

Poly bd[®] Resins in the Coatings Industry

Introduction

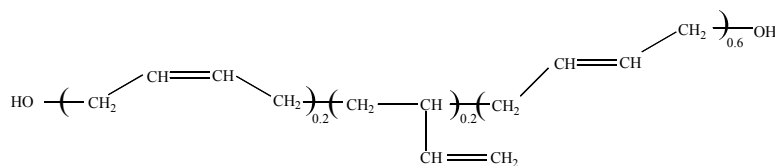
Poly bd Resins are not commonly associated with coatings, especially when to most, coatings means paints. However, when thought of in a broader sense, the highly flexible compositions made from these resins demonstrate outstanding performance in water proofing coatings, electrical varnishes and anticorrosive barrier membranes. Hydroxyl functional polybutadiene oligomers are better known as binders in solid rocket fuel, insulated glass sealants and electrical potting. Do they have utility in paints?

Poly bd resin was originally conceived as a synthetic drying oil in the late 1950's by Dr. O.W.

Burke of Burke Research Company¹ while working for Texas Butadiene and Chemical Company. The product was commercialized in 1971 when a semi-works plant was constructed by ARCO Chemical Co.

These resins are liquid, low molecular weight polymers of 1,3-butadiene. Multi functionality is the distinguishing characteristic of Poly bd resins and a variety of reactions can occur at the olefinic and hydroxyl centers. A generalized structure is shown in Figure 1. Poly bd resins have been used in various applications in which polyurethanes are formed by reaction of the hydroxyl groups with polyfunctional isocyanates to give materials with resistance to aqueous chemicals, low temperature flexibility and high adhesion to metals and glass.²⁻⁶

Figure 1.



Traditional Coatings of Poly BD Resins

Despite outstanding resistance to aqueous chemicals and utility in metal protection, especially where resistance to acid, caustic or moisture is required, Poly bd coatings were rarely used in thin film coatings because they were perceived to form only soft polyurethanes. Based on historical information a formulator might expect only a 5B pencil hardness from a pigmented, two part

polyurethane paint and despite good adhesion, would consider this low hardness below what is reasonably accepted by the industry. However, Poly bd resins are easy to formulate and tolerate high solids loadings, are readily extended with asphalts, are soluble in common solvents, and most importantly for paint thinking, can participate in oxidative cross-linking, the original use perceived by O.W. Burke in 1966.

Moisture Proof Membranes

Spray applied, self leveling and trowellable coatings are easily formulated with Poly bd resins and are used, for example, in construction to water proof basements, roofs, garage decks and oil water separator tanks. Spray coatings with an thixotropy index of 4.5 to 7.6 give a 30.5 N/mm (173 pli) tear resistance at a Shore A 80 hardness. A self leveling coating for roller or squeegee application can accept 80 parts of soft asphalt to 100 parts Poly bd resin and a trowellable composition with a similar resin backbone is easily made by addition of 100 parts filler and 100 parts asphalt per 100 parts of Poly bd resin.

Electrical Coatings

With free radical initiation and heat cure, Poly bd resin, formulated with a vinyl monomer and a polyfunctional methacrylate produces a H to 6H coating, depending on component ratio, with outstanding electrical insulation properties that will meet Class F (continuous 150°C) in motors and Class H+ (continuous 220°C/aluminum conductors) in high voltage transformers. Adhesion and protection from moisture are maintained.

New Opportunities

Air Dry Systems

The use of Poly bd resin in air dry rust inhibitive primers was described by J.J. Salitros⁷ in 1992. With no modification, Poly bd resins will dry at room temperature to a tough, flexible film, in about thirty days, providing dry film thickness (dft) is less than 25 microns. The addition of typical, organometallic paint driers shortens the dry time to a reasonable time frame. Nevertheless, only thin films will through dry and 50 microns (2 mil) is the practical limit. These primers recoat easily with a variety of topcoats.

