

As defined by Louis H. Sharpe(1), an adhesive is a substance capable of holding materials together in a useful manner by surface attachment. An adhesive is always part of a structure or composite. It does not function as a separate entity, but influences and is influenced by the materials it contacts.

It is usually not possible to select an adhesive by using a tabular display of adhesive classes and characteristics. There are great variations of properties within each type of adhesive, a great overlap of properties, between types, and a lack of industry wide classification and standardization.

However, four general considerations should be observed.(2,3) The first consideration is the materials to be bonded, including the chemical nature of the surfaces, the chemical nature of the adhesive, and the condition of the surfaces. The second is the conditions of service to which the bond will be subjected. These conditions include extremes of temperature, pressure, impact, corrosive elements, and other environmental conditions. The third factor is a combination of adhesive properties and production requirements. There must be ample time between application and bonding, the desired tack, the desired curing or drying time, etc. The last

is the cost of the adhesive material. However, the cost per gallon is not the only factor, since solids content, the amount necessary for adequate coverage, reduction of rejects, and efficient application are also important.

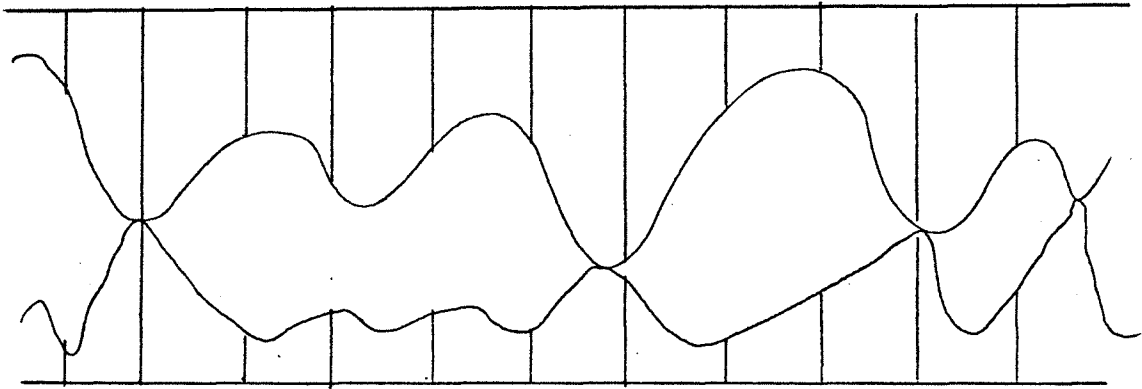
Although no work has been done in the area, acrylic ester polymers possess certain properties that would make them good adhesive materials for rubber to rubber bonding. These polymers are inherently tacky and produce films with very good flexibility. This film flexibility would lend itself very well to the bonding of materials like rubbers. Polyacrylic esters also have good long term aging properties. The reason for the lack of work using polyacrylic esters for the bonding of rubber substrates is the prohibitively high cost of the acrylic ester monomers.

THEORIES OF ADHESION

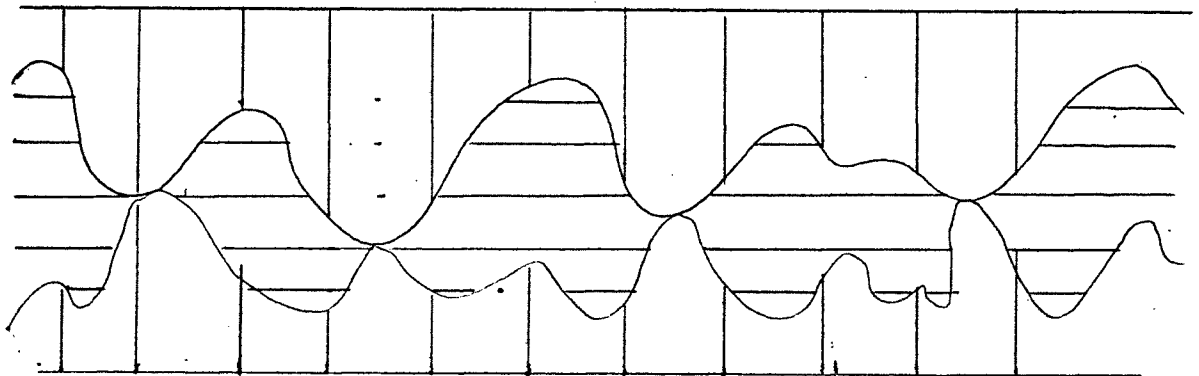
The actual term "adhesion" can be considered to have two different connotations. To a physical chemist, this refers to the molecular forces acting across an interface. To an adhesives chemist, this term refers to the forces required to separate two surfaces bonded together by an adhesive material. These forces depend on factors other than the molecular forces across an interface.(4,5,24)

Most surfaces may seem quite smooth on a macroscopic scale, but even the most highly polished surfaces are extremely irregular on a microscopic scale. When the surfaces are brought together without the presence of an adhesive material, there is very little actual contact between the surfaces(see Fig. 1). For this reason, the total forces of attraction are very small and the surfaces are easily separated. The purpose of an adhesive is to fill at least some of the surface irregularities. In this way, it acts as a bridge between the surfaces.(6)

The adhesive must be initially fluid enough to fill all the surface irregularities, but it must solidify enough to withstand the applied forces it will encounter in service. This solidification can be accomplished by solvent evaporation; cooling, as in the case of hot melts; and polymerization.



contact between two surfaces



two solids joined by an adhesive

Fig. 1 Microscopic View of an Interface
(See Ref. 4)

The viscosity of an adhesive is its most important property from a physical viewpoint.(37) It must be low enough so that the adhesive takes up at least the larger voids in the substrate surfaces, and yet must be high enough so that the adhesive will stay where it is applied. When the voids are filled there results an increase in the molecular contact and the area of bonding. The presence of voids is extremely undesirable since they are points of stress concentration, which can lead to premature bond failure.

In general, the degree of contact between the substrate surfaces is proportional to the viscosity of the adhesive; i.e., lower adhesive viscosities lead to higher bond strengths. However, reducing the viscosity of certain types of adhesives can lead to increased stress concentration in the final bonded joint. In the case of hot melt adhesives, stresses are introduced on cooling due to the differences in the coefficients of thermal expansion of the adhesive and the substrate. These stresses tend to increase when the adhesive viscosity is decreased by increasing the application temperature. Solvent cements, whose viscosity is reduced by increased solvent concentration, can develop increased stress concentrations by leaving an increased number of voids when the solvent evaporates. From this it can be seen that adhesive

viscosity must be lowered enough to make void filling easy, but excessive lowering of viscosity may lead to a lowering of the strength of the final bond.(4)

The surface energy of the substrate has a great bearing on the strength of the final bond. It affects the degree of contact between the adhesive and the substrate. The contact angles of the adhesive and the substrate are useful measures of the degree of contact achieved. The contact of pure liquids and low energy, smooth surfaced substrates, including many polymers, have been determined. A linear relationship exists between the cosine of the contact angle, θ , and the surface tensions of a homologous series of organic liquids. This observation led to the idea of a critical surface tension of wetting, γ_c .(28,29, 30,31,32) This quantity represents the intercept of the line $\cos \theta = 1$ with the extrapolated plot of $\cos \theta$ vs. surface tension. A liquid with a lower surface tension than γ_c will spread on a given substrate. This critical surface tension of wetting is a useful quantity since it gives a readily determined indication of the surface energy of a polymer(see Fig. 2).

Since real surfaces are irregular, it is necessary to consider how the surface energy of the substrate affects the filling of irregularities. This can be estimated by the Washburn-Rideal Equation(4), which relates

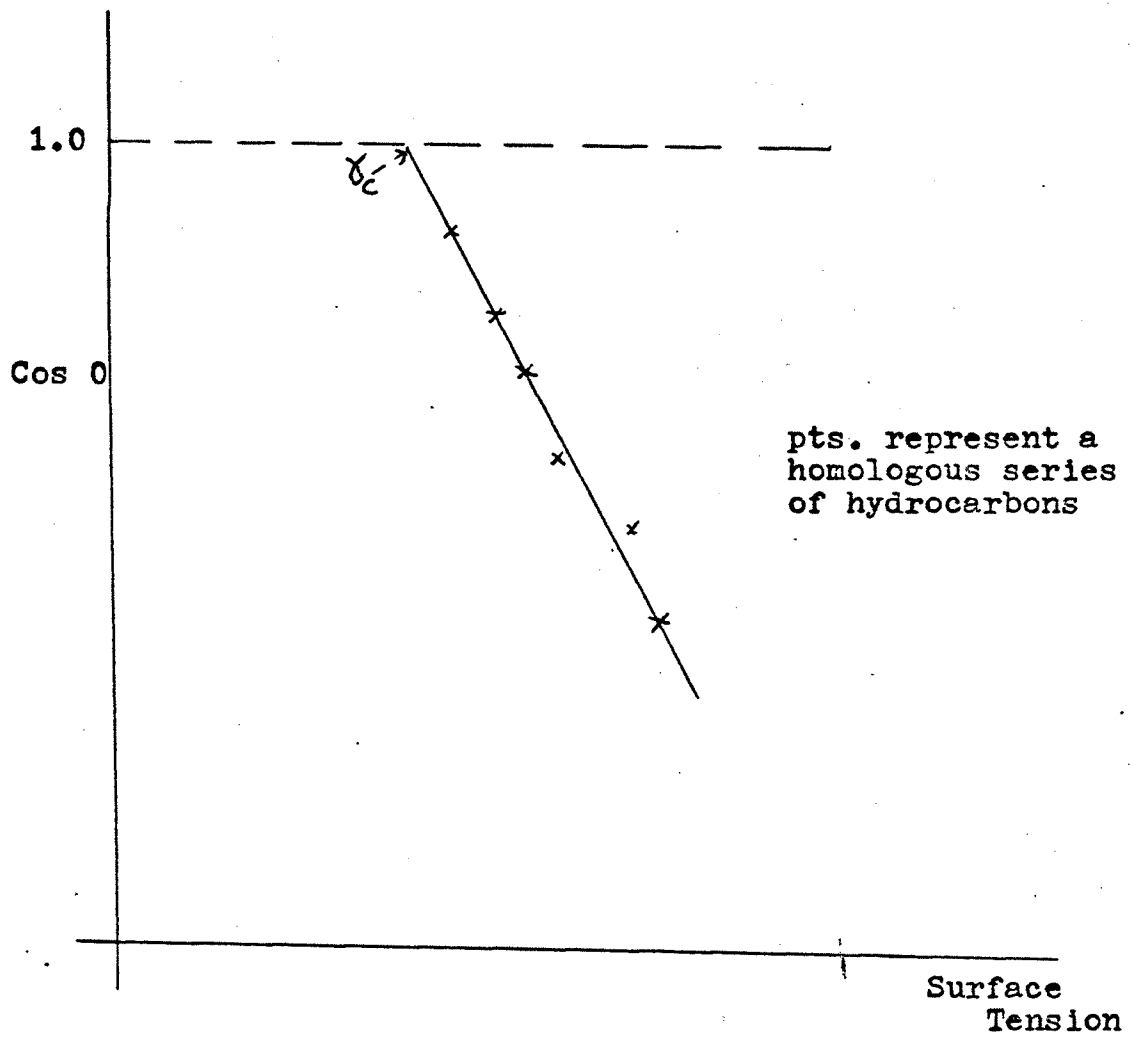


Fig. 2 Relation Between Cos θ and Surface Tension
(see Ref. 4)

the time t of the filling of a capillary of radius r and length x with a liquid of viscosity n , surface tension γ , and contact angle θ . The equation is:

$$t = \frac{2nx^2}{\gamma \cos\theta r}$$

As can be seen, the contact angle not only affects the final degree of contact, but also the the rate which wetting is achieved.

