

hydroxyl terminated

Poly bd[®] Resins

functional liquid polymers

in urethane elastomers

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Introduction

Poly bd⁷ resins are liquid, hydroxyl terminated homopolymers of butadiene. Through the use of an isocyanate cure reaction to produce novel urethane products, they offer a route to castable, general-purpose elastomers. They can be reinforced with various fillers, and extended with a variety of low cost process oils.

The unique structure of the Poly bd resins provides properties which surpass both conventional polyether and polyester urethane systems, as well as conventional, general-purpose rubbers. These novel Poly bd resins can be used in preparing castable elastomers, caulks, sealants, membranes, sponges, foams, adhesives, coatings, propellant binders, potting and encapsulating compounds, as well as other rubber fabricated materials.

Some of the more prominent features of Poly bd urethane systems are:

1 Castable. General-Purpose Elastomers.

The facile reaction of Poly bd resins with curing agents such as conventional di- and polyisocyanates provides an economical liquid or semisolid route to general purpose rubbery elastomers.

2. Efficient Reinforcement with Carbon Black and Other Fillers.

The molecular structure of Poly bd liquid polymers resembles that of polybutadiene rubber, hence, these polymers respond to reinforcement with carbon black and other fillers in similar manner.

3. Oil Extendability.

Poly bd liquid resins are compatible with a wide variety of hydrocarbon oils and resins. Oil extension, therefore, provides formulation flexibility in controlling properties of the uncured liquid systems such as pot life, gel time, etc., as well as the properties of the cured products; e.g., tensile and tear strengths, and elongation.

Oil extension in combination with filler reinforcement provides unique formulation flexibility for preparing low cost urethane products.

4. Improved, Low-Temperature Properties.

Many elastomeric products derived from Poly bd resins have brittle points as low as -70°C.

5. Excellent Hydrolytic Stability.

The hydrophobic backbone of Poly bd resins imparts excellent hydrolytic stability to urethane products. Thus, elastomers, caulks, sealants, foams and other products can be made which are resistant to hydrolysis, even in boiling water.

6. Excellent Electrical Insulation Properties.

A discussion of the benefits of Poly bd resins in electrical applications is found in the Electrical Applications bulletin.

7. Chemical Resistance.

Poly bd resins can be used to prepare polyurethane elastomers with excellent resistance to aqueous inorganic acids and bases.

8. Toxicity.

Poly bd resins have a low order of toxicity.

These features, as well as others to be described, show Poly bd urethane systems to combine the advantages of general purpose rubbers and urethane elastomers within the same polymer network.

Physical Properties

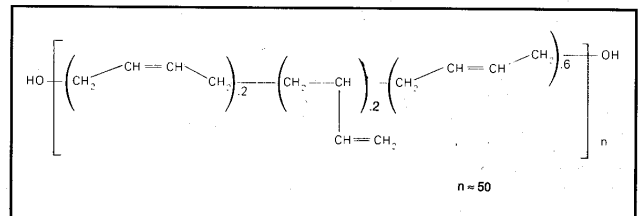
Typical physical properties of these hydroxylterminated polybutadiene resins are given in Table 1. Their simplified structure is represented in Figure 1. The polybutadiene microstructure of both homopolymers is analogous to that of diene polymers prepared by emulsion techniques. These polymers possess predominantly primary, terminal hydroxyl groups of the allylic type. This structural combination accounts for their high reactivity, especially with aromatic diisocyanates. The hydroxyl functionality of Poly bd R-45M resin is typically in the range of 2.2 to 2.4, whereas that of Poly bd R-45HTLO resin is somewhat higher, typically 2.4 to 2.6.

Storage stability for both resins is excellent in the absence of air, and their low moisture content allows them to be used directly from containers without further pretreatment in many systems. The typical viscositytemperature relationship is given in Figure 2.

Table 1 Typical Properties of Poly bd7 Resins

| Poly bd Resin | R-45HTLO | R-45M |
|-------------------------------|----------|-------|
| Nonvolatile Material, Wt. % | 99.9 | 99.9 |
| Viscosity, mPa-s @ 30°C | 5000 | 4300 |
| Hydroxyl Value, meq/g | 0.86 | 0.73 |
| Hydroxyl Number, mg KOH/g | 48.2 | 41.0 |
| Molecular Weight, No. Average | 2800 | 2800 |
| Water, Wt.% | 0.03 | 0.03 |
| Specific Gravity @ 30°C | 0.901 | 0.899 |
| Iodine Number, g/100g | 400 | 400 |
| Polybutadiene Microstructure | | |
| Cis- | 20% | |
| Trans- | 60% | |
| Vinyl- | 20% | |

Figure 1 Homopolymers



Low Temperature Behavior of Poly bd Resin Based Urethanes

Polyurethane elastomers based on Poly bd resins also exhibit outstanding low temperature properties. This characteristic is attributable to the "rubbery" polybutadiene backbone. Many polyurethane elastomers derived from Poly bd resins have brittle points as low as 70°C.

To demonstrate this characteristic, the physical properties of a Poly bd resin prepolymer system prepared from a 15% free NCO Poly bd R-45HTLO/TDI prepolymer chain extended with equal equivalents of Voranol 220-530 and Pluracol TP-340 were tested over a temperature range of -20° F to +140° F. Table 2 shows a nearly constant elongation over this temperature range, while other properties behaved consistently with usual polyurethane systems. An elongation of 130% at -20° F demonstrates that the Poly bd based polyurethane elastomer is not brittle and indeed still possesses elastomeric properties at this temperature.