Melamine Coil Coatings

Poly bd resins react with aminoplasts to give highly flexible coatings that cure under the high speed, coil coating conditions. Greater than 160 in lb impact and zero T-bend is obtained with an anti-corrosive, barium chromate containing formulation.

Polyurethane Anti-corrosive Primers

The film thickness restrictions of air dry systems is easily circumvented by incorporating an aromatic or aliphatic isocyanate into the system at a greater than 1/1 NCO to OH ratio. Cobalt, zirconium or calcium dryer package is used to catalyze alkydlike chemistry and the urethane formation allows variable dry time and traditional coating weights. Impact resistance, flexibility and resistance to aqueous chemicals is retained. In addition, resistance to organic solvents, typically deficient in the well documented, traditional Poly bd urethanes elastomers, is realized. These breakthroughs were described by J.J. Salitros in an exhaustive study of isocyanates, pigments driers and UV stabilizers.⁸

Secondary Containment Coatings

The resistance of Poly bd coatings to acid and caustic has been demonstrated in many applications. In secondary containment, adhesion to concrete and flexibility to bridge cracks in a concrete containment dike with a 250 micron (25 mil) coating is necessary. With a clay filler, a simple polyurethane of Poly bd resin withstood penetration by 70% sulfuric acid for 96 hours and by 98% sulfuric acid for 48 hours.

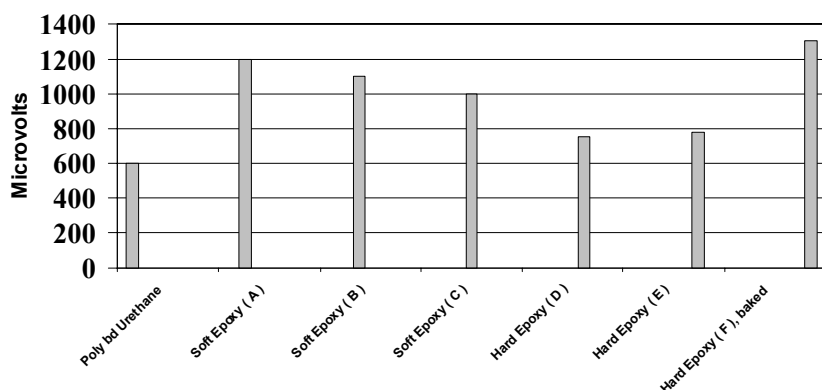
In a baked, high build coating, a Poly bd polyurethane exposed to 190°F, 50% caustic and saturated sodium chloride for 24 hours did not change in hardness and maintained dimensional stability.

New Chemistry and New Discoveries

The urethane modified anti-corrosive primer, which contains no chromate additive, outperformed several epoxy primers for reinforcing bar. The "Pore-Cell Test" for rebar is similar to cathodic disbonding. The test involves immersion of a coated and uncoated bar in separate cylinders containing alkali solution, one of which also contains sodium chloride. The bars are connected by a resistor and salt bridge, thus setting up an electrolytic cell. Voltage measured across the resistor reflects corrosion. The lower the voltage, the less the electrolytic corrosion. Figure 2 shows a comparison among the Poly bd primer and several epoxies containing strontium chromate.

Figure 2.

Electrolytic Corrosion of Rebar



Water dispersed polyurethanes can be made from Poly bd resins, despite their intensely hydrophobic nature, by a patented process. These dispersions quickly air dry to form tough films with excellent adhesion to galvanized steel. Aziridine crosslinkers are not needed. These dispersions were described in 1997 by R.H. Boutier.⁹

Unsaturated polyesters can be prepared from Poly bd resins and undergo peroxide initiated cure in baked coatings that have high hardness while maintaining excellent flexibility. This is another route to single component systems for baked coatings.

Epoxidized Poly bd resins offer the formulator a variety of chemistries to use singly or simultaneously. Anhydride curing agents produce excellent coatings when reacted with the internal oxiranes of these unusual resins. In addition, these resins are appropriate for cationic UV cured coatings, as demonstrated by F. Cazaux, et al.¹⁰

A vinyl functional urethane oligomer of Poly bd resin cures with either peroxide initiation or by free radical, UV techniques. Depending on the cure conditions, this resin can form soft conformal coatings or hard coatings for metals.