It is necessary that there be good contact between adhesive and adherend. If a region of relatively low strength exists in the adhesive layer, joint strength will be poor even if there is good adhesive-substrate contact.(7) If this region of low strength exists right at the interface, it is termed a weak boundary layer, It can originate in either the adhesive or the adherend. Possible causes of weak boundary layers are impurities arising during the polymerization process, a low molecular weight tail in the polymer, the presence of additives(plasticizers, antioxidants, etc.), external processing aids, and surface contamination(contact angle measurements show how easy it is to transfer mold release agents to polymeric surfaces).

Surface pretreatments are necessary to satisfactorily bond a number of polymers. Some of these surface pretreatments are solvent stripping, sanding, flame treatment, and electrical discharges. Many pretreatments involve an

oxidizing action and it is assumed that their success is due to an increase in the surface energy of the substrate. Evidence indicates that these oxidative surface treatments introduce polar groups onto the surface of nonpolar polymers.(35,36) However, the situation is complicated because an oxidizing pretreatment may alter not only the surface energy of the substrate, but the surface geometry as well.(4)

The stress-strain characteristics of both the adhesive and the adherend have a great affect on the strength of the final bond. If the substrate is very rigid compared to the adhesive material, the mechanical properties of the adhesive largely determine the strength of the final bond. If both the adhesive and the substrate are either rigid or flexible, the mechanical properties of both interact.(4) The properties of the final joint may differ considerably from the properties of the bulk material due to stress concentrations at or near the surface. Therefore, the strength of the joint is dependent on the strength of its weakest region.

The testing conditions can have a very great affect on the strength of an adhesive joint. Strain rate, temperature, humidity, thickness of the adhesive layer, and the type of test are all very important.(4) On the average, bond strength increases with increasing strain rate. It may increase or decrease with increasing temperature.

In shear and direct tension testing, the cohesive strength of an adhesive is decreased by increased temperature. This leads to a marked decrease in the strength of the final bond. Increasing the thickness of the adhesive layer adversely affects the bond strength when tested in shear or direct tension. It has been postulated that a thin adhesive layer tends to minimize stress concentrations.(4) Results obtained using different testing methods are not directly comparable. An adhesive which gives relatively high values when tested for peel strength, may give low values when tested in shear or direct tension. For example, flexible adhesives give high peel strengths (7 kg./cm.) despite low cohesive strengths, while giving low values in shear or direct tension(7 kg./cm.²). Epoxy resins have a very high modulus, so high bond strengths are obtained in shear or direct tension, and low strengths are obtained in peel tests. Also, peeling tests are important with flexible substrates, e.g., films; and shear and direct tension are important with rigid substrates, e.g., molded parts.

There are four generally accepted theories of the mechanism of adhesion.(8,9,10,20,52) The Mechanical Theory is the oldest and is widely regarded in Great Britain. The Adsorption Theory is the most widely regarded theory in the United States. The Electrostatic Theory and the

Diffusion Theory are both Russian in origin.

The Mechanical Theory stems from early work that was done for the aircraft industry that involved joints between wooden airframe components. In this theory there is a distinction made between specific adhesion and mechanical adhesion. It was suggested that in the case of wood or any other porous substrate, the prime factor in the strength of the bond is the imbedding of the glue in the pores and irregularities of the bonded surfaces. In other words, the adhesive has to key into the porosity. If this is true, then two factors become apparent: the first is that an increase in the surface porosity and irregularity increases the bond strength; the second is the adherend is stronger than the adhesive, so the joint strength is proportional to the film strength of the adhesive.

It is common knowledge in carpentry that a glued joint involving the end grain of a piece of wood is more liable to be a weak joint. The more open grained the wood, the weaker the joint. This can be seen in the following table which shows data based on the shear testing of maplewood bonded with a urea-formaldehyde resin glue at 5 PSI:

<u>Surface Quality</u>	<u>Shear Strength, PSI</u>	
planed	3120	roughness increases (8) ↓
sanded	2360	
sawed	2690	
combed	2400	

This shows that a smoother surface leads to a stronger

joint. In the case of wood, sanding and combing raise fibers in the surface and remove the softer material between. These raised fibers are damaged to a great extent. If these fibers are firmly incorporated into the adhesive bond, they can be removed from the bulk of the material by the application of a very small force. It is thought that surface cavities are not involved, since the adhesive would be kept out of them by trapped air.(8)

There is confirmatory evidence for this theory which stems from work done on experimental precast concrete air raid shelter components, during World War II. These components were molded in cavities lined with Portland Stone. It was found that on hardening, there was almost complete adhesion between the castings and the molds. This effect was traced to the similarity in size between the particles of cement and the natural pores in the stone. More complete analysis showed some chemical interaction, but there remained 90% of the bond strength that was mechanical in nature. It has also been found that there is mostly mechanical adhesion acting in the bonding of rubber to textiles. The bond strength in this case depends heavily on the number of textile fibers imbedded in the adhesive.

The Adsorption Theory depends mostly on surface forces to explain the phenomena that are observed. It is based on the assumption that adhesion is one property of a phase

interface where polar molecules or groups are oriented in an ordered way. The forces that are usually involved in this mechanism are van der Waals forces. A molecule large enough to contain a polar group and a non-polar group as separate entities orients itself when it approaches an interface where the dielectric constant changes. It sets itself up so the non-polar end is in the medium of low dielectric constant and the polar end is in the medium of high dielectric constant. This is basically the theory of adsorption and must take place if the theory is to be considered valid.(42,43,44)

It has been argued that this theory is impractical since space limitations in a solid adhesive would prevent this mechanism from operating and that thermal agitation would destroy this ordered arrangement. However, in practice adhesives are used in an easily deformable form.

If this theory were completely correct, there would be a direct correlation between the energy of adsorption and the strength of the adhesive bond. This is generally observed, but not often enough to form the basis of a precise and quantitative theory. Adsorption requires that an active molecule be preferentially deposited from a solution onto an adsorbing surface. This cannot be rigorously demonstrated.(8)

When two surfaces are brought into intimate enough contact for molecules to really approach and interact, van der Waals Forces start to act and the surfaces stick more strongly than the strengths of each of the separate materials. Therefore, one must arrange to get the materials close together over a really useful area. This is done by making the substrate surface roughness correspond on both faces. This essentially means that one surface must be a fluid. However, fluidity is not sufficient in itself. A viscous liquid with a large contact angle will not make effective contact, since it will bridge surface depressions and trap air. In this way, stress concentrations due to this large contact angle will become significant. A mobile liquid with a very small, or a zero contact angle, will spread easily, flow into crevices, and achieve true contact. Therefore, stress concentrations will approach zero.. From this it can be seen that wettability is of prime importance.

The Electrostatic Theory arises from two observations made during peel testing. The first was that the work expended to separate a film from a surface was of the order of 10^4 - 10^6 ergs/cm.². The second observation was that the adhesion of a film to a substrate was dependent on the speed at which it was peeled. Neither of these observations was consistent with any theory based on surface tension

effects. (45, 46, 47)

The basis of this theory is the idea of an electrical double layer being formed at the interface between two materials. The consequent coulombic attraction accounts for the adhesion and the resistance to separation. The theory begins with Paschens Law of Electrical Discharge:

$$V \propto lp \qquad \begin{array}{l} V = \text{potential} \\ l = \text{spark length} \\ p = \text{gas pressure} \end{array}$$

The substrate plus the adhesive are considered one plate of a parallel plate condenser, with the film being considered the second plate. This would lead to an electrical discharge on separation.

For a parallel plate condenser:

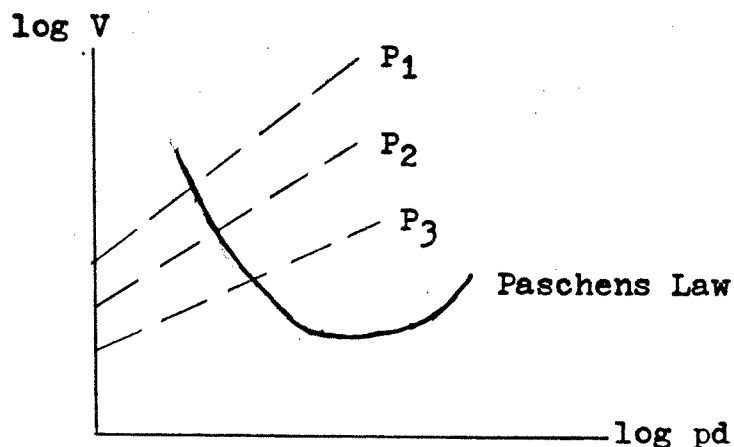
$$\text{Energy, } W = \frac{1}{2}eV = \frac{1}{2}cV^2 \text{ and } c = Ka/4d$$

$$V^2 = \frac{8\pi Wd}{Ka} = \frac{8\pi Wpd}{Kap}$$

e = total charge
 V = potential difference
 c = capacity
 K = dielectric constant
 d = plate separation
 a = plate area

Assume a value for W, then for various values of p, work isobars can be calculated relating potential difference and the quantity pd, which is the amount of gas between the plates. The isobars are then plotted on the same graph as the curve given by Paschens Law. Further, the energy

Fig. 3



of a condenser is given by the expression, $W = 2\pi\epsilon^2 d/K$ with ϵ = surface energy density. If the quantity d is eliminated by combining the two expressions for W , the following quantity is what results:

$$W = \frac{1}{2}V\epsilon$$

It was assumed that the energy, W , could be equated with the work of adhesion. The following is the data for the adhesion of PVC to glass in an atmosphere of Argon:

Atm. Pressure mm. Hg	Work of Adhesion erg/cm. ²	Discharge Energy	Charge Density
760	18	18	29
175	31	31	30
100	40	41	28
50	50	51	28

(48)

The constant value for the charge density suggests the soundness of the theory.