Figure 2 Poly bd7 R45HTLO Resin Viscosity as a Function of Temperature

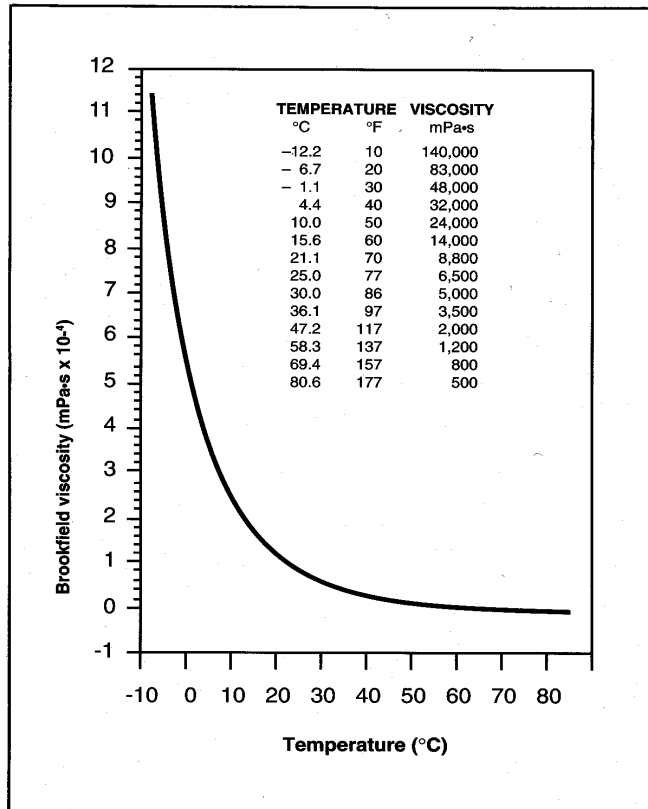


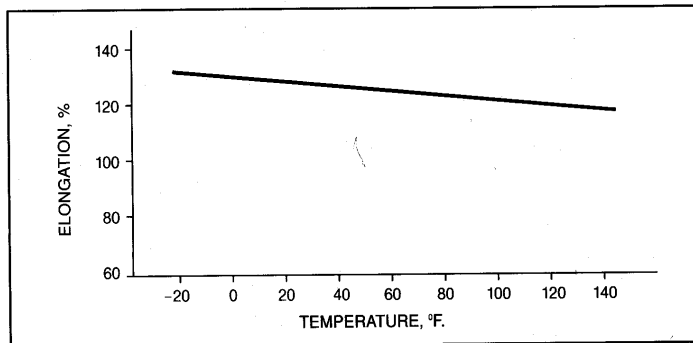
Table 2

| Temp., °F | Tensile (psi) | Elongation (%) | Modulus (psi) | | |
|-----------|---------------|----------------|---------------|------|------|
| | | | 50% | 100% | Tear |
| 140 | 2060 | 117 | 960 | 1775 | - |
| RT | 3250 | 122 | 1748 | 2800 | 275 |
| 0 | 5090 | 125 | 2800 | 4390 | - |
| -20 | 6080 | 130 | 3500 | 5250 | 423 |

Thermal Shock/Embedment Stress

Retention of flexibility at low temperatures is a prominent feature of Poly bd resin based systems. This feature allows for encapsulation of fragile electrical components in a medium that retains cushioning properties. Embedment stress at -40° F is significantly lower than many competitive materials. This same characteristic of the Poly bd resin also imparts excellent thermal cycling properties to components potted or encapsulated with a Poly bd resin based system. Figure 3 shows the elongation of a typical Poly bd compound to be essentially constant over a wide temperature range.

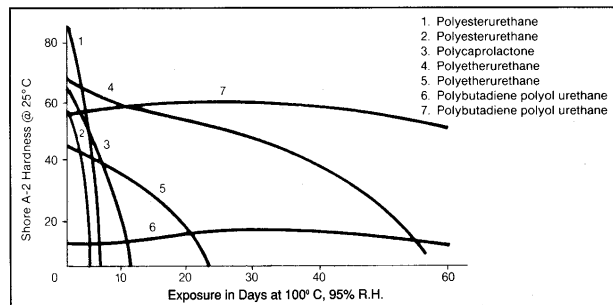
Figure 3 Elongation vs Temperature



Hydrolytic Stability

The hydrocarbon backbone in Poly bd resin imparts hydrolytic stability to the finished product, surpassing that of any other type of polyurethane. Electrical integrity is maintained in the presence of moisture, even at high temperatures. Poly bd resin systems far exceed the 28 day requirement of the Naval Avionics test. By measuring hardness vs. time at 100°C and 95% relative humidity, it can be shown that Poly bd based systems are essentially unaffected by moisture at high temperature, whereas other typical urethanes actually liquify (revert) during the test period, as shown in Figure 4.

Figure 4 Comparative Hydrolytic Stability of Conventional vs. Polybutadiene Polyol Urethanes



Hydrolytic Stability of Poly bd Resins in Combination with Polyether Polyols

Polyurethane elastomers based on Poly bd resins exhibit outstanding hydrolytic stability. Again this characteristic is inherent in the nature of the hydrocarbon polybutadiene backbone of the Poly bd resin. There are no ester or ether linkages to hydrolyze.

The addition of even moderate amounts of Poly bd resins to polyether based polyurethanes markedly improves the hydrolytic stability of the cured elastomer. Figures 5, 6 and 7 show the test results on two comparable elastomer systems. One contains 24.4 weight percent Poly bd resin, whereas the other is based only on the same polyether polyols without Poly bd resin.

Test specimens were totally immersed in water at 75°C for the periods shown. Elastomers containing

Poly bd resin had excellent retention of all physical properties after 75 days. Note that hardness and tensile strength were virtually unchanged after 50 days immersion.

Figure 5 Hydrolytic Stability @ 75°C % Change in Tensile Strength

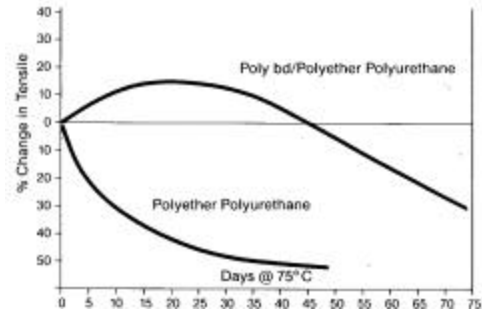


Figure 6 Hydrolytic Stability @ 75°C % Change in Hardness

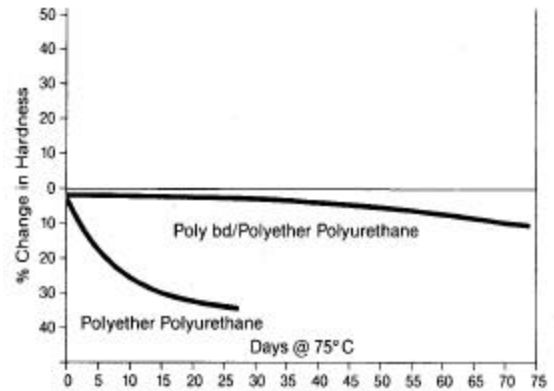
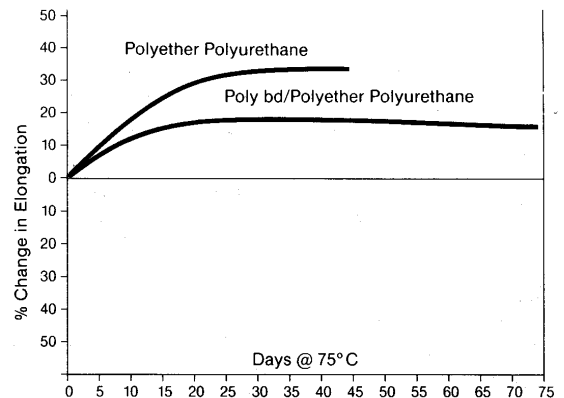


Figure 7 Hydrolytic Stability @ 75°C % Change in Elongation



Chemical Resistance

Poly bd resins can be used to prepare polyurethane elastomers with excellent resistance to aqueous inorganic acids and bases. This characteristic is also attributable to the hydrophobic nature of the polybutadiene backbone.

To demonstrate this resistance, an elastomer prepared from a 9% free NCO Poly bd R45HTLO/TDI

prepolymer cured with 2-ethyl-1, 3 hexanediol was totally immersed in the test media shown for one week at 160° F. The results are summarized in Table 3 which, in addition to absolute values, shows in parentheses, the percent change for tensile strength, elongation and tear strength. The physical properties showed minimal change after exposure. Note also that there was no significant dimensional or weight change.

These data indicate that Poly bd resin can be used to formulate chemically resistant urethane elastomers. Physical properties of the elastomer can be varied by techniques discussed later in this bulletin. The added chemical resistance obtained from the hydrocarbon Poly bd polymer will vary, of course, depending upon the concentration in a given formulation.