Conclusion

The unusual versatility of Poly bd resins makes them an excellent choice for the coatings formulator. Few resins can meet the demands of

so many application areas. Whether those demands be for corrosion resistant coatings without chromate pigments, tough waterborne urethanes without aziridines, coatings with excellent electrical resistance, or environmental coat resistant to aqueous chemicals, Poly bd resins perform as few others can.

References

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Viscosity Reduction Table for Poly bd[®] R45HTLO Resin

The following tables show the approximate of Poly bd R45HTLO in common coatings solvents. Measurements were made at 20°C.

Poly bd R45HTLO									
Viscosity, Brookfield cP (mPa)	% SOLIDS								
	10	20	30	40	50	60	70	80	90
Ordorless mineral spirits		50	90	100	180	290	575	2150	4400
Mineral spirits	34	40	70	96	130	230	470	825	1450
Xylene	30	32	57	70	88	168	350	850	2080
Aromatic 100	34	50	60	85	105	175	350	1075	1225
Aromatic 150	40	65	80	89	160	230	460	1175	2600
Methyl ethyl ketone	29	30	32	60	77	103	220	580	1850
Methyl isoamyl ketone	30	35	40	70	100	170	340	880	2200
Butyl acetate	32	45	65	80	90	170	370	790	1660
Tetrahydrofuran		30	57	73	88	125	350	790	2560
EXXATE 600	32	35	60	86	110	220	490	1100	1660
Viscosity, Seconds #4 Ford Cup									
Ordorless mineral spirits		15	19	26	56	110	236	528	1845
Mineral spirits	12	13	17	23	39	82	169	450	993
Xylene	10	11	13	15	23	46	100	244	649
Aromatic 100	12	14	16	21	34	60	124	288	743
Aromatic 150	13	15	18	23	41	76	167	360	979
Methyl ethyl ketone	10	10	11	14	16	26	63	168	498
Methyl isoamyl ketone	11	11	13	17	24	46	93	237	614
Methyl isobutyl ketone				15	19	37	72	195	518
Butyl acetate	11	12	14	17	25	49	97	227	529
Tetrahydrofuran		10	13	16	23	40	100	217	670
Exxate 600	11	12	14	19	30	58	134	337	730
Ektasolve EEP				20	34	67	138	327	903

Poly bd[®] Resin Waterproof Membrane Spray Applied

This two part polyurethane formulation is recommended as a starting point for a spray applied, industrial membrane. Formulations containing Poly bd resins exhibit excellent moisture vapor and water resistance. Poly bd resins also impart excellent low temperature flexibility and are resistant to aqueous acid and caustic.

Resin Component	Parts by Weight	Supplier
Poly bd [®] R45HTLO	100.0	Cray Valley Co.
Voranol [®] 220-530	18.0	The Dow Chemical Company
Regal [®] 660 carbon black, dry	0.5	Cabot Corporation
Thixcin [®] R/Xylene (3:1)	10.0	Elementis
Cyanox [®] 2246 antioxidant	1.0	Cytec Industries
Byk [®] 070 defoamer	0.1	BYK – Chemie USA
Curing Agent	Parts by Weight	Supplier
Isonate [®] 143L*	38.6	The Dow Chemical Company

* 1.05 NCO/OH Equivalent Ratio

Procedure and Related Information

Charge polyols, defoamer and antioxidant and mix at 85°C until homogeneous. Add Thixcin[®] R thixotrope and mix at 95°C until dissolved. Add carbon black and mix until color is homogeneous. Stop mixer and allow to degass at temperature to 15 to 20 minutes. Cool. Add Curing Agent and mix thoroughly. Pot life for a 100g batch approximately 40 minutes.