However, this theory has been criticized on two observations. An electrical double layer arises due to the different pressures of the electron gas within the two surfaces. The difference should be minimal, or zero, if

the two adherend surfaces are of the same material. This would suggest that adhesion should be least between identical materials, and increase as the materials become more and more different. Actually, the opposite is seen. In the case of rubber adhesives, the addition of carbon black should increase the materials electrical conductivity and cause the reduction in the adhesive properties due to charge leakage. The presence of a small amount of sulfur and the vulcanization process would not be expected to alter the contact potential and decrease the adhesive properties. Actually, the opposite is observed. Carbon black loaded rubbers retain their adhesive properties, while vulcanized rubbers lose them.

The Diffusion Theory is interesting in that it emphasizes the essential similarity in origin of the strength of an adhesive and the strength of the bulk material. The fundamental concept of this theory is that adhesion arises due to the interdiffusion of the adhesive and the adherend. This idea is applied principally to joints involving polymeric substrates, and is very difficult to apply anywhere else. It is based on the fundamental theories of high polymers, including the chain nature of the polymer structure with its inherent flexibility, And the ability of the polymer chains to undergo Brownian Movement on a sub-molecular scale.(49,50,51)

Adhesive molecules are more mobile than the molecules of the substrate, and play a more active role in the diffusion process. When an adhesive material in solution is applied to a substrate that is also soluble in the solvent, the substrate molecules will be loosened from the bulk and will also diffuse to an appreciable extent into the adhesive layer. On the whole, the clear cut boundary between the adhesive and the substrate disappears, either by one-way diffusion of adhesive molecules, or by two-way diffusion of adhesive molecules and substrate molecules. The boundary is replaced by a layer representing a gradual transition from one polymer to another. The point of most importance is that the mechanism of adhesion is changed from a two dimensional area process to a three dimensional volume process. However, this mechanism depends on the mutual solubility of the polymer molecules of the adhesive and the polymer molecules of the substrate.

LITERATURE SURVEY

Acrylic polymers are not only polymers and resins made from acrylic ester monomers, but also polymerizable derivatives of both acrylic and methacrylic acids, acid anhydrides, nitriles, and amides. The major constituent of most commercial acrylic materials is methyl methacrylate, since the homopolymers and copolymers of this material are best as far as the properties of weatherability, hardness, and clarity. Acrylics can be used as unmodified materials containing only the basic polymer, or as modified materials with other polymers present. Unmodified acrylics are transparent and extremely stable against discoloration. These properties give this material superior dimensional stability, desirable structural and thermal properties, and light weight.

Although acrylic polymer adhesives have not been used much for the bonding of rubber to rubber, they have found widespread use as specialty and pressure sensitive adhesives. The specific advantages of the acrylics are their lack of color and their good aging properties. These advantages tend to outweigh their high price. The two research objectives that have received the greatest amount of attention are the increase of tack without the loss of cohesive strength, and the lowering of prices. It is estimated that prices must be cut by 50% to make

acrylics competitive with natural rubber and other elastomers as general purpose adhesives.(11)

There are major differences in the chemical natures of acrylics and elastomers.(11,21) Most rubbers and elastomers are highly branched macromolecules with very high molecular weight. They possess very high residual unsaturation. They can also be readily tackified by the addition of plasticizers and tackifying agents without much loss of their cohesive strength. The acrylic resins are linear polymers containing short side chain branches. They are generally lower in molecular weight, and in the case of copolymers, have a wide molecular weight distribution. They are usually self-tackified by their short side chain branches, but they possess lower cohesive strength. When it is attempted to increase the tackiness of these materials through the use of external plasticizers, compatibility problems are encountered before any significant effect is observed.

If all acrylic polymers fitted this model, they would probably never have stirred any interest. This fortunately is not the case. It was found that certain acrylic monomers yielded homopolymers of higher tack than others. In the case of these materials, the mode of plastification is different from that previously outlined. Certain bulky ester groups enable the polymer chains to slide along one

another without the bulk material losing all of its cohesive strength.(11) A great deal of the acrylic polymers used for pressure sensitives over the last ten years have been based on butyl acrylate or its copolymers. These resins generally exhibit very good tack properties combined with an acceptable amount of cohesive strength.

Briefly, there are three ways of upgrading the cohesive strength of an acrylate adhesive. They are the use of cohesive monomers, the copolymerization of different monomers, and crosslinking.(11) The first two are never used alone. However, the use of tackifying monomers, like butyl acrylate, plus cohesive monomers is necessary due to the need for high tack adhesives in this application.

The most interesting method for increasing cohesive strength is crosslinking. This term is misleading since it implies the desirability of a rigid, three dimensional network of covalent bonds. Actually, this would be the least desirable condition of all, since it would lead to a material that is anything but a tacky and plastic polymer capable of forming a pressure sensitive film. What is wanted is a sufficient increase in the average molecular weight combined with a certain amount of branching. This would yield an adhesive that is resistant to high temperatures and solvents, and still have good tack properties.(11)

There are many theories relating to crosslinking. They all depend on the copolymerization of a monomer having strongly reactive functional groups with the basic acrylate monomer. Some modes go by self-crosslinking, while others depend on an added crosslinking agent. The reactions are usually brought on by the heating of the dried adhesive film, but can be initiated in solution, where they are catalysed by something as simple as a change of pH. (11)

Modern acrylic based adhesives utilize a combination of all three methods of cohesive strength enhancement. Using these techniques, it has been possible to produce polymers of consistently hightack, and 100 times the cohesive strength of original butyl acrylate polymers. However, there still remain certain shortcomings to be overcome. The most serious remaining problem is the difficulty of compounding with the acrylics, especially tackifiers. In some cases, the resulting adhesives still fall short of fully compounded rubber based solvent adhesives in their tack/cohesion ratio. (11)

Another industry research aim is the lowering of the prices of acrylic adhesives. The first step toward this goal was the introduction of vinyl acetate as a copolymer in pressure sensitive adhesives. However, the results have only been partially satisfactory. The performance of these copolymers with respect to aging and

color is drastically lower than acrylic homopolymers, while the resulting price decrease was still insufficient. Still, it was found that the copolymers exhibited good cohesive strength.

Research is still going on using special monomers which have different copolymerization reactivity ratios than the normal acrylic ester monomers. However, the preparation of homogeneous copolymers, free of monomer residue, is a very difficult matter.

A new line of research has not been done into the price or performance of an adhesive, but into the physical state. The attention of adhesives chemists is turning toward the area of pressure sensitive hot melts.(11) To clarify, the term "hot melt" implies nothing about the nature or type of adhesive, but that it is applied in the molten state.

These adhesives can be offered in the form of thick sheets, slabs, or drums that are hot filled at the production reactor. The materials are applied at temperatures ranging upward from 100°C by roller coaters or sheet extruders on paper, plastic films, etc. Before being wound on rolls, the finished product must be protected by a release paper. The economy of this type adhesive is the gain in productivity due to the extreme shortening of the

drying time. Instead of heating to evaporate a solvent, heat is applied to melt and maintain the adhesive at an elevated temperature.

There are various problems that are involved in the development of a hot melt adhesive. The adhesive supplier must sell these materials completely ready for use. Hot melts give rise to handling difficulties when it comes to compounding. This involves the metering of high viscosity products and their homogenation with additives. These are operations which at their best are lengthy and could be uneconomical for an adhesives user. A supplier has the choice of compounding, or designing a polymer having the desired combination of end use properties, e.g., tack, adhesion, and cohesive strength. If he decides to compound his adhesive, the risk is taken that the good aging and color properties of the acrylic will be lost on the addition of a tackifier.(11)

If the decision is made to synthesize, a supplier must decide what adhesive properties are desired. This problem stems from the fact that there are about as many pressure sensitive adhesives as there are adhesive problems. Careful market research is needed so as not to waste much time, effort, and money. A particular difficulty encountered with hot melts is to find a compromise between a workable viscosity in the molten state and good cohesive strength

at service temperatures. High cohesive strength is needed for all pressure sensitive adhesives, whether permanent or removable. Permanent types need it for high service temperature ratings, and removable types need it so there are no residual traces of adhesive left on the substrate after removal.

The polymers of a pressure sensitive adhesive must not only be completely fusible, but they must have a low melt viscosity at not too high a temperature. Apart from the danger of the thermal decomposition of the polymer, it would be uneconomical to apply a pressure sensitive hot melt adhesive at temperatures of the order of 200°C, since it is not necessary to bring about a rapid set by a big difference with room temperature. Also wanted is a low temperature gradient of viscosity. An example of a desirable span would be 1,000 poises at 100°C and 100 poises at 150°C. Without this property, slight variations in temperature would greatly affect the properties of the applied film.(11)

A natural prerequisite for hot melt adhesives is that they not discolor or alter their viscosity after a prolonged period of heating. This property makes it impossible to alter the cohesive strength of the polymer by thermal crosslinking, as is done with classical pressure sensitives in solution or dispersion. All cohesive strength must come from the monomers used, and it must be wholly built up

during polymerization. This stability requirement is a severe limitation on the choice of possible monomers. In the case of low priced adhesives, vinyl acetate used in large doses confers bad aging properties since it is particularly subject to hydrolysis. Therefore, this monomer must be ruled out for hot melts, because it causes rapid discoloration after only a short heating period, even if it is present at low percentages. The same applies to nitrogen containing monomers, like acrylonitrile or acrylamide.

Frequently an applications chemist is asked to characterize a new polymer. This new polymer might have adhesive properties. The exploratory research department might have prepared a few grams of it, and they found that it sticks to the wall of the flask or to the fingers. He must plan a test program to determine if this new material is marketable as an adhesive. This test program must yield the maximum amount of data with the absolute minimum use of material.