Table 3
Chemical Resistance of Poly bd Resin Based Urethanes

| | Untreated | 20% HZ S04 | 20% NaOH |
|-----------------------|------------------|-------------------|-----------------|
| Tensile Strength, psi | 1450 | 1420 | 1470 |
| Elongation, % | 315 | 335 | 335 |
| Modulus, psi | | | |
| 100% | 775 | 765 | 770 |
| 200% | 1020 | 1010 | 1020 |
| 300% | 1340 | 1280 | 1350 |
| Tear Strength, pli | 224 | 227 | 228 |
| Hardness, Shore A | 89 | 89 | 89 |
| Dimensional Change, % | - | +0.10 | +0.40 |
| Weight Change, % | - | +0.18 | 0 |

Low Exotherm/ Ambient Temperature Cure

Poly bd resin based systems can be cured at ambient temperatures by reaction with di- or polyisocyanates. Pot life/cure time can be readily adjusted by using typical urethane catalysts. Even when employing catalysts to increase reaction rates, exotherms are low, typically in the range of 30° to 60° F (300 g mass).

Minimal Shrinkage

Poly bd systems cured at ambient temperature exhibit little or no shrinkage.

Toxicity

Poly bd resins have been tested for Acute Oral Toxicity. Primary Skin Irritation and Eye Irritation. Specific data are available from **ATOFINA Chemicals, Inc.**

For typical applications, low vapor pressure polymeric isocyanates are recommended. Toxicity and proper handling information on this component of the formulation can be obtained from the manufacturer. Material Safety Data Sheets should be obtained from each manufacturer for all ingredients prior to formulation.

Formulating Flexibility

Unlike preformulated potting and encapsulating compounds, Poly bd resins provide fabricators or formulators a wide degree of flexibility to develop products suitable for their particular needs. Desired physical properties can be achieved by formulating with short chain diols, fillers and extenders.

Chemistry

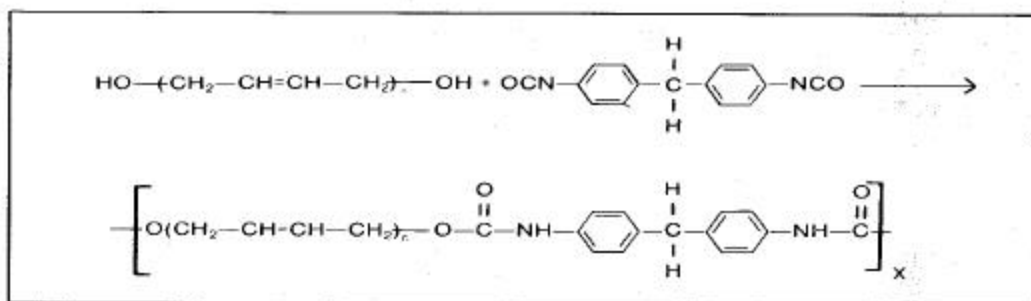
The systems herein described are divided into two categories-one-step urethanes and two-step urethanes. One-step systems are based upon the direct reaction of Poly bd resin with an isocyanate. The one-step systems offer the advantages of versatility, simplicity, and low cost fabrication techniques for preparing urethanes having a wide range of physical properties. Such applications as caulks, sealants, elastomers and foams are possible via these systems.

Two-step Poly bd resin systems are based upon the intermediate formation of a prepolymer which can be further chainextended and crosslinked with auxiliary diols and diamines to form the final polyurethane. These systems usually provide higher performance urethanes and have the advantage of lowering the overall toxicity of the system. Again, a variety of products is possible.

One-Step Urethane Reactions

Poly bd liquid polymers offer distinct advantages in preparing one-step urethane products. The primary, allylic nature of the hydroxyl groups, combined with their controlled functionality (hydroxyl functionality estimated between 2.2-2.6 depending upon the particular Poly bd resin) enables products to be rapidly and completely cured at ambient or elevated temperatures. The cure reaction of Poly bd resins with 4, 4' methyl diphenyl diisocyanate is illustrated in Figure 8.

Figure 8



Procedure for Reacting Poly bd Liquid Polymers with Isocyanates

When producing simple, unfilled elastomers from Poly bd resins and isocyanates, the liquid polymer and the isocyanate are blended with good mixing. The mixture is poured into a mold or applied to a substrate and permitted to cure at ambient or elevated temperature. To prepare castings which are bubble-free, vacuum degassing is recommended. Refer to Appendices for additional details concerning calculations and procedures.

Table 4 shows typical properties of unfilled gumstocks prepared by reacting Poly bd resins with commercial isocyanates. The use of NCO/OH ratios lower than unity results in softer, lower modulus materials. At NCO/OH ratios above 1, lower modulus materials may also be prepared. However, the latter materials will gradually increase in hardness with time, since the free NCO groups can undergo further reaction with moisture to give urea structures, or can form allophanate crosslinks (especially at elevated temperatures).

Unfilled urethane systems of the type described may be cured at ambient temperatures within 24 hours with no catalyst. However, using either typical urethane catalysts and /or elevated temperatures, cure rates may

be greatly accelerated. Catalysts such as dibutyltin dilaurate and 1,4-diazo [2.2.2.] bicyclooctane (Dabco) have been used successfully with these systems. Catalyst concentrations are usually in the range of 0.05-0.5 weight %, depending upon the particular system. The tin catalysts are recommended for fast cures at elevated temperatures. For example, with 0.2 phr of dibutyltin dilaurate, Poly bd R-45HTLO resin and an isocyanate will cure completely at ambient temperatures in approximately 12-16 hours, at 75° C. in 812 hours, and at 125° C. in 15-30 minutes.

The properties of the unfilled urethanes in Table 4 resemble those of an unreinforced SBR vulcanizate. Whereas the tensile and tear strengths are low, the gumstocks show good compression set, impact resilience and low temperature properties.

Table 4

Properties of Typical One-Step Unfilled Urethanes Based on Poly bd Resin

| Formulation (pbw) | <u>1</u> | <u>2</u> |
|--------------------------|-----------------|-----------------|
| Poly bd R-45HTLO resin | 100 | 100 |
| Toluene Diisocyanate | 7.0 | - |
| Isonate 2143L | - | 12.5 |
| DBTDL | 0.2 | 0.2 |

Physical Properties of Gumstocks

| | | |
|--|----------|--------|
| Tensile Strength, psi | 140 | 179 |
| Ultimate Elongation, % | 120 | 101 |
| Modulus, psi, 100% | 90 | 179 |
| Tensile Set, % | 0 | — |
| Hardness, Shore A | 45 | 53 |
| Tear Strength, ph | 20 | 16 |
| Compression Set, % Method B, 22 hrs. @ 158°F | 5.5 | — |
| Compression Set, % Method B, 22 hrs. @ 212°F | 30 | - |
| Impact Resilience Goodyear-Healey Rebound, % | 71 | |
| Low Temperature Brittleness (B) at -70 C | passed-F | passed |
| Chemical Resistance-Volume Change, +% 10% NaOH, 72 hrs. @ 216°F | 4.4 | - |
| 10% HCl, 72 hrs. @a 216° F | 3.0 | - |

Filled, One-Step Urethanes

Poly bd resin based urethanes have a polymer backbone structure similar to conventional diene rubber vulcanizate. Just as these conventional systems respond to carbon black reinforcement, Poly bd resin based urethane systems can also be reinforced with various carbon blacks, as well as a variety of other fillers. Although carbon blacks must be masterbatched into conventional elastomers with the aid of highshear mixers for efficient dispersion, they may be dispersed readily into liquid Poly bd resins before curing with minimum energy requirements. Thus, new lower cost fabrication techniques are now offered to rubber goods manufacturers.