Properties

Thixotropic index (1/10 rpm)	4.5
Tensile Strength, MPa (psi)	5.8 (840)
Elongation, %	550
Hardness, Shore A	83
Tear resistance, N/mm (pli)	30.5 (173)

Poly bd[®] Resin Waterproof Membrane Self Leveling

Asphalt extended, two part polyurethanes form excellent moisture barriers. The starting point formulation shown here is designed to be applied to horizontal surfaces by roller or squeegee and has sufficient flow to be self leveling. This prototype formula uses a soft (high penetratin) asphalt. Harder asphalts such as AC20 will increase tensile strength by approximately 20%.

Resin Component	Parts by Weight	Supplier
Poly bd [®] R45HTLO	100.0	Cray Valley Co.
Voranol [®] 220-530	16.8	The Dow Chemical Company
AC5 Asphalt	80.0	Koch Materials Company
Foamkill [®] 8D defoamer	1.0	Crucible Chemical Comapany
Cyanox [®] 2246 antioxidant	1.0	Cytec Industries
Curing Agent	Parts by Weight	Supplier
Isonate [®] 143L*	40.7	The Dow Chemical Company

* 1.06 NCO/OH Equivalent Ratio

Procedure and Related Information

Charge components of Resin Component portion and melt mix at 85°C until homogeneous, generally 15-20 minutes. Allow to cool. Add Curing Agent and mix thoroughly. Pot life for a 100g batch is 35-40 minutes. Full cure is accomplished overnight.

Properties

Tensile Strength, MPa (psi)	1.73 (250)
Elongation, %	700
Hardness, Shore A	50

Polybd[®] Resin Waterproof Membrane Trowel Applied

Asphalt extended, two part polyurethanes form excellent moisture barriers. The starting point formulation shown here is designed to be applied by trowel by vertical surfaces. This prototype formula uses a soft (high penetration) asphalt. Harder asphalts such as AC20 will increase tensile strength by approximately 20%. Formulations containing Poly bd resins also impart excellent low temperature flexibility and are resistant to aqueous acid and caustic.

Resin Component	Parts by Weight	Supplier
Poly bd [®] R45HTLO	100.0	Cray Valley Co.
2-Ethyl-1,3-hexanediol	20.0	Dixie Chemical Company
AC5 Asphalt	100.0	Koch Materials Company
Atomite CaCO ₃ , dry	100.0	Imerys
Foamkill [®] 8D defoamer	1.0	Crucible Chemical Comapny
Cyanox [®] 2246 antioxidant	1.0	Cytec Industries
Aerosil [®] 202, dry	5.0	Degussa Corporation
Curing Agent	Parts by Weight	Supplier
Isonate [®] 143L*	54.6	The Dow Chemical Company

* 1.16 NCO/OH Equivalent Ratio

Procedure and Related Information

Charge polyols, asphalt, defoamer, filler and antioxidant and melt mix at 85 °C until homogeneous, generally 15-20 minutes. Add the dried Aerosil 202 fumed silica thixotrope while mixing. Allow to cool. Add Curing Agent and mix thoroughly. Pot life for a 100g batch is 35-40 minutes. Full cure is accomplished overnight.

Properties

Thixotropy indes (5/50 rpm)	2.4
Tensile Strength, MPa (psi)	4.1 (600)
Elongation, %	260
Hardness, Shore A	87
Tear resistance, N/mm (pli)	18.8 (107)

Polybd[®] Resin Coating for Electric Motors and Transformers

Poly bd resin is recommended for dip tank or vacuum impregnation coatings for motors or transformers where superior insulating characteristics, moisture resistance and formulation flexibility are necessary. Simple ratio adjustments offer the compounder a pencil hardness range of H to 6H without loss of adhesion.

In motors, insulation is rated as Class F, continuous operation at 150 °C. In high voltage transformers, Class H+, continuous operation at 220 °C, is met when aluminum conductors are used and Class H, continuous operation at 180 °C, with copper conductors. This starting point formulation is stable at 45 °C for at least 70 days.

Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	100.0	Cray Valley Co.
Vinyl toluene	22.0	The Dow Chemical Company
SR350*	8.0	Sartomer Co.
Luperox [®] 101*	3.0	Atofina Chemicals Inc.