Many physical properties can be used as measures of the adhesive potential of a material. These properties include the modulus of elasticity, plasticity, T_g , molecular weight, contact angle with a given substrate, and cohesive energy density. The chemist will already know the properties that clearly indicate the magnitude

of the pressure sensitive adhesion of the polymer, and he wants to use simple tests that yield a large body of data relating to the end use. Five tests that he might use would be 180° peel, creep resistance, butt tensile tack, quick stick, and adhesive specificity.(12,13,14)

The 180° peel test is run on six inch lengths cut from a tape coated with the adhesive under test. The tests are run in triplicate according to The Pressure Sensitive Tape Council's peel adhesion test, PSTC-1. A ten inch per minute peel rate is called for, but the test can be modified to run at either two or ten inches per minute. A record is made of the high, low, and median readings. "Noise" on the test record reveals valuable information about the viscoelasticity of the polymer and the degree of wetting of the substrate. An assumption of adhesive failure can be made at the end of this test if the substrate appears free of residual adhesive when examined under low magnification.

Both Wetzel(33) and Hammond(34) have developed methods for measuring butt tensile tack. Hammond's method employs a test unit which is the more versatile of the two, since dwell time, separation rate, pressure, and temperature can be varied. In this method, one measures the viscoelastic behavior and adhesive proclivity of the polymer, while avoiding the complex mechanics of the 180°

peel test. A minimum of ten readings are taken and the face of the steel probe must be examined and cleaned after each reading.

Creep resistance is tested in accordance with PSTC-7 and is a practical measure of the viscoelasticity of the adhesive. The test is run at 50°C. The samples are run in triplicate and at the end of the test are examined to determine whether the mode of failure was cohesive or adhesive. Automatic timers are connected to the "shear adhesion" apparatus to stop the test the moment the adhesive fails.(12)

The adhesive property known as "quick stick" is dependent on pressure, time, and temperature. To illustrate, when an adhesive tape is brought into contact with a substrate it may behave in several ways. It may stick aggressively or sluggishly. The adhesive bond may develop immediately or it may develop over a period of time. The bond may develop faster in a warm environment than in a cold one. The adhesive consumers concept of quick stick is the adhesive will grab almost instantaneously under almost negligible load at room temperature. This property is measured using the Chang Test, PSTC-5. However, other tests may be used. They are the rotating cylinder method, inclined plane method, and curved track method. All these secondary tests suffer from the same shortcoming. The

cylinder and ball tend to become contaminated with residual adhesive at the beginning of the test. Therefore, it becomes a test of the adhesive's ability to wet and adhere to itself.

When adhesive specificity is studied, the determinations serve a dual purpose. They reveal how well the adhesive will bond to substrates that differ in their surface free energies. Also, they show how well the adhesive will key to a backing material used to make an adhesive tape. The basis of adhesion selectivity and the rate dependence of adhesion both rest on the same basic phenomenon. This is the wetting efficiency of the adhesive system on the substrate.(12) The test method in this case consists of a set of plastic probes that vary in their critical surface tensions of wetting. Each is touched to the adhesive film and it is determined which achieved the strongest bond.

Over the past few years adhesive applications have become very diverse.(15,16,17) Our new technology is putting adhesive materials to the test in very severe and hostile environments. At one time, the demand for a variety of adhesives was satisfied by compounding a few base polymers with various additives. These additives included fillers, tackifiers, plasticizers, etc. However, uncompounded polymers are replacing these compounded adhesives. In the field of pressure sensitive adhesives,

uncompounded polyacrylates and their copolymers, along with polyvinyl ethers have made strong inroads.

These single component systems have various advantages over multicomponent systems. There are no low molecular weight components that could migrate and form weak boundary layers. Since adhesive bond formation is a surface phenomenon, the minimizing of composition variations at the surface by minimizing of formulation components is very desirable. Also, uniformity is much easier to achieve in a one component system. The aging behavior of an uncompounded polymer is easier to predict than that of a compounded adhesive.(18)

In the end, if a manufacturer wishes to produce a one component, uncompounded polymer adhesive, there are many factors that have to be considered. They must be handled one at a time and reviewed in the light of the end use properties that are desired.

The choice of the monomers to be used is determined by the physical properties required. In the case of pressure sensitives, the main property required is tackiness, or the ability to form an adhesive bond almost instantaneously at low contact pressure. In this case, the tack can be thought of as the limiting property relating to the bond strength formed at zero contact pressure and at zero

contact time, and as such is not measureable. However, this allows tack to be considered away from the properties of peel resistance and shear resistance.(18)

Most polymers of sufficiently low molecular weight or sufficiently high plasticizer concentration are tacky. However, the mere presence of tackiness does not constitute pressure sensitivity.(38) The polymer should have sufficient cohesive strength to allow its removal from a smooth surface without apparent residue. The drawback to this requirement is it unnecessarily restricts the scope of adhesives. There is no single criterion for the behavior of an adhesive during the breaking of a bond. Many applications require a clean separation, but cohesive failure is not objectionable in other applications, and there is always the possibility of substrate failure. The adhesive must also resist peeling and support a load in shear. As can be seen, the application determines a multitude of properties.(19,22,23)

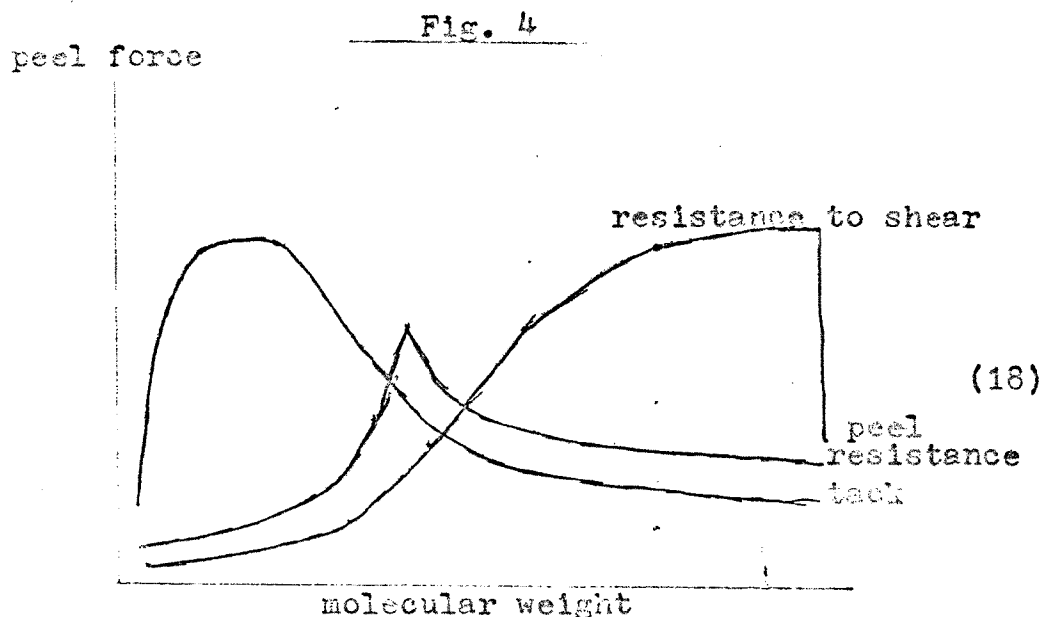
Most single component adhesives are copolymers of at least two or more monomers. Higher molecular weight acrylic monomers, from butyl acrylate up, yield pressure sensitive polymers. However, copolymerization enhances chain flexibility, increases the rate of chain relaxation, and improves tack and resistance to peel. The general rule for copolymerization is that monomers with bulky side

chain groups enhance the tack and peel resistance of a polymer without affecting its shear strength. Short side chain monomers form a harder and more rigid product.(39)

The method of polymerization has a great affect on the adhesive properties of the polymer. Acrylics polymerize easily by a free radical process in bulk, solution, emulsion, or suspension. However, bulk polymerization is rarely used. Emulsion or suspension being the main methods of polymerization. The main difference between emulsion and solution polymers is the emulsion polymers develop higher molecular weights. Emulsion polymers are desireable for coatings due to their high solids content, and low cost, nonflammable, nonpolluting carrier-water. The drawback to this technique is the required use of emulsifiers. These low molecular weight substances tend to migrate to the adhesive surface and cause loss of tack due to surface contamination. A current active area of research is the development of a polymerization technique without the use of surface active agents, or one using an emulsifier that can be removed during the drying process, or one which uses an emulsifier that is incorporated into the final polymer so it cannot migrate.(18)

The molecular weight and molecular weight distribution are the most important properties affecting the performance of a polymer. The performance characteristics of tack,

peel resistance, and shear resistance are affected most by changes in molecular weight. Tack measurements tend to increase with increasing molecular weight. The trend is a levelling at low molecular weights and then a decrease. This decrease continues or levels off with increasing molecular weight.(18) These quantities are obtained by either a probe or rolling ball technique, and the inconsistency is due to the measuring techniques which include either resistance to shear or peel components.



The tack properties at high molecular weights differentiate a good pressure sensitive adhesive from a bad. An adhesive whose tack is not sensitive to increased molecular weight or to an increase in intermolecular bonding indicates a polymer with high chain flexibility or a predominant effect of long side chains. A good pressure sensitive adhesive will show only a minor change

of tack with increased molecular weight or increased intermolecular bonding. If this were not true, large property variations would occur from batch to batch.

An adhesives resistance to peel changes shows a more complicated pattern than other properties. There can be a shift in the mode of failure cohesive to adhesive or near adhesive with increasing molecular weight.(13) The resistance of the adhesive to creep in shear can increase with increasing molecular weight, until the polymer becomes sufficiently rigid to cause stress concentrations at the interface. A good adhesive should show a wide shear resistance plateau as a function of molecular weight.

It is really not possible to exactly state the minimum molecular weight range for a pressure sensitive polymer. The physical properties of a polymer can be greatly affected by hydrogen and other types of non-covalent bonding. However, high molecular weight polymers are desirable for applications requiring high resistance to shear. It is easier to maximize this property without affecting the tack and peel resistance of an adhesive by increasing the molecular weight of the polymer and then crosslinking it.

The molecular weight of the polymer can be regulated by controlling the polymerization conditions. A slow

polymerization rate and low concentration of chain transfer agent give long polymer chains. The choice of the proper free radical catalyst, a low catalyst concentration, and low reaction temperatures all give low reaction rates. Higher molecular weight polymers are obtained by emulsion polymerization than by solution polymerization.(18)

Solvents are subject to chain transfer, thus causing lowered molecular weights. Therefore, it is desirable to use pure solvents having low chain transfer constants. In emulsion polymerization, the type and concentration of surface active agent can contribute to the properties of the polymer.