The properties of representative carbon black reinforced elastomers are shown in Table 5. Comparison of these data with those of Table 4 illustrates that tenfold increases in tensile strengths are obtainable along with general increases in elongation and other strength properties.

A three roll mill was used to prepare the dispersions employed in obtaining these data. The use of conventional compounding equipment for high shear, such as Hochmeier or Cowles mixers results in the lowering of values at least 50%.

Calcium Carbonate

Calcium carbonate is used quite extensively to extend general purpose elastomers. More common designations for various calcium carbonates include limestone, chalk, whiting any ground oyster shell.

In general, calcium carbonates are quite soft and may be used at rather high levels. In fact, addition of calcium carbonate enhances the extrusion properties of general purpose goods Elastomers prepared using this filler are suitable for many caulk and sealant applications where high elongation and moderate tensile properties are required.

Various levels and types of calcium carbonates were investigated to determine the effects on Poly butadiene resin based elastomers. The results of this investigation are shown in Table 5.

Silica

In general, silicas contribute a great increase in tensile strength than other nonblack fillers. Silicas also have a profound stiffening effect as indicated by the increased modulus and hardness and the decrease in ultimate elongation and tear strength shown in Table 5.

Clay

Clays, like calcium carbonates, are low cost, high bulking fillers widely used in the rubber industry. In general, clays give only a moderate degree of reinforcement, only fair abrasion resistance but a relatively high stiffening effect. Clays are used as fillers in stocks requiring hardness and high modulus; e.g., shoe soles and heels, mats, and floor tile.

The use of clays as non-black fillers for Poly butadiene resin based elastomers has been investigated. Data describing the use of clay in Poly butadiene based elastomers are shown in Table 5.

Zinc Oxide

In addition to reinforcement, zinc oxide also provides resilience and heat conductivity. Its use as a reinforcing filler in general purpose elastomers is rather limited, however, due to high density and cost.

The data in Table 5 show zinc oxide to have a reinforcing effect on Poly butadiene resin based elastomers. Increasing the zinc oxide content improves tensile and tear strength, increases hardness and modulus but decreases elongation. The effect of oil extension on the physical properties of zinc oxide reinforced Poly butadiene resin based elastomers is discussed on page 8.

Combination of Zinc Oxide and Carbon Black

Zinc oxide can be effectively employed as a reinforcing filler in conjunction with carbon blacks. There is a progressive increase in tensile, modulus, tear, and hardness as carbon black loading is increased. However, at a constant black level, increasing the concentrations of zinc oxide also increases tensile, tear, modulus

and hardness until maximum values are reached, after which there is a decrease in overall physical properties. The abrasion resistance of elastomers filled with combinations of zinc oxide and carbon black were generally superior to those filled using carbon black alone. It is important to note that at a constant carbon black level, increasing the concentration of zinc oxide decreases the workable pot life after the isocyanate component is added; i.e., gelation occurs more rapidly.

In addition to carbon black, other fillers may be incorporated into Poly bd resin urethane systems to alter physical properties and reduce costs.

Although the degree of reinforcement using calcium carbonate or zinc oxide fillers is not as great as with carbon black, the non-black systems can be more highly loaded; i.e., 300 phr and higher are feasible, and in combination with oil extension (see Table 6) can provide starting points for a wide variety of low cost caulks, sealants, elastomers and foams. In addition, a wide variety of fillers, including clays, talcs, etc., can be employed with these systems, either alone or in combination to provide the formulator versatility in compounding for specific properties.

Table 5

| Formulation (pbw) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------------------------|------|------|-----|-----|-----|-----|-----|------|------|-----|-----|-----|
| Poly bd R-45HTLO resin . | 100 | | | | | | | | | | | |
| Toluene Diisocyanate | 7.0 | | | | | | | | | | | |
| DBTDL | 0.05 | | | | | | | | | | | |
| Elftex-5 (HAF-Fluffed) | 30 | | | | | | | | | | | |
| Regal 600 (ISAF-L3) | | 50 | | | | | | | | | | |
| Calcium Carbonate | | | 100 | | | | | | | | | |
| Zinc Oxide | | | | 100 | | | | | | | | 150 |
| Calcene (CaCO ₃) | | | | | 100 | | | | | | | |
| Calcene NC (CaCO ₃) | | | | | | 50 | | | | | | |
| Calcene CO (CaCO ₃) | | | | | | | 100 | | | | | |
| Silica Filler | | | | | | | | 100 | 50 | | | |
| Clay | | | | | | | | | | 50 | 100 | |
| Physical Properties | | | | | | | | | | | | |
| Tensile Strength, psi | 1700 | 1740 | 350 | 510 | 510 | 680 | 560 | 1800 | 1100 | 520 | 560 | 770 |
| Elongation, % | 570 | 460 | 320 | 420 | 610 | 630 | 700 | 60 | 170 | 280 | 270 | 210 |
| Modulus, psi | | | | | | | | | | | | |
| 100% | 210 | 280 | 240 | 190 | 330 | 210 | 260 | | 800 | 310 | 430 | 470 |
| 200% | | | | | 420 | 310 | 340 | | | 460 | 560 | 750 |
| 300% | 777 | 1030 | 330 | 420 | 450 | 450 | 380 | | | | | |
| Tear Strength, pli | 139 | 179 | 53 | 94 | 128 | 89 | 99 | 52 | 78 | 55 | 72 | 60 |
| Hardness, Shore A | 53 | 58 | 55 | 52 | 69 | 55 | 58 | 90 | 76 | 62 | 71 | 71 |

Note: All Poly bd systems used in thermal cycling conditions in air should contain 1 phr of an antioxidant such as Cyanox 2246 or Irganox 1076. The antioxidant should be added at a temperature above its melting point.

Conclusions

In most cases, non-black fillers contribute less reinforcement to Poly bd resin based elastomers than carbon black fillers. However, there are several advantages inherent in using nonblack fillers. Some of the more prominent advantages are as follows:

Ease of dispersion Lower viscosity build-up Light color High loadings-lower cost

Oil Extension

Poly bd resins, because of their hydrocarbon backbones, are compatible with conventional hydrocarbon oils, chlorinated oils, asphalts and other related low cost materials. Such mixtures can be cured with conventional diisocyanates to yield oil-extended elastomers.

The quantity of oil which can be incorporated into a Poly bd resin system is a function of the oil and the type of filler, if present. Cured Poly bd resin systems may be formulated which incorporate in excess of 100 parts oil per 100 parts Poly bd resin and do not "bleed" oil in the final product.

Table 6 demonstrates the effect of oil extension of a zinc oxide-reinforced Poly bd resin system. With the addition of up to 50 parts oil, there is a moderate decrease in tensile strength and modulus, and elongation is greatly improved while the tear strength is unaffected. No bleeding of oil was noted. These data demonstrate that the combination of oil extension and filler reinforcement provides a means to improve overall properties of Poly bd resin based urethanes while reducing formulation costs.

Oil extension provides many other advantages such as further improvement in hydrolytic stability, control of premix viscosities, gel time, cure time, and the ability to attain higher filler loading. The use of materials such as chlorinated waxes and oils also incorporates fire retardant properties into the finished product.

The effect of oil extension on gel time is shown in Figure 9 for an unfilled one-step urethane cured with Isonate 2143L. The addition of 60 parts oil extended the gel time in an uncatalyzed reaction from 50 to 110 min. As shown with catalyzed systems, the trend to lengthen gel times is maintained. However, the relative effect is diminished.