Cure conditions: 350 °F for 90 min.

Film thickness: 2 mil dft

Properties

Viscosity at 25°C, mPa.sec	900
Cross hatch adhesion, %	100
Reverse impact, in lb	>120
Pencil hardness	6H

* Trimethylolpropane trimethacrylate

** 2,5-dimethyl-2,5-di-[t-butylperoxy] hexane

Poly bd® Resin Clear Coil Coating

This melamine cure, clear, low VOC coating provides good adhesion to steel and has very high flexibility.

Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	448.0	Cray Valley Co.
Cymel 303	79.0	Cytec
Aromatic 150	230.0	Exxon Mobil
DBE	130.0	DuPont
Nacure 5225	4.0	King Industries

Cure conditions: 42 sec at 350 °C

Peak metal temperature: 216 °C

Substrate: Bondrite 37 cold rolled steel

Properties

Weight per gallon, lb	7.91
VOC, lb/gal	2.64
Percent solids by weight, %	66.6
Percent solids by volume, %	67.7
T-bend, adhesion	0T
T-bend, crack free	0T
Cross hatch adhesion, %	100
Reverse impact, in lb	>160
Pencil hardness	H

**Poly bd® Resin Rust Inhibitive Red Iron Oxide Primer
Urethane Modified**

This primer provides excellent cathodic corrosion protection without incorporation of chromate pigments. The primer exhibits excellent flexibility and ease of recoating with polyurethane, epoxy or acrylic topcoats.

Part A		
Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	139.5	Cray Valley Co.
Xylene	134.8	
Bentone 38 *Mix for 10 min	4.7	Elementis
1475 Red iron oxide	69.7	Reade Advanced Materials
Barytes	139.5	Elementis
Talc	139.5	Whittaker, Clark & Daniels
Butrol 22 *Disperse to 4-5 Hegman	93	Buckman Laboratories
Poly bd R45HTLO	69.7	
Xylene	207.7	
Cobalt drier, 6%	3.5	
Zirconium drier, 6%	6.7	
Calcium drier, 5%	7.0	
Anti-skinning agent	3.5	
Part B		
IPDI (1.0 NCO/OH)	62.0	Degussa

Properties

Weight per gallon, lb	10.81
VOC, lb/gal (g/L)	3.75 (450)
PVC	31.7
Cross hatch adhesion, %	100
Reverse impact, in lb	>160

Poly bd® Resin Rust Inhibitive Red Iron Oxide Primer

This air dry primer should be applied at 2 mil dft or less to insure through dry before recoating. The primer exhibits excellent flexibility and ease of recoating with polyurethane, epoxy or acrylic topcoats.

Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	150	Cray Valley Co.
Xylene	145	
Bentone 38 *Mix for 10 min	5	Elementis
1475 Red iron oxide	75	Reade Advanced Materials
Barytes	150	Elementis
Talc	150	Whittaker, Clark & Daniels
Butrol 22 *Disperse to 4-5 Hegman	100	Buckman Laboratories
Poly bd R45HTLO	75	
Xylene	223.4	
Cobalt drier, 6%	3.8	
Zirconium drier, 6%	7.2	
Calcium drier, 5%	7.5	
Anti-skinning agent	3.8	

Properties

Weight per gallon, lb	10.96
VOC, lb/gal (g/L)	3.83 (459)
PVC	35
Cross hatch adhesion, %	100
Reverse impact, in lb	>160

**Poly bd® Resin Zinc rich Primer
Urethane Modified**

This low VOC primer provides good adhesion to steel and has a high zinc content to give corrosion protection. The primer exhibits excellent flexibility and ease of recoating with polyurethane, epoxy or acrylic topcoats.