The addition of chain transfer agents can have a great affect on the final polymer. The molecular weight is appreciably lowered by the addition of these materials.(18)

Even minute amounts of mercaptans will lower the molecular weight drastically. A more sensitive and controllable way of varying the molecular weight is to vary the reaction conditions. One could increase the reaction temperature or the catalyst concentration, or in the case of a solution polymerization, start with a higher monomer concentration.

The effect of the molecular weight distribution is much more elusive than the effect of molecular weight. Resistance to creep comes from the high molecular weight

fraction. Tackiness and resistance to peel come from the low molecular weight fraction. Polymer blending serves to tailor the final properties of an adhesive from both of these fractions.(18)

As has been mentioned, covalent crosslinking is a convenient way of increasing the performance properties of an adhesive composition. Low crosslink densities are desirable, since high crosslink densities are possible only if carried out after the application of the adhesive tape. Intermolecular crosslinking increases the cohesive strength in the same way as an increase in molecular weight. Also, the improvement in creep resistance, even at low crosslink densities, can be quite significant.(40)

Crosslinking tends to decrease the free movement of the polymer chains in the bulk material. Since adhesive polymers are viscoelastic materials, this effect tends to increase the effect of the elastic component at the expense of the viscous component.(18)

The introduction of divinyl monomers is a well known method of obtaining a crosslinked polymer. Divinyl benzene and dimethacrylate monomers are the ones most widely used. The maintenance of a low concentration of these materials allows one to obtain the low crosslink densities needed to retain tack properties. A divinyl

monomer with the vinyl groups separated by a long carbon chain is introduced into the reaction. The reactivities of both vinyl groups are the same until one is incorporated into the polymer. At this time, the reactivity of the unreacted vinyl group is reduced. This means that at the end of the reaction, there remains a number of unreacted vinyl groups, which can, when exposed to higher temperatures, also crosslink. This stems from the fact that when exposed to elevated temperatures these groups and the whole polymer network are increased in mobility. In this way, the unreacted vinyl groups can come into very close contact with one another.(41)

Two basic avenues of approach can be used. The first is single functional groups can be introduced into the chain and then crosslinked with a multifunctional molecule added later that is capable of reaction with the polymer functionalities. The second is functionalities capable of reaction with each other are introduced into the polymer chain. Besides choosing the proper functional groups to be used, their distribution along the polymer chain is important. Choosing monomers that are as close as possible in their reactivities is helpful in assuring that the distribution of functional groups is uniform. The order of addition of the monomers into the reaction vessel can also help to control the functional group

distribution.(18)

Natural rubber, when used as the binder material in a solvent cement, makes an excellent adhesive. Public awareness of rubber cements began with the introduction of pneumatic tires. During attempts to devulcanize or regenerate rubber back to its natural state, it was noted that devulcanized rubber dissolved in benzene or naphtha formed an adhesive.(3) This cement had excellent adhesive properties and qualities that could not be obtained with crude natural rubber. The use of reclaimed rubber for adhesives is very high, since the demand for adhesives increased at a faster rate than the production of synthetic materials.(3)

There is a variety of natural rubbers which can be used for the production of adhesives. Pale crepe and smoked sheets are rubbers obtained from plantations in East India. Para is a South American rubber that is not used much due to its higher cost, but does give higher strength and better aging qualities than other types of rubber. Balatta and Gutta Percha are the trans form of natural rubber, and give stiffer film qualities than natural rubber.

Solvent solution cements based on natural rubber are quick drying and are adaptable to high speed production

processes due to their ease of application, fast drying, fast tack, good film resiliency, and high impact strength. They can also be made in a wide range of viscosities varying from a thin solution to a thick paste.(3)

Recent applications find these adhesives being used to bond paper, rubber, plastic films, leather, wood, ceramic and plastic tile, plasterboard, metals, etc. to each other and to other materials. Major applications are in the automotive, shoe, and building industries. For example, in the building industry these adhesives have three main uses. The first is as a weatherproofing in the form of a thick paste or extruded ribbon. It can seal brick, wood, metal, or concrete. The second use is for the attachment of interior trim. Rubber flooring or linoleum can be bonded to wooden subflooring using this type of adhesive. The final use is in the construction of prefabricated panels.

Styrene-butadiene copolymer rubber possess relatively low polarity compared to other types of rubber. Due to this, it should not be an effective polymer for adhesive uses, and it is the least often employed.(3) When it is employed, due to its resistance to atmospheric oxidation, it is compounded with natural rubber.

SBR is tougher and more difficult to process than

natural rubber, so softening is necessary. This can be done by adding plasticizer or by mechanical working. This can impart the tackiness of natural rubber, but this material is still characterized by low tensile and film strengths in the form of pure gums and vulcanizates.

In spite of all its negative properties, SBR still has properties which make it useful in adhesives. Compounds reinforced with SBR retain their strength better. SBR compounds have good abrasion resistance. They absorb less water than natural rubber compounds. SBR compounds, vulcanizing and non-vulcanizing, possess atmospheric and heat aging properties superior to those of natural rubber, and comparable to those of polychloroprene and nitrile rubbers. (3)

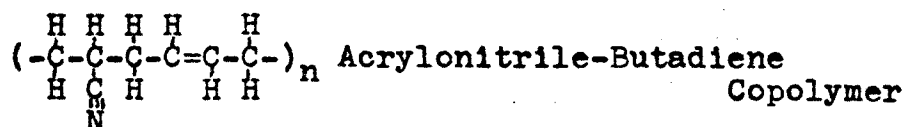
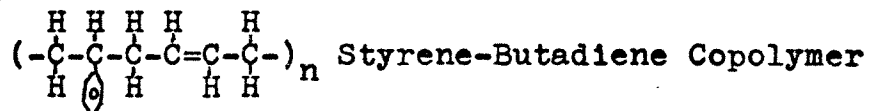
As an indication of the properties now being obtained with natural rubber adhesives, one could consult the government specifications covering these materials. Federal specification MMM-A-00182 (GSA-FSS) calls for a cold patching rubber adhesive of at least 6% natural rubber in benzene that will withstand at least 12.5 PSI in shear. Military specification MIL-C-12850 calls for a rubber cement of 12-14% smoked, pale crepe, or para rubber in petroleum naphtha, with a peel strength of at least 5 lbs./in. at 75°F.

EXPERIMENTAL

Substrate Material Selection

Since the ultimate aim of this project was the chemical crosslinking of the substrate to the adhesive, substrates had to be selected for the retention of some residual unsaturation even after they had been cured. For this reason, a nitrile rubber and a styrene-butadiene copolymer rubber were chosen. Another reason for choosing the nitrile rubber is its high oil resistance and its consequent bonding difficulty.

The chemical structures of these two materials are as follows:



B.F. Goodrich Chemical Co., Cleveland, Ohio was contacted as a possible supplier of these materials. They were able to provide 6" x 6" tensile sheets of both types of rubber. The SBR had the tradename of Ameripol 1500 and the NBR had the tradename of Hycar 1000X88. The Ameripol 1500 started out as a cold, non-pigmented, general purpose SBR. Before compounding it contained 23.5% bound styrene and had a specific gravity of 0.94. The Hycar 1000X88 contained a nominal 43% acrylonitrile and had a

specific gravity of 1.00. However, to obtain the desired tensile strength for this series of tests, these rubbers had to be compounded with other materials. The following are the formulaes that were used:

Ameripol 1500(NBS-386)	100.0	phr
NBS EPC Black S-300	40.0	"
NBS Zinc Oxide	5.0	"
NBS Sulfur	2.0	"
NBS Benzothiazl Disulfide	3.0	"
NBS Stearic Acid	1.5	"
Total	151.5	"

Hycar 1000X88	100.0	phr
Zinc Oxide	5.0	"
Sulfur	1.5	"
Stearic Acid	1.0	"
SRF-Black	65.0	"
DOP	15.0	"
TMTM	0.4	"
Total	187.9	"

After receiving the samples of these materials, I ran tensile strength tests on them. The samples were standard dog bone shape. At the narrow part of the sample the width was 0.25 inch and the thicknesses were 0.092 inch for the SBR and 0.078 inch for the NBR. The results of this test were that the NBR had a tensile strength of 3,870 PSI and the SBR had a tensile strength in excess of 4,350 PSI. The value for the SBR is not exact since the elongation of the sample was greater than the capacity of the Instron it was tested on.

Testing of Solvent Cements

To gain a point of reference, it was decided that the testing would begin with rubber based solvent cements. It

was felt that solvent cements based on the same rubbers as the substrates would give the best results, since there would be a maximum of compatability between the adhesive and the substrate.

These samples and all subsequent adhesive samples were tested by a procedure outlined in ASTM D-816-55.(26) The part of this test that was used was Method B-Adhesion Strength in Shear. This method calls for the substrate to be cut into strips 25 mm.(1 in.) in width and 125 mm. (5 in.) in length. These samples are to be bonded over an area of 625 mm.²(1 in.²). The lap bonded samples are then tested using an Instron to determine their breaking strengths. Shims are placed in the sample holders to maintain the applied force in the plane of the bonded area. The sample holder jaws are seperated at a rate of 0.8 mm./sec.(2 in./min.). The breaking strengths are reported in units of either Kilopascals or pounds per square inch of bonded surface area. Two samples must be tested, with the higher reading being reported as long as the two readings agree within 10%. If there is no agreement of this sort, up to six specimens can be run. If after running six specimens there is no agreement, an average of all six readings can be reported as the average adhesion strength in shear.

The Adhesives and Coatings Dept. of Uniroyal, Inc.,

Mishawaka, Ind. was contacted in order to procure samples of rubber based solvent cements. Three samples were ordered. The first was Royal M-6213, which is a light amber colored liquid with SBR as the adhesive binder and rubber solvent naphtha as the solvent. It contains approximately 22.0% solids and has a viscosity of 4,000 centipoises. The second was Royal M-6230, which is a dark brown colored liquid with NBR as the adhesive binder and acetone as the solvent. It contains approximately 30.0% solids and has a viscosity of 1,350 centipoises. The third was Royal M-6262, which is a black liquid with natural rubber as the adhesive binder and rubber solvent naphtha as the solvent. It contains approximately 13.0% solids and has a viscosity of 400 centipoises. Although it does not contain one of the substrate rubbers as the binder, it was chosen because it is recommended as an adhesive for cured SBR rubber.