The addition of an electrical grade hydrocarbon oil or ester plasticizer will serve to extend the formulation by a dilution effect. These materials are generally utilized to reduce viscosity and lower cost. Increasing levels of oil or plasticizer will tend to increase elongation and lower tensile and tear strengths. Very high levels of oil or plasticizer (up to 80 parts-per 20 parts by weight of polymer) will result in a jellylike cured material with minimal physical properties but still retaining electrical insulation characteristics. The addition of liquid extenders will also tend to extend pot life and cure times.

The selection of the extender oil will depend on compatibility parameters as well as the viscosity and volatility characteristics desired. Hydrocarbon process oils of the aromatic and naphthenic type are most compatible with Poly bd resin. As a general rule, oils with at least 40% aromatic content are highly compatible and can be used at relatively high levels. Process oils that have a high paraffinic component are the least compatible.

Plasticizers are also effective as extenders for Poly bd resin and they tend to be lower in viscosity than process oils. Aromatic ester plasticizers such as dioctyl and diundecyl phthalate as well as triisononyl mellitate can be used. Linear esters such as ditridecyl adipate are also useful.

A list of generally compatible extenders for Poly bd resin follows:

- Dioctyl Phthalate
- Diundecyl Phthalate
- Tricresyl Phosphate
- Chlorinated Paraffin
- Aromatic Process Oil
- Naphthenic Process Oil
- Alkyl Naphthalenes
- Asphalt
- Coal Tar
- Linseed Oil
- Tung Oil
- Detergent Alkylate

Table 6
Effect of Oil-Extension on Zinc Oxide Reinforced Poly bd Based Elastomers

| Formulation (pbw) | 1 | 2 | 3 |
|----------------------------|----------|----------|----------|
| Poly bd R-45M resin | 100 | 100 | 100 |
| NCO: OH | 1:1 | 1:1 | 1:1 |
| DBTDL | 0.2 | 0.1 | 0 |
| Process Oil (A) | | 25 | 50 |
| Zinc Oxide | 300 | 300 | 300 |
| Physical Properties | | | |
| Tensile Strength, psi | 1030 | 750 | 510 |
| Elongation, % | 160 | 240 | 650 |
| Modulus, psi | | | |
| 100°/a | 890 | 570 | 220 |
| 200% | | 730 | 330 |
| 300% | | | 370 |
| Tear Strength, pli | 93 | 89 | 92 |
| Hardness, Shore A | 82 | 73 | 49 |

(A) Naphthenic type oil; viscosity 121 cp @ 100°F

Asphalt Extension

In addition to extender oils and fillers common to rubber processing, asphalt modification provides the basis for formulating many low-cost elastomeric caulks, sealants and coatings. Tables 7 and 8 show the properties of a series of asphaltextended products

prepared by adding a mixture of carbon black, Poly bd R-45HTLO resin and polymeric, PAPI 901 (f=2.6) or PAPI 27 (f=2.3), or modified MIDI, Isonate 2143L, products to either AC-20 or AC-5 straight run asphalt. The 1.1 NCO/OH ratio used included the isocyanate equivalency of the asphalt. These data indicate that, while the tensile strength of the elastomers is only moderately affected, the elongation changes significantly with the level of asphalt and the functionality of the isocyanate.

Table 7
Poly bd Resin/Asphalt Urethanes

| Formulation (pbw) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|
| Poly bd R-45HTLO resin | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Asphalt AC-20 | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 | 100 | 400 |
| Carbon Black Sterling R | 6.0 | 9.0 | 12.0 | 15.0 | 6.0 | 9.0 | 12.0 | 15.0 | 6.0 | 15.0 |
| DBTDL, drops | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| PAP1 27 | 13.26 | 14.73 | 16.20 | 17.67 | - | - | - | - | - | - |
| PAP 1901 | - | - | - | - | 13.02 | 14.46 | 15.91 | 17.36 | - | - |
| Isonate 2143L | - | - | - | - | - | - | - | - | 14.21 | 18.94 |
| Physical Properties | | | | | | | | | | |
| Tensile Strength, psi | 189 | 222 | 319 | 226 | 224 | 340 | 354 | 309 | 265 | 258 |
| Elongation, % | 183 | 303 | 437 | 413 | 291 | 600 | 720 | 785 | 506 | >800 |
| Tensile Set, % | 4 | 7 | 18 | 13 | 5 | 17 | 17 | 25 | 8 | 56 |
| Modulus, psi | | | | | | | | | | |
| 100% | 158 | 132 | 108 | 89 | 158 | 127 | 100 | 80 | 125 | 72 |
| 200% | - | 161 | 122 | 107 | 190 | 145 | 106 | 91 | 160 | 81 |
| 300% | - | - | 169 | 145 | 220 | 164 | 122 | 101 | 185 | 88 |
| Tear Strength, pli | 34 | 44 | 46 | 35 | 42 | 54 | 48 | 40 | 54 | 42 |
| Hardness, Shore A | 49 | 48 | 50 | 43 | 44 | 49 | 45 | 45 | 41 | 25 |

NCO/OH ratio=1.1 AC-20 (77° F)=72 penetration, straight run asphalt

Table 8
Poly bd Resin/Asphalt Urethanes

| Formulation (pbw) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Poly -bd R-45HTLO resin | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Asphalt AC-5 | 100 | 200 | 300 | 400 | 100 | 200 | 300 | 400 | 100 | 400 |
| Carbon Black Sterling R | 6.0 | 9.0 | 12.0 | 15.0 | 6.0 | 9.0 | 12.0 | 15.0 | 6.0 | 15.0 |
| DBTDL, drops | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| PAP 127 | 13.26 | 14.73 | 16.20 | 17.67 | - | - | - | - | - | - |
| PA P I 901 | - | - | - | - | 13.02 | 14.46 | 15.91 | 17.36 | - | - |
| Isonate 2143L | - | - | - | - | - | - | - | - | 14.21 | 18.94 |
| Physical Properties | | | | | | | | | | |
| Tensile Strength, psi | 174 | 174 | 202 | 219 | 214 | 275 | 292 | 249 | 266 | 230 |
| Elongation, % | 170 | 287 | 403 | 570 | 300 | 562 | 688 | 650 | 593 | 930 |
| Tensile Set, % | 3 | 5 | 11 | 12 | 4 | 11 | 12 | 14 | 9 | 35 |
| Modulus, psi | | | | | | | | | | |
| 100% | 140 | 105 | 76 | 59 | 133 | 111 | 79 | 60 | 111 | 56 |
| 200% | - | 134 | 97 | 74 | 173 | 128 | 88 | 72 | 142 | 65 |
| 300% | - | - | 134 | 97 | 207 | 146 | 100 | 90 | 165 | 75 |
| Tear Strength, pli | 34 | 33 | 35 | 29 | 38 | 46 | 37 | 30 | 50 | 30 |
| Hardness, Shore A | 43 | 41 | 39 | 34 | 42 | 45 | 39 | 34 | 37 | 25 |

NCO/OH ratio=1.1

AC-5 (77° F)=141 penetration, straight run asphalt

Short Chain Reinforcing Diols

Physical properties of Poly bd resin based elastomers can be improved by the addition of auxiliary polyols to the formulation. A wide variety of short chain diols may be employed, however, Voranol 220530 (phenyl diisopropanolamine) was found to be most effective.