Part A		
Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	136.6	Cray Valley Co.
Xylene	26.4	
Bentone 38 *Mix for 10 min	5.5	Elementis
Carbon black	9.1	Columbian Chemicals Co.
Poly bd R45HTLO *Disperse 30 min	128.4	
Zinc dust *Disperse until smooth	1639.6	U.S. Zinc Corporation
Xylene *Cool to room temperature	150.1	
Cobalt drier, 6%	3.5	
Zirconium drier, 6%	6.6	
Calcium drier, 5%	6.8	
Anti-skinning agent	3.5	
Part B		
IPDI (1.0 NCO/OH)	78.6	Degussa

Properties

Weight per gallon, lb	21.95
VOC, lb/gal (g/L)	2.13 (256)
Zinc in dry film, %	82.5
Cross hatch adhesion, %	100
Reverse impact, in lb	>160

Poly bd® Resin Zinc Rich Primer

This low VOC primer provides good adhesion to steel and has a very high zinc content to give corrosion protection. The primer exhibits excellent flexibility and ease of recoating with polyurethane, epoxy or acrylic topcoats. To insure adequate through dry, application should be at 2 mil dft or less.

Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	150	Cray Valley Co.
Xylene	29.0	
Bentone 38 *Mix for 10 min	6.0	Elementis
Carbon black	10.0	Columbian Chemicals Co.
Poly bd R45HTLO *Disperse 30 min	141.0	
Zinc dust *Disperse until smooth	1800.0	U.S. Zinc Corporation
Xylene *Cool to room temperature	164.8	
Cobalt drier, 6%	3.8	
Zirconium drier, 6%	7.2	
Calcium drier, 5%	7.5	
Anti-skinning agent	3.8	

Properties

Weight per gallon, lb	23.22
VOC, lb/gal (g/L)	2.16 (259)
Zinc in dry film, %	85.4
Cross hatch adhesion, %	100
Reverse impact, in lb	>160

Poly bd® Resin Corrosion Resistant Coil Coating

This melamine cure, high solids and low VOC coating provides good adhesion to steel and has very high flexibility.

Component	Pounds/100 gal	Supplier
Poly bd R45HTLO	158	Cray Valley Co.
Aerosil R 972	4.0	Degussa Chemical Co.
Ti-Pure® R-900	91.0	DuPont
Barium chromate	116.0	Atlantic Equipment Engineers
Acematt® OK 412	5.0	Degussa Chemical Co.
M-P-A 2000-X	5.0	Elementis
Aromatic 150 *Disperse to Hegman 7	27.0	Exxon Mobil
Poly bd R45HTLO	156.0	Sartomer Co.
Cymel 303	45.0	Cytec Industries
Aromatic 150	185.0	Exxon Mobil
DBE	26.0	DuPont
Nacure 5225	2.0	King Industries

Cure conditions: 42 sec at 350 °C

Peak metal temperature: 216 °C

Properties

Weight per gallon, lb	8.2
VOC, lb/gal	2.44
PVC, %	31.5
Percent solids by weight, %	70.3
Percent solids by volume, %	68.0
Viscosity at 25°C	76 sec, #4 Ford cup
T-bend, adhesion	0T
T-bend, crack free	0T
Cross hatch adhesion, %	100
Reverse impact, in lb	>160
Pencil hardness	H

Poly bd[®] Resin Underground Steel Pipe Coating
100% Solids

This 100% solids, polyurethane pipe coating is designed for application by two stream, hot airless spray. This prototype formula uses a Poly bd R20LM resin, a low molecular weight polyol that gives high hardness while maintaining flexibility and impact resistance. Formulations containing Poly bd resins have excellent resistance to aqueous acid and base.

Resin Component	Parts by Weight	Supplier
Poly bd [®] R20LM	100.0	Cray Valley Co.
Voranol 220-530	33.3	The Dow Chemical Company
Barytes	33.3	Elementis
Dibutyltin Dilaurate	0.13	Atofina Chemicals
Curing Agent	Parts by Weight	Supplier
Isonate [®] 143L*	69.0	The Dow Chemical Company

Properties

Hardness, Shore D	60
Elongation, %	50
Cross-hatch Adhesion to cold rolled steel, %	50
Impact Resistance, direct & reverse	
at 25°C	>160 in-lb
at 0 °C	>160 in-lb

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