The substrate was cut into strips one inch wide. Then one square inch of the substrate was roughened with emery paper and cleaned with carbon tetrachloride. The adhesives were applied in the following order: M-6213 with SBR, M-6230 with NBR, and M-6262 with SBR. The samples were held in intimate contact by a ten pound weight for 72 hours. The samples, still held in place by the weight, were placed in an oven (Despatch style V-15, electric forced

air, serial 48084) at 300°F for thirty minutes to insure proper curing.

The samples were tested in accordance with ASTM D-816-55. The combination of SBR substrate with Royal M-6213 gave a breaking strength of 40 pounds per square inch of bonded area. The combination of SBR substrate and Royal M-6262 gave a breaking strength of 40 pounds per square inch of bonded area. Finally, the combination of NBR substrate and Royal M-6230 gave a breaking strength of 50 pounds per square inch of bonded area. These results will serve as a reference point for judging the results of further work.

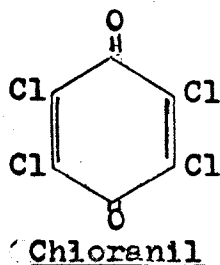
Monomer Selection and Preparation

At the beginning of the experimentation stage, the decision was made to work mainly with polyacrylic ester materials. This was due to several reasons. The acrylic esters were chosen over the methacrylic monomers due to the inherent stiffness of the polymethacrylates and the inherent flexibility of the polyacrylates. The presence of adhesive flexibility would be a definite plus in the bonding of rubbers. Another factor in favor of the polyacrylates is their good tack properties. The acrylic ester monomers are also readily available.

As has been stated earlier, the longer the carbon

chain of the alcohol that is esterified to form the monomer, the more flexible the final polymer will be. The highest degree of flexibility is wanted, so the monomers chosen were ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate.

The monomers were vacuum distilled to remove any polymerization inhibitor that might have been added to the monomer by the producer. However, before heating the monomers, they were further inhibited with chloranil to prevent high temperature polymerization during distillation. After the distillation was completed, the monomers were kept in a refrigerator to prevent spontaneous polymerization.



Solution Acrylic Polymers

To gain another point of reference, since it was decided to experiment with acrylics, testing had to be done with commercial acrylic solution polymers. A line of these materials is produced by B.F. Goodrich Chemical Co., and they were contacted for samples. The materials they make are intended as pressure-sensitive and laminating adhesives and as compounding bases for special adhesive

systems.

The materials that were sent are known as Hycar 2100X20, 2100X29, and 2100X33. Hycar 2100X20 is a clear, carboxylated acrylic polymer, 50% solids in methyl ethyl ketone. It has a medium syrup viscosity and the solids have a specific gravity of 1.05. This material was tested with the NBR rubber due to its advertised excellent compatibility with this material. Hycar 2100X29 is a carboxylated acrylic polymer, supplied as 30% solids in methylene chloride. Its viscosity is approximately 10,000 centipoises at 25°C. This material was tested on the SBR substrate. Hycar 2100X33 is a self-curing acrylic polymer, supplied as 45% solids in an 80/20 mixture of cyclohexane/methyl ethyl ketone. This material was tested with both types of substrate rubber.(27)

The substrate samples were roughened with emery paper and cleaned with carbon tetrachloride. The polymer solutions were then applied and the samples were held in intimate contact for 12 hours. They were then cured for 15 minutes at 300°F still held in intimate contact. The samples were allowed to cool and then tested.

<u>Rubber/Polymer</u>	<u>Strength, lbs./sq. in.</u>
NBR/2100X20	10
SBR/2100X29	12 + ₁
NBR/2100X33	6 -
SBR/2100X33	8

Polymer Preparation

The initial polymerizations were carried out by a solution process in 500 ml. glass stoppered boiling flasks. The flasks were immersed in a constant temperature bath maintained at 60°C. The following is the original formulation used:

Monomer	100.0	gms.
Benzene	200.0	"
Benzoyl Peroxide(catalyst)	0.5	"
2-Mercaptoethanol(chain transfer agent)	0.5	"

In the first polymerization run, there was no visible reaction, so the benzoyl peroxide was replaced with 2,2'-Azobis(2-methyl propionitrile) for further runs. Before stoppering the flasks, they were purged with nitrogen for 10 minutes. The stoppers were held in by spring tension hooks, while the reaction was allowed to proceed for 24 hours.

Using this formulation, the process gave an 80% yield of polybutyl acrylate, a 70% yield of polyethyl acrylate, and an 80% yield of poly2-ethyl hexyl acrylate.

A second set of polymerizations were carried out in order to obtain higher molecular weight polymers. To do this, the concentration of chain transfer agent used in the polymerizations was cut to 0.15 gms. The process that was carried out used 2-ethyl hexyl acrylate as the monomer. The yield from this process was 65%.

Adhesive Preparation

At this point, it was decided to eliminate the polyethyl acrylate from testing. This was done since it was felt that the polymer would probably not be flexible enough for this application. Further, there was a time limitation and thus an extensive test program was not possible. Therefore, the decision was made to limit this work to polybutyl acrylate and poly2-ethyl hexyl acrylate.

Before beginning the preparation of the test adhesives, it would be useful to know the viscosity of the polymers. This property was measured with a Brookfield Model RVF Viscometer, using a number 7 spindle at 4 RPM. The low molecular weight polybutyl acrylate had a viscosity of 26,400 centipoises. The viscosities of the low molecular weight and high molecular weight poly2-ethyl hexyl acrylates were 65,000 and 220,000 centipoises respectively.

The first adhesives tested were prepared to determine the optimum concentration of catalyst to be used.

The formulation was as follows:

Polymer	3.0 gms.
Monomer	2.0 "
Benzoyl Peroxide	varied
N,N-dimethyl paratoludine	0.15 gms.

The polymer and monomer used were polybutyl acrylate and butyl acrylate monomer. The concentration of benzoyl

peroxide was varied as follows: 0.20 gms., 0.225 gms., 0.25 gms., and 0.30 gms. The adhesives were applied to both the SBR and the NBR.

The test specimens were left held in close contact for 12 hours, and then, still held in contact, were cured at 300°F for twenty minutes. Due to the fact that there was no crosslinking agent present in the adhesive, there was not enough bond strength developed to warrant testing on the Instron. However, it was observed that the greatest bond strength was developed by the adhesive that contained 0.30 gms. of benzoyl peroxide.

The next step was to prepare adhesives containing a crosslinking agent. The crosslinker chosen was ethylene dimethacrylate. The formulation used was as follows:

Polymer	3.0 gms.
Monomer	2.0 gms.
Benzoyl Peroxide	0.3 gms.
N,N-dimethyl paratoluidine	0.15 gms.
Ethylene Dimethacrylate	0.15 gms.

Three adhesives were prepared using this formulation. The polymers and monomers used were polybutyl acrylate, low molecular weight and high molecular weight poly2-ethyl hexyl acrylate; each with its corresponding monomer. Each adhesive prepared was spread on samples of SBR and NBR. Then each test specimen was held in close contact for 12 hours and cured at 300°F for 20 minutes. The results these tests were as follows:

<u>Sample</u>	<u>Strength, lbs./sq. in.</u>
SBR/low m.w. P2EHA	0.70
NBR/low m.w. P2EHA	0.95
SBR/high m.w. P2EHA	2.85 +0.25
NBR/high m.w. P2EHA	0.50 -0.25
SBR/PBA	1.95
NBR/PBA	1.30

These results emphasize the difficulty in bonding NBR rubbers, that stems from their high oil resistance property. These values are well below those obtained with the commercial materials, but should improve with further experimentation.

When preparing these adhesives, great difficulty was observed in trying to dissolve the benzoyl peroxide in the polymer-monomer solution. For this reason, 1 gram of benzoyl peroxide was dissolved in 5 grams of benzene prior to its addition. The appropriate amount of solution was then blended into the adhesive to attain the desired concentration of catalyst. It was also hoped that the presence of a small amount of benzene would swell the surface of the substrate rubber and thereby improve the bonding by increasing the mobility and diffusion of the polymer chains of the substrate. The adhesive was prepared using the same formulation and then applied to two pieces of SBR. The pieces were brought into intimate contact and held for 12 hours. The test specimen was then cured at 300°F for 20 minutes. This was done also to drive off any benzene that still might be present. When tested,

this sample had a breaking strength of 3.20 lbs./sq. in.. This is an appreciable increase over the previous preparations, but still lower than the commercial materials.

Bulk Polymers

Since the lower molecular weight polymers did not give very good results, it was decided to prepare some very high molecular weight samples. A bulk type polymerization process was decided on using butyl acrylate and 2-ethyl hexyl acrylate. The monomers, 100 gms., were mixed with 0.50 gms. of 2,2'-Azobis(2-methyl propionitrile) and were allowed to polymerize for 24 hours at 60°C.

Before bonding was attempted, the substrate rubber was allowed to soak overnight in monomer. This was done to swell the rubber and thereby facilitate the interdiffusion of the molecules of the rubber and the molecules of the adhesive.

The adhesives were prepared according to the formulation used in the last set of adhesives, using poly2-ethyl hexyl acrylate. One set was prepared with crosslinker and one set without. After the adhesives were applied to the substrate, the samples were held in intimate contact overnight. They were then placed in an oven for 3 hours at 300°F to drive off any monomer that

remained in the rubber and to cure the adhesives. The set prepared without a crosslinking agent was not expected to develop very good properties; and they did not. The results of the tests were:

<u>Sample</u>	<u>Strength, lbs./sq. in.</u>
SBR w/o EDMA	2.50
SBR w/ EDMA	2.90 + 0.50
NBR w/o EDMA	1.90 - 0.50
NBR w/ EDMA	7.30

The value obtained with the NBR substrate and a crosslinked adhesive was the highest so far obtained in this test program. The values obtained with the SBR substrate were lower than expected. It was observed that very little adhesive remained on the rubber surface, and it appeared that the adhesive had been absorbed into the rubber. For this reason, there remained very little material to bond the samples together.

The next set of substrate samples were allowed to soak overnight in butyl acrylate monomer since the adhesive would be based on polybutyl acrylate. The adhesives were prepared using a crosslinking agent. The samples in this case were also left in intimate contact overnight and cured at 300°F for 3 hours.