The use of a short chain diol in conjunction with the required additional isocyanate increases the urethane concentration in the final polymer backbone. This combination leads to increased hydrogen bonding between polymer chains and thus higher strength properties in the cured elastomer. These same effects can be noted when short chain diamines or mixed alcohol diamines are employed as auxiliary reactants with Poly bd resins.

The Voranol 220-530 chemically reinforces the cured Poly bd elastomer, increasing hardness and improving tensile and tear strengths. Table 9 shows the effect of increasing levels of Voranol 220-530 in a Poly bd system. Other effective short chain diols are 2-ethyl-1, 3-hexanediol and bishydroxyethyl dimerate.

Isocyanates such as PAPI, PAPI 901 or others may be used with Voranol 220-530 systems, but the Isonate 2143L produced elastomers with better physical properties.

Note:

Don't forget that oil extension and filler reinforcement can be used with short chain reinforcing diols to allow maximum property and cost modification.

Two-Step Urethanes and Urea-Urethanes

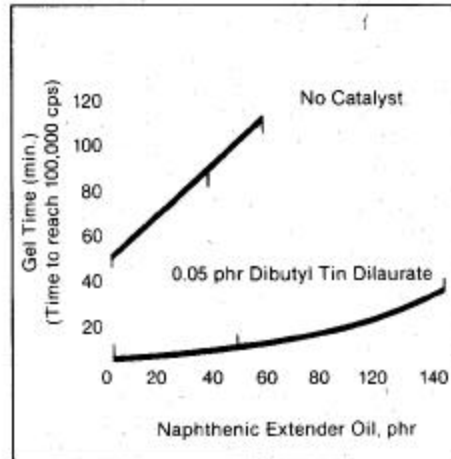
Previous sections described the preparation of diverse one-step urethane and ureaurethane products based on Poly bd resins. In many conventional urethane applications, it is desirable or essential to utilize a two-step reaction sequence, wherein an isocyanateterminated prepolymer (quasiprepolymer) is first formed and subsequently converted to a high molecular weight elastomer by further reaction with glycols, diamines, or other chainextending agents.

Isocyanate prepolymers are widely used for producing high performance elastomers of castable, millable, and moldable types. Other applications include foams, and one and two component coatings, caulks, sealants, etc.

The chemistry of Poly bd resin based prepolymer systems is outlined in Figure 10.

Prepolymers of Poly bd resins can be prepared with excellent storage characteristics when the recommended reaction and handling precautions are observed. See Appendix C for further detailed information.

Figure 9 Gel Time vs. Extender Oil



Reaction of isocyanate-terminated prepolymers with diol or diamine extenders produces solid elastomers. In addition to the normal chain extension reaction, cross-linking occurs in these systems because the functionality of the Poly bd resins is in excess of two. Accordingly, when a diol extender is employed, crosslinking occurs via urethane and allophanate formation. With diamine extenders, further crosslinking is possible thru urea and biuret formation.

Two-Step Urethanes

Use of the prepolymer technique in preparing Poly bd resin urethanes provides a method for preparing elastomers having improved physical properties over unmodified or unreinforced one-step Poly bd resin systems. A wide variety of chain-extending diols can be employed, and this choice will affect the cure rate and the final physical properties of the urethane. Two particularly good diols for use with Poly bd resin based prepolymers are 2-ethyl, 1,3 hexanediol, and Voranol 220-530. Properties of some typical systems are shown in Tables 10 and 11.

As can be seen from these data, maximum properties for both systems in tensile and tear strengths occur at NCO/OH ratio is changed, other properties such as elongation and hardness can be altered to the formulators desire. Also at devreased NCO/OH the degree of thermoplasticity of the system increases so that thermoplastic and millable gumstocks are feasible.

Alteration of the free NCO content of the prepolymer provides a further means of changing the physical properties of the cured gumstocks.

Table 9
Effect of Voranol 220-530 Content NCO/OH ratio = 1.05

| Formulation (pbw) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Poly bd R-45HTLO 9 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Voranol 220-530, g | - | 2.22 | 4.45 | 8.89 | 11.85 | 17.78 | 26.67 | 35.56 |
| DBTDL, drops | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| Cyanox 2246, g | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| Isonate 2143L, g | 12.76 | 15.45 | 19.14 | 25.53 | 29.78 | 38.29 | 51.05 | 63.81 |
| Equivalent ratio - | | | | | | | | |
| Poly bd/Voranol 220-530- | | 4/1 | 2/1 | 1/1 | 3/4 | 1/2 | 1/3 | 1/4 |
| Tensile Strength, psi | 179 | 242 | 377 | 902 | 1192 | 2021 | 2695 | 3476 |
| Tear Strength, pli | 16 | 40 | 46 | 114 | 150 | 231 | 308 | 411 |
| Elongation, % | 101 | 151 | 195 | 238 | 245 | 300 | 325 | 297 |
| Modulus, psi | | | | | | | | |
| 100% | 179 | 192 | 124 | 247 | 465 | 1073 | 1609 | 2182 |
| 200% | - | - | 195 | 382 | 763 | 1492 | 2126 | 2814 |
| 300% | - | - | - | - | - | 2010 | 2641 | 3784 |
| Hardness, Shore A | 53 | 56 | 62 | 75 | 82 | - | - | - |
| Shore D | - | - | - | - | - | 43 | 51 | 53 |

Elastomer sheets cured for 0.5 hr. at 80°C in press; post-cured for 64 hrs. at 49°C.

Table 10
**Two-Step Urethane Elastomers from Poly bd R-45M Resin -TDI
 Prepolymer and 2-Ethyl-1, 3-Hexandiol**

| Formulation | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| Percent fRee NCO of Prepolymer | 6.39 | 6.56 | 6.56 | 6.56 | 8.71 | 8.71 | 8.71 | 8.72 |
| Reaction NCO/OH Ratio | 0.8 | 0.9 | 1.0 | 1.1 | 0.8 | 0.9 | 1.0 | 1.1 |
| Formulation (pbw) | | | | | | | | |
| R-45M Prepolymer | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2-Ethyl-1,3-hexanediol | 13.9 | 12.6 | 11.4 | 10.4 | 19.0 | 16.9 | 15.2 | 13.8 |
| DBTDL | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Elastomer Properties | | | | | | | | |
| Tensile strength, psi | 310 | 550 | 1140 | 990 | 340 | 1300 | 2270 | 2200 |
| Tear Strength, pli | 55 | 105 | 140 | 145 | 90 | 230 | 215 | 210 |
| Elongation, % | 950+ | 635 | 460 | 335 | 1130 | 615 | 470 | 410 |
| Hardness, Shore A | 45 | 58 | 70 | 74 | 45 | 80 | 84 | 88 |
| Modulus, psi | | | | | | | | |
| 100% | 95 | 185 | 365 | 480 | 195 | 555 | 770 | 865 |
| 200% | 110 | 235 | 495 | 665 | 220 | 680 | 1010 | 1145 |
| 300% | 125 | 280 | 650 | 890 | 235 | 795 | 1270 | 1470 |