The results of the tests indicated that the rubbers were swelled to a greater degree with butyl acrylate than with 2-ethyl hexyl acrylate. They were swollen to such a

degree that the adhesion was lessened. The strength developed on the SBR substrate was negligible and the strength developed on the NBR substrate was only 4.80 lbs./sq. in.. This was a lower value than was obtained with the poly2-ethyl hexyl acrylate.

Primer Coating

It was felt that the strengths of the adhesive bonds could be improved by the application of a primer coating consisting of polymer, monomer, and catalyst to the rubber prior to the application of the adhesive. This primer would be cured for 20 minutes at 300°F. The coating was applied to samples of the rubbers that had been roughened and cleaned and to samples that had soaked in monomer for 4 hours. It was hoped that the short soaking period would prevent excessive swelling of the rubber.

The primer coatings were prepared according to the formula-2.50 gms. polymer, 2.50 gms. monomer, 0.30 gms. benzoyl peroxide. These mixtures were made both with polybutyl acrylate and poly2-ethyl hexyl acrylate. The mixtures were applied to the rubbers and allowed to cure. Then, to make the adhesives, 0.15 gms. ethylene dimethacrylate and 0.15 gms. N,N'-dimethyl paratoluidine were added to the polymer-monomer-catalyst blends. This mixture was then applied to the rubbers. The specimens

were held in close contact overnight and then cured for 3 hours at 300°F.

The specimens were removed from the oven, allowed to cool, and then tested. The results obtained from the monomer soaked samples were:

<u>Substrate/Polymer</u>	<u>Strength, lbs./sq. in.</u>
SBR/PBA	4.20
SBR/P2EHA	negligible + 0.50
NBR/PBA	2.00 - 0.50
NBR/P2EHA	7.20

The results for the roughened and cleaned samples were:

<u>Substrate/Polymer</u>	<u>Strength, lbs./sq. in.</u>
SBR/PBA	7.00
SBR/P2EHA	5.50 ±0.50
NBR/PBA	8.80
NBR/P2EHA	8.10

As can be seen from these results, the soaking of the rubber in the monomer must be further limited in time. Even shortening the soaking time to 4 hours was not a sufficient reduction. The swelling of the rubber is still so severe that it has a detrimental effect on the adhesion. However, it can be seen that although the values obtained with the samples that had been roughened and cleaned were not as high as the commercial rubber based solvent cements, they compare favorably with the solution acrylic polymers of commercial manufacture.

The next set of tests that was prepared was meant to evaluate the effect of shorter exposure times for the

rubber soaked in the monomer, and the effect of elevated curing temperatures. the soaking time was reduced to 30 minutes to prevent excessive swelling of the rubber. The temperature used for curing the primer coatings and the adhesives was raised to 350°F. This was done in hopes of obtaining a faster and more complete curing of the adhesives.

The formulation used for the primers and the adhesives was the same as was used in the last set of tests. The primer was cured for 20 minutes at 350°F and the adhesives were cured at 350°F for 3 hours. The samples were removed from the oven, allowed to cool, and tested. The results of the testing were as follows for the monomer soaked samples:

<u>Substrate/Polymer</u>	<u>Strength, lbs./sq. in.</u>
SBR/PBA	11.75
NBR/PBA	10.25
SBR/P2EHA	6.75 +0.50
NBR/P2EHA	4.25 -0.50

The results of the testing of the unsoaked samples were:

<u>Substrate/Polymer</u>	<u>Strength, lbs./sq. in.</u>
SBR/PBA	10.50
NBR/PBA	9.25
SBR/P2EHA	4.25 +0.50
NBR/P2EHA	4.50 -0.50

The shorter soaking time and higher curing temperature improved all the values, except for the NBR substrate bonded with poly2-ethyl hexyl acrylate. It would appear that the 2-ethyl hexyl acrylate monomer did not have sufficient time to swell the highly oil resistant NBR.

For this combination of rubber and monomer, it would appear a 3-4 hour soaking time is optimum. For other materials, the short soaking period gives the best results. It can also be seen that the soaked rubber tends to be bonded more strongly than rubber that is just roughened and cleaned.

The increased curing temperature seems to have had a detrimental effect on the bonding power of the poly2-ethyl hexyl acrylate. This can be seen when this set of results is compared with the set previously run. This effect is not seen with the polybutyl acrylate. This could be due to the higher molecular weight of the polybutyl acrylate helping to retain the properties of the material even after exposure to the higher curing temperature.

The next of samples was prepared to determine the effect of an even higher curing temperature. The pretreatment, primer coating, and adhesive formulations were the same here as in the last set of samples. The primer coatings and bonded specimens were cured at 375°F. The results of the testing of the roughened and cleaned samples were:

<u>Substrate/Polymer</u>	<u>Strength, lbs./sq. in.</u>	
NBR/PBA	7.25	
NBR/P2EHA	4.25	+0.50
SBR/PBA	15.25	-0.50
SBR/P2EHA	5.50	

The testing of the monomer soaked samples resulted in the

following:

<u>Rubber/Polymer</u>	<u>Strength, lbs./sq. in.</u>
NBR/PBA	11.50
NBR/P2EHA	5.25 +0.50
SBR/PBA	15.50 -0.50
SBR/P2EHA	8.50

As can be seen, the trend of the soaked samples being stronger than the roughened and cleaned samples is continued. The poly2-ethyl hexyl acrylate still displayed inferior properties when compared to the polybutyl acrylate, as expected at this even higher curing temperature.

A peel test was run on the best formulation tested up to this point. This was an adhesive based on bulk polymerized butyl acrylate applied to a substrate of monomer soaked styrene-butadiene copolymer rubber. The test was run on 1 inch wide strips of rubber that were bonded and cured at 375°F for 3 hours. The peel rate was 2 inches per minute. The result was a peel strength of 41 ounces per inch.

Polyswell

As a final test, it was decided that the rubber substrate pieces should be swelled with butyl acrylate monomer containing 0.20% 2,2'-Azobis(2-methylpropionitrile), AIBN. After swelling the samples for one hour, they were placed in an oven at 60°C for 24 hours to polymerize the butyl acrylate that had been absorbed.

To evaluate the effect of this pretreatment on the substrate rubber, two dogbone shaped specimens were prepared from both the SBR and NBR polyswells. They were tested on an Instron in the same way as the original tests that were run at the beginning of this work. The results of this test were the SBR polyswell had a tensile strength of 4,100 PSI and the NBR polyswell had a tensile strength of 5,500 PSI. This compares to an original strength for the SBR of 3,900 PSI and for the NBR 4,350 PSI.

As part of this test, a new sample of polybutyl acrylate was prepared. To remove the inhibitor, a 250 ml. portion of monomer was washed twice with 0.50% potassium hydroxide solution and twice with deionized water. The monomer was then dried overnight with anhydrous sodium sulfate. The inhibitor free monomer was mixed with 0.20% AIBN and placed in an oven overnight at 60°C. The resulting polymer was then dissolved 50:50 with monomer. This polymer-monomer solution was the base from which the test adhesive was made.

The swelled and polymerized rubber samples were bonded using an adhesive that consisted of 5 gms. polymer-monomer solution, 0.30 gms. benzoyl peroxide, 0.30 gms. ethylene dimethacrylate, and 0.15 gms. N,N'-dimethyl paratoluidine. Another set was prepared using the same formulation without ethylene dimethacrylate. The specimens

were put under ten kilograms per square inch pressure overnight and then cured, under pressure, for three hours at 375°F. The results were as follows:

<u>Rubber/Adhesive</u>	<u>Strength, lbs./sq. in.</u>
SBR w/ EDMA	14.80
SBR w/o EDMA	11.50 + 0.50
NBR w/ EDMA	6.40 - 0.50
NBR w/o EDMA	1.50

These results show this pretreatment to be inferior to the one that consisted of precoating the samples with polymer, monomer, and catalyst.

A dogbone shaped specimen averaging 0.13 inch thick by 0.25 inch wide was prepared from a sample of set adhesive of the type used in this section of work. The sample was allowed to dry in a sheet, cured at 375°F for three hours, and the dogbone was die cut. The tensile strength of the dogbone was 160 pounds per square inch.

The following three pages are a tabulation of the total data generated in this study. Table 1 is a summation of the data generated using the commercial materials used as reference standards. Table 2 is a summation of the data generated using polybutyl acrylate adhesives with the various modifications of bonding technique. Table 3 is the same as Table 2, except that it summarizes the data generated using poly2-ethyl hexyl acrylate.

TABLE 1Testing of Commercial Adhesive Materials

<u>Adhesive</u>	<u>Breaking Strength, lbs./sq.in.</u>	
	<u>SBR</u>	<u>NBR</u>
Royal ¹ M-6213	40	-
Royal ¹ M-6262	40	-
Royal ¹ M-6213	-	50
Hycar ² 2100X20	-	10
Hycar ² 2100X29	12	-
Hycar ² 2100X33	8	6

¹ - Solvent cement

² - Solution Acrylic Polymer

TABLE 2Experimental Results Using Polybutyl Acrylate

<u>Adhesive Polymer</u>	<u>Breaking Strength, lbs./sq.in.</u>	
	<u>SBR</u>	<u>NBR</u>
Solution Polymerized Substrate Roughened and Cleaned	1.95	1.30
Bulk Polymerized Substrate Swelled 24 hr. in Monomer	Negligable	4.80
Bulk Polymerized Primer Coated Substrate Swelled 4 hr. in Monomer	4.20 ¹	2.00 ¹
Bulk Polymerized Primer Coated Substrate Swelled 30 min. in Monomer	11.75 ² 15.50 ³	10.25 ² 11.50 ³
Bulk Polymerized Primer Coated Substrate Roughened and Cleaned	7.00 ¹ 10.50 ² 15.25 ³	8.80 ¹ 9.25 ² 7.25 ³

¹ - Cured at 300°F

² - Cured at 350°F

³ - Cured at 375°F

TABLE 3

Experimental Results Using Poly 2-ethyl Hexyl Acrylate

Adhesive Polymer	Breaking Strength, lbs./sq.in.	
	SBR	NBR
Low Mol. Wt. Solution Polymerized Substrate Roughened and Cleaned	0.70	0.95
High Mol. Wt. Solution Polymerized Substrate Roughened and Cleaned	2.85	0.50
Bulk Polymerized Substrate Swelled 24 hr. in Monomer	2.90	7.30
Bulk Polymerized Primer Coated Substrate Swelled 4 hr. in Monomer	Negligable ¹	7.20 ¹
Bulk Polymerized Primer Coated Substrate Roughened and Cleaned	5.50 ¹ 4.25 ² 5.50 ³	8.10 ¹ 4.50 ² 4.25 ³
Bulk Polymerized Primer Coated Substrate Swelled 30 min. in Monomer	6.75 ² 8.50 ³	4.25 ² 5.25 ³

¹ - Cured at 300°F

² - Cured at 350°F

³ - Cured at 375°F

CONCLUSIONS

When the data generated in this study is taken together, certain trends can be seen. The first trend is that for maximum adhesion to be developed, the highest possible molecular weight polymer must be used as the binder material. A bulk polymerization technique is superior to solution polymerization in this case, since higher molecular weight polymers are generated.