Table 11
Two-Step Urethane Elastomers from Poly bd R-45M Prepolymers and Voranol 220-530

| Formulation (pbw) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
|----------------------------|----------|----------|----------|----------|----------|----------|----------|----------|------|
| Poly bd R-45M Prepolymer | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | |
| Tinuv_in 327 | - | - | - | 1.0 | - | - | - | - | |
| Cyanox _2246 | - | - | - | 1.0 | - | - | - | - | |
| DBTDL Catalyst | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | |
| Vorano1220-530 | 15.0 | 21.3 | 29.6 | 36.0 | 26.7 | 24.0 | 21.3 | 19.3 | |
| NCO/OH ratio | 1.0 | 1.0 | 1.0 | 1.0 | 0.83 | 0.94 | 1.04 | 1.15 | |
| Percent NCO of Prepolymer | 6.0 | 8.9 | 11.9 | 14.5 | 8.9 | 8.9 | 8.9 | 8.9 | |
| Physical Properties | | | | | | | | | |
| Tensile Strength,psi | | 1280 | 3140 | 2970 | 1920 | 1090 | 3170 | 3140 | 2160 |
| Elongation, %_ | | 400 | 495 | 400 | 400 | 705 | 595 | 495 | 575 |
| Modulus, psi | | | | | | | | | |
| 100% | | 570 | 1040 | 1485 | 1690 | 805 | 990 | 1040 | 880 |
| 200% | | 765 | 1340 | 1950 | 1650 | 890 | 1235 | 1340 | 1120 |
| 300% | | 970 | 1685 | 2200 | 1670 | 910 | 1475 | 1685 | 1310 |
| Tear Strength, pli | | 195 | 295 | 340 | 290 | 275 | 345 | 295 | 305 |
| Hardness, Shore D | | 34 | 42 | 51 | 50 | 40 | 42 | 42 | 40 |

Applications for Poly bd Resin Systems

A wide range of properties is attainable in Poly bd based urethanes. These features, combined with their versatility in formulating with compatible oils and inexpensive fillers, enhance their value for many elastomer applications. General-purpose rubber parts can easily and inexpensively processed from Poly bd resin based systems. These systems can vary from completely castable liquids to millable gumstocks. Oil and Asphalt-extended Poly bd resin based systems permit low-cost systems for elastomer coatings, linings, adhesives, caulks, and sealants.

Compounding flexibility permits viscosity control for sprayable coatings and adhesives, with excellent moisture and chemical resistance. Other advantages of Poly bd resin based 100% polymer systems over many conventional systems include the elimination of the use of solvents and solvent removal equipment and capability for room temperature cures or very fast oven cures. The liquid Poly bd resin prepolymer systems, cured with Voranol 220-530, provide excellent high performance coatings having good abrasion, impact and low temperature properties.

Both rigid and flexible products can be produced by chemical blowing techniques identical to those used in foaming polyether and polyester urethanes. Sponge products can be produced with blowing techniques used in sponge rubber production. In addition, Poly bd resin based systems can be mechanically frothed to obtain medium density, closed cell, flexible and nonflexible end-products.

Potting and encapsulating compounds exhibit excellent electrical properties. Further information on the electrical properties of these materials are available on request.

The ability of Poly bd resins to accept high filler loadings and to be extended with asphalts and oils allows the formulation of many low-cost, good performance caulks and sealants.

A list of applications where Poly bd urethane elastomers are typically used follows.

- Electrical/Electronic Potting & Encapsulation**
- Construction**
 - Asphalt Extended Membranes**
 - Waterproofing Membrane**
 - Roofing**
 - Mastics**
 - Highway Sealants**
 - Architectural Sealants**
 - Chemically Resistant Coatings**
 - Adhesives**
 - Pond Liners**
 - Athletic Surfaces**
 - Insulating Glass Sealants**
- Adhesives**
- Rubber Parts**
- Military/Aerospace**
- Reaction Injection Molding (RIM)**
- Automotive**

Appendix A-Urethane Calculations

In all urethane calculations the reactants should be expressed in terms of equivalent weight. The basis for this approach is that one equivalent of OH, or other active H will react with one equivalent of NCO. In general, an NCO/OH equivalent ratio of approximately 1

$$\begin{array}{l} \text{For Hydroxyl Compounds: EW} = \frac{\text{Molecular Weight}}{\text{Functionality}} \\ \text{EW} = \frac{56100}{\text{Hydroxyl Number}} \\ \text{EW} = \frac{1000}{\text{Hydroxyl Value}} \\ \text{EW} = \frac{1700}{\% \text{ Hydroxyl}} \end{array} \quad \begin{array}{l} \text{For Isocyanate Compounds: EW} = \frac{\text{MW of NCO Compound}}{\text{Functionality}} \\ \text{EW} = \frac{4200}{\% \text{ NCO in compound}} \end{array}$$

$$\text{Also: Hydroxyl Value} = \frac{\text{milliequivalent OH}}{\text{g}} \frac{\text{Hydroxyl Number}}{56.1}$$

Examples of Urethane Formulation Stoichiometry follow:

General Formula

$$\frac{\text{Weight NCO Compound}}{100 \text{ g Hydroxyl Compound}} = \frac{(\text{Hydroxyl Value}) (\text{EW NCO compound}) (\text{NCO/OH ratio})}{10}$$

- Find the weight of Isonate 2143L1(EW=143) needed to prepare a gumstock from Poly bd R-45HTLO resin (Hydroxyl Value=0.83 meq/g) at an NCO/OH ratio of 1.1.

$$\frac{\text{Weight Isonate 2143L}}{1008 \text{ Poly bd R-45HTLO Resin}} = \frac{(0.83) (143) (1.1)}{10} = 13.0\text{g}$$

For each 1008 of R-45HTLO resin, 13.0g of Isonate 21431-mould be required.

- Find the weight of Isonate 2143L needed to make a Poly bd resin system reinforced with Voranol 220-530, at a Poly bd/Isonol equivalent of 1/2 and NCO/OH ratio of 1.1.

$$\text{Equivalents Poly bd R-45HTLO Resin} = \frac{\text{Weight Poly bd R-45HTLO Resin}}{\text{EW Poly bd R-45HTLO Resin}}$$

$$\frac{100\text{g}}{1000/0.83 \text{ meq/g}} = 0.083 \text{ equivalents}$$

$$\text{Equivalents Voranol 220-530} = (2) (\text{equivalents Poly bd R-45HTLO Resin}) (2) (0.083 \text{ eq}) = 0.166 \text{ equivalents}$$

$$\text{Weight Voranol 220-530} = (\text{Equivalents Voranol 220-530}) (\text{EW Voranol 220-530}) = 0.083\text{g} + 0.166\text{g} (143\text{eq/eq}) = 17.3\text{g}$$

$$\begin{array}{l} \text{Weight Isonate} \\ \text{2143L required} \end{array} = \begin{array}{l} (\text{total OH equivalents}) (\text{EW Isonate 2143L}) (\text{NCO/OH}) \\ = (0.0838 + 0.1668) (143\text{eq/g}) (1.1) = 39.28 \end{array}$$

Formula would be:

| | |
|------------------------|-------|
| Poly bd R-45HTLO resin | 100g |
| Voranol 220-530 | 17,38 |
| Isonate 2143L | 39.28 |

- Prepolymers of Poly bd resins may be prepared at various % free NCO by use of the following equation:

$$\frac{\text{Weight Isocyanate}}{100\text{g Poly bd Resin}} = \frac{100 (\text{EW Isocyanate})}{\text{EW Poly bd Resin}} \times \frac{100 (\text{EW NCO}) + (\text{EW Poly bd Resin}) (\% \text{ Free NCO})}{100 (\text{EW NCO}) - (\text{EW Isocyanate}) (\% \text{ Free NCO})}$$

Appendix B-Preparation of Elaston

1. One-Step Urethanes

- A. Weigh out the components of the desired formulation; e.g., Poly bd resin, filler(s), extender oil, antioxidants, and tin catalyst.
- B. Charge the weighed components to a suitable mixing device and mix until the ingredients are well dispersed.* Mixing time may vary with the efficiency of the mixing device.
It is advisable to degas the "masterbatch" during the mixing steps under vacuum. It may also be necessary to dry fillers at elevated temperatures to remove moisture.
- C. Add the calculated amount (See Appendix A) of di- or polyisocyanate to the mixture to give the desired NCO/OH ratio in the final formulation. In elastomer systems, optimum properties are usually obtained at NCO/OH ratios between 1.0 and 1.1.
- D. Mix the completed formulation until homogenous and pour or pump into molds or apply to desired substrate.
- E. If multi-component mixing-metering equipment is utilized, the filled Poly bd resins and isocyanate components may be metered separately into the mixing head of the metering device
- F. Permit the formulation to cure. Longer cure times are required at lower temperatures. The elastomers described in this bulletin were arbitrarily cured at 175-212F for 1/2 hours unless otherwise stated. No differences in properties were noted between elastomers which were cured at ambient or elevated temperatures.