The second trend noted is that a very high temperature must be used for the curing of rubbery acrylic polymer adhesives. A temperature of 375°F is not too high. If a high enough temperature is not used, an incomplete cure will be the result, with a consequent lowering of bond strength.

The results obtained in this study tend to agree with the Diffusion Theory of adhesion and disagree with the Mechanical Theory. They disagree with the Mechanical Theory since on the most part the bond strengths obtained with a smooth surfaced substrate were higher than with a substrate that had been roughened. Higher curing temperatures and the presence of a prime coating would aid in the interdiffusion of the polymer chains of the substrate and the adhesive. This would be exhibited by an increase in the bond strength with increased curing temperature and the application of a prime coating. This was seen.

After an intensive search of Chemical Abstracts in search of data generated by other sources to compare with the data generated here, it has been determined that none is available. Acrylic ester homopolymers are not seeing much use as adhesive binder materials. They are being copolymerized with vinyl acetate, methyl methacrylate, or other acrylic monomers to improve their performance properties. For this reason, no comparisons can be made, due to the radical differences in the natures of the polymers.

One interesting use of an adhesive system similar to the one used in this project was disclosed in patent Fr. 1,572,744, issued to Imperial Chemical Industries Ltd., June 27, 1969. A crosslinkable polymer-monomer mixture of 2-ethyl hexyl acrylate was spread 1.5 mm. thick on both sides of five glass sheets 4 mm. thick. The glass sheets were then laminated together with outer layers of rigid poly(vinyl chloride) 4.6 mm. thick. The composite was cured for five hours. The cured composite was resistant to steel balls fired at a distance of 40.6 cm. from a 0.357 caliber pistol.

RECOMMENDATIONS

Further work can be done on the optimization of the curing conditions for the primer coatings and the adhesives. Since the trend seems to be toward increasing bond strength with increasing curing temperature, I feel that a curing temperature of 400°F should be tried. Longer curing times for the primer coatings and adhesives should also be evaluated.

Another possibility for further work is the evaluation of copolymers of butyl acrylate and 2-ethyl hexyl acrylate. A 50-50 or 60-40 copolymer would probably be best to combine the the good adhesion of the butyl acrylate and the polymer flexibility of the 2-ethyl hexyl acrylate.

It was noted in the "polyswell" phase of the experimental work that the rubber substrates had improved tensile strength after being swelled with butyl acrylate monomer and catalyst and then heated at 60°C for twelve hours. This observation should be verified and pursued as a possible way of obtaining improved properties with cured rubber stocks.

REFERENCES

- 1) Sharpe, Louis H., "Adhesive Bonding". Machine Design, September 11, 1969.
- 2) Gould, Bernard, "Guide to Adhesives Selection", Adhesives Age, March, 1959
- 3) Handbook of Adhesives, Irving Skeist (ed.), New York, Reinhold Publishing Co., 1962
- 4) Polymer Science, A.D. Jenkins (ed.), Vol. II, Chap. 13, New York, American Elsevier Publishing Co., 1972, p.933-957
- 5) Iyengar, I. and D.E. Erickson, "Role of Adhesive-Substrate Compatibility in Adhesion", Journal of Applied Polymer Science Vol. 11, p.2311-2324 (1967)
- 6) Kutscha, Dieter, "Mechanisms of Bonding and Joint Performance", Adhesives Age, November, 1968, p.37-40
- 7) Schonhorn, Harold, F.W. Ryan, Tsuey T. Wang, "Effects of Symmetrical Bonding Defects on Tensile Shear Strength of Lap Joints Having Ductile Adhesives", Journal of Applied Polymer Science, Vol. 15, p.1069-1078 (1971)
- 8) Aspects of Adhesion, D.J. Alner (ed.), Vol. 5, "Theories of Adhesion Surveyed", 1969, London, Univ. of London Press. 1965
- 9) DeLollis, N.J., "Theory of Adhesion, Parts 1 and 2", Adhesives Age, December 1968 and January, 1969, p.21-25 and p.25-29
- 10) Schneberger, Gerald L., "Chemical Aspects of Adhesive Bonding, Parts I, II, and III", Adhesives Age, February, March and April, 1970, p.21-24, p.28-31, and p.41-44
- 11) Weber, A., "Acrylic Pressure Sensitive Polymers", Adhesives and Coatings Conference-Brussels, April 13, 1971
- 12) Uffner, M.W., "Characterizing and Utilizing Pressure-Sensitive Adhesive Polymers", Adhesives Age, December, 1967, p.30-33
- 13) Satas, Don, "How to Test Adhesive Bonds", Adhesives Age, June, 1970, p.38-40
- 14) Wetzel, Frank H., "The Characterization of Pressure Sensitive Adhesives", ASTM Bulletin No. 221, April 1957
- 15) Newman, George V., William H. Snyder, Charles E. Wilson, "Acrylic Adhesives for Bonding Attachments to Tooth Surfaces", Angle Orthodontist, Vol. 38, No. 1, January, 1968

- 16) Newman, George V., William H. Snyder, Charles E. Wilson, and Deran Hanesian, "Adhesives and Orthodontic Attachments", Journal of the New Jersey State Dental Society, November, 1965
- 17) Snyder, William H., Charles E. Wilson, George V. Newman, and John Semen, "Investigation of Fast Setting Acrylic Adhesives for Bonding Attachments to Human Tooth Surfaces", Journal of Applied Polymer Science, Vol. 11, p.1509-1527 (1967)
- 18) Satas, Don, "Tailoring Pressure-Sensitive Adhesive Polymers", Adhesives Age, October, 1972, p.19-23
- 19) Mooncai, Wallace W., "Properties and Applications of Pressure-Sensitive Adhesives", Adhesives Age October, 1968, p.28-35
- 20) Encyclopedia of Polymer Science and Technology, Vol. 1, "Acrylic Ester Polymers", New York, Interscience Publishers, 1964, p.246-342
- 21) Encyclopedia of Polymer Science and Technology, Vol. 1, "Adhesion and Bonding", New York, Interscience Publishers, 1964, p.445-550
- 22) McCart, Bernard A., "How to Improve Tack Properties, Elastomeric Adhesives", Adhesives Age, October, 1970, p.53-55
- 23) Petersen, Kenneth C., and Robin A. Martin, "Tack and Adhesion of Uncured Elastomers", Adhesives Age, March, 1969, p.22-25
- 24) Treatise of Adhesion and Adhesives, Robert L. Patrick (ed.), New York, M. Dekker Publishing, 1967
- 25) B. F. Goodrich Chemical Co., Ad No. M-022R
- 26) ASTM D816-55. "Standard Methods of Testing Rubber Cements"
- 27) B.F. Chemical Co., Technical Service Bulletins ASP-1 and 2
- 28) Physical Chemistry of Surfaces, Arthur W. Adamson, p.366-368, New York, Interscience Publishers, 1967
- 29) Shafrin, E.G., and W.A. Zisman, Journal of Physical Chemistry, 64, 519 (1960)
- 30) Fox, H.W., and W.A. Zisman, Journal of Colloid Science, 5, 514 (1950)
- 31) Fox, H.W., and W.A. Zisman, Journal of Colloid Science, 7, 109 (1952)
- 32) Fox, H.W., and W.A. Zisman, Journal of Colloid Science, 7 428 (1952)

- 33) Wetzel, F.H., Rubber Age, Vol. 82, 291-295 (1957)
- 34) Hammond, F.H., ASTM Special Technical Publication No. 360 (1964)
- 35) DeBruyne, N.A., Aero Research Technical Notes, Bulletin No. 168 (1956)
- 36) Rossman, K., Journal of Polymer Science, 19, 141 (1956)
- 37) Wake, W.C. Adhesion, edited by D.D. Eley, Oxford University Press, Chap. 8
- 38) Hendricks, J.O. and C.A. Dahlquist, Adhesion and Adhesives, Vol. 2, R. Howwink and G. Solomon (eds.) p.387, Second Edition, New York, American Elsevier Publishing Co., 1967
- 39) Mendelsohn, M.A., Industrial and Engineering Chemistry, Product Research and Development, Vol. 3, p.67-72 (1964)
- 40) Damusis, A., W. Ashe, and K.C. Frisch, Journal of Applied Polymer Science, Vol. 9, p. 2965-2983 (1965)
- 41) Loshaek, S. and T.G. Fox, Journal American Chemical Society, Vol. 75, p. 3544 (1953)
- 42) deBruyne, N.A., Aircraft Engineering, 16, 115, 140 (1944)
- 43) deBruyne, N.A., Aircraft Engineering, 18, 1 (1939)
- 44) deBruyne, N.A., Materialenkenntis, 51, 551 (1947)
- 45) Deryagin, B.V., and N.A. Kratova, Adhesion, Izd. Akad. Nauk, M-L, 1949 (in Russian)
- 46) Deryagin, B.V., and N.A. Kratova, Doklady Akad. Nauk SSR, 61, 849 (1948)
- 47) Deryagin, B.V. and N.A. Kratova, Usphekhi Fiz. Nauk, 36, 387 (1948)
- 48) Kratova, N.A., Yu. M. Kirillova, and B.V. Deryagin, Zhur, Fiz. Khin, 30, 1921 (1951)
- 49) Voyutskii, S.S., Kauchuk i Rezina, No. 7, 23 (1957)
- 50) Voyutskii, S.S., Vysokomolekul. Soedin, 1, 230, (1959)
- 51) Voyutskii, S.S., A.I. Shapovalova, and A.P. Pisarenko, Doklady Akad. Nauk SSR, 105, 1000 (1955)
- 52) Voyutskii, S.S. Autohesion and Adhesion of High Polymers, p.126-147, New York, Interscience Publishers, 1963, p.126-147