Catalyst concentration and/or level of oil extension permit wide latitude in pot lives and cure times of specific formulations as previously discussed.

Moreover, the type of filler greatly affects workable pot life and cure time. For example, zinc oxide catalyzes the reaction and, therefore, shortens pot life. But acidic fillers such as silicas may have a retarding effect on pot life and ultimate cure time.

2. One-Step Urea-Urethanes

Procedure is identical as for the onestep urethanes, except that diamines are added to the Poly bd resin formulation during the initial mixing cycle.

3. Two-Step Urethanes

The weighed prepolymer is mixed with weighed amounts of catalyst, filler and polyol, such as Voranol 220-530, or more Poly bd resin (or diamine if urea-urethanes are desired) and cured at ambient or elevated temperatures.

*Note: A three-roll paint mill was used to prepare the filled formulations presented in this bulletin. However, experimental work has shown that filler can be satisfactorily dispersed with conventional mixers.

Appendix C-Preparation of Prepoly

Prepolymers from Poly bd resins can be prepared with excellent shelf-life when the following reaction and storage precautions are observed:

1. The Poly bd resin must be thoroughly degassed. It is recommended that the resin at 100°C be evacuated at low vacuum for a minimum of 30 minutes with efficient stirring.
2. The addition of benzoyl chloride (0.03% based on Poly bd resin) prior to the addition of the diisocyanate greatly enhances the stability of the prepolymer product. The same amount of benzoyl chloride may be added to the prepolymer at the completion of the reaction to further insure shelf stability.
3. When storing the prepolymer, containers with plastic lids should be avoided. Narrowmouthed solvent cans which can be plugged and then capped are the most satisfactory containers. The product should always be purged with nitrogen before sealing.

The procedure below has been employed successfully in preparing Poly bd prepolymers. The equipment used was a five-gallon working capacity 316 stainless steel jacketed autoclave equipped with an anchor type stirrer, thermowell, charging port, vacuum and nitrogen lines, and a bottom flush valve. The autoclave was heated by circulating a lubricating oil heat transfer fluid through a 6 kW electric heater and then through the autoclave jacket. Cooling was effected by circulating the oil through a water cooled heat exchanger and through the autoclave jacket.

Procedure

The Poly bd resin was charged to the autoclave, and the autoclave sealed. The agitator was turned on, the vessel evacuated to 20 mm mercury absolute pressure, and heating begun.

About two hours time was required to heat the charge from 76° to 230° F, with a maximum jacket temperature of about 245° F. The autoclave internal pressure was 5 mm mercury absolute pressure at the 230° F internal temperature. The autoclave contents were degassed and stirred at 230-232° F and 5 mm mercury absolute pressure for thirty minutes. The autoclave contents were then cooled to 107° F over a two-hour period.

The autoclave internal pressure was increased to 55 mm mercury absolute pressure and benzoyl chloride added. After stirring five minutes, the diisocyanate was added. The addition required about three minutes. The exothermic reaction increased the internal temperature from 103° F to 123° F over a twelve minute time interval. The autoclave contents were then heated to 140° F with stirring, at 50 mm mercury absolute pressure, over a one hour period.

The reactor contents were maintained at 140° F/50 mm mercury, with stirring, for two hours.

A second portion of benzoyl chloride was then added with stirring, and the product withdrawn into three twogallon screw-top cans. The cans were thoroughly flushed with prepurified nitrogen before sealing.

For low NCO pre-polymers (6% Free NCO) it is recommended that 1% Cyanox 2246 also be added for package stability.

Appendix D-Product Identification

| Tradename | Chemical Name | Supplier |
|-------------------|-------------------------------------|---------------------------------|
| Voranol 220-530 | (phenyl diisopropanoamline) | The Dow Chemical Company |
| IsonateO" 2143L | Polyfunctional liquid isocyanate | The Dow Chemical Company |
| PAPlo | Polymethylene polyphenyl isocyanate | The Dow Chemical Company |
| Cyanox,#, 2246 | Antioxidant | Cytec Industries |
| Tinuvin* 327 | U.V. Stabilizer | CibaCorporation |
| Lead Octoate | Catalyst | Nuodex Chemical Company |
| DBTDL Catalyst | Dibutyltin Dilaurate | Air Products & Chemicals, Inc. |
| Dabco(-) | Triethylene Diamine | Air Products & Chemicals, Inc.. |
| Pluracolck TP-340 | Urethane triol | BASF Corporation |

Appendix E

The following tests were used to determine properties of Poly bd elastomers described in this brochure.

| Physical Property Tested | Method |
|--------------------------------|-----------------------|
| Tensile Strength | ASTM D-412-61T |
| Ultimate Elongation | ASTM D-412-61T |
| Tensile Modulus | ASTM D-412-61T |
| Tear Strength | ASTM D-624-51 (Die C) |
| Shore Hardness | ASTM D-676-59T |
| Flexural Cut Growth Resistance | ASTM D-1052-55 |
| Low Temperature Brittleness | ASTM D-746 |
| Compression Set | ASTM D-395 |
| Oil and Solvent Resistance | ASTM D-471-64T |
| Abrasion Index | ASTM D-1630-61T |
| Impact Resilience | ASTM D-1054-55 |

Applications of Poly bd * Resins

General

Adhesives
Binders
Ball Cores
Foams
Liquid Castable
 General Purpose
Rubbers
Reaction Injection Molding
Reinforcement of Rubber/
 Urethane Elastomers
Rollers
Urethane Elastomers

Coatings

Can Coatings
High Solids Coatings
Maintenance Coatings
Pipeline Coatings
Urethane Asphalts
Water Based Electrocoatings
Waterproof Deck Coatings

Construction Products

Athletic and Recreational
Surfaces
Caulks and Mastics
Elastomeric Asphalts
Insulating Glass Sealants
Jint and Crack Sealant
Urethane-Asphalt Emulsions

Waterproof Membranes

Architectural Membranes
Pond and Waste Treatment
Linings
Roofing
Spray-on Membranes

Electrical Applications

Cable Filling Compounds
Coil Impregnants
Conformal Coatings
General Purpose Potting &
 Encapsulating
Compounds
HighVoltage Insulating
Elastomers

Automotive

Adhesives
Brake Linings
Electrical Potting &
Encapsulation
Sealants
SoundNibration Damping

For additional information and/or samples, please call one of the offices listed below.