Primers & Adhesion

August 2008

Primers: Coupling Agent

- Definition: Silicone primers are formulated silanes, supplied in a solvent. They are used to improve the bond strength between a silicone rubber or adhesive and another substrate surface (silicone, metals, and plastics). After evaporation of the carrier solvent, the resultant deposited silicone layer crosslinks by hydrolysis from atmospheric moisture.
  - Two different reactive groups are present on the coupling agent; one group is reactive to the substrate, the other to the adhesive
- Process: Wiping (Kim wipe paper), brushing, dipping or spraying techniques.
- Examples:
  - MED-160 and MED-164 are designed to improve bonding of RTV condensation cured and peroxide-cure silicones to various materials
  - MED1-161 and MED6-161 are designed to improve bonding of platinum-cured silicones.

Adhesives & Sealants

- Definition: Silicone adhesives are widely used to bond silicones to other materials such as metals, thermoplastics, ceramics, and urethanes. These products can be formulated into both one-part and two-part systems. All one-part systems require atmospheric moisture to cure, two-part systems can employ either moisture-or platinum-curing agent .
- Process: Dispensing guns
- Examples:
  - MED-1137: Non-slump
  - MED-2000: Self-leveling
  - MED-1511: Flowable
  - MED1-4213 / MED2-4213: Fast cure platinum catalyzed adhesive.
  - MED-1356: Pressure sensitive adhesive. For topical use only.

Primers and Adhesion Promoters

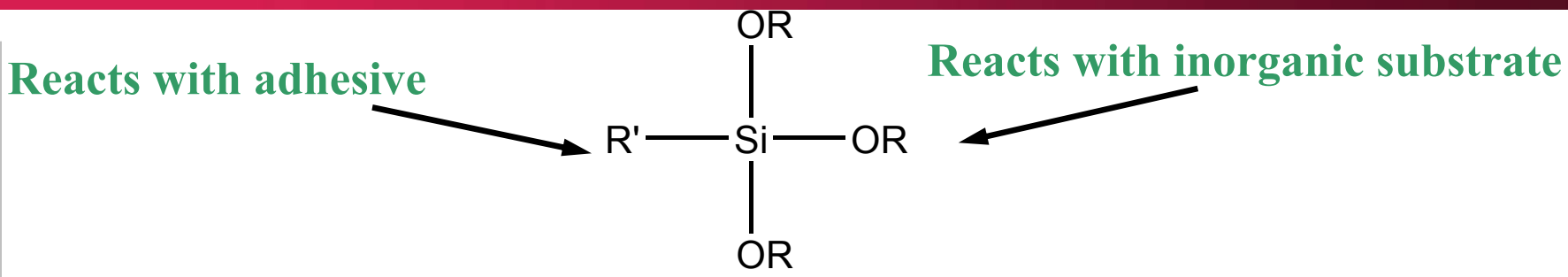
- Silane Coupling Agents
  - Silicone Primer
  - Adhesion Promoter
- Mechanical and Chemical Factors Affecting Bonding
- Failure Modes
- Primer Application and Handling

Silane Coupling Agents

- Provides a stable bond between two non-bonding surfaces.

- Typically, two different reactive groups are present on the coupling agent; one group reactive to the substrate, the other to the adhesive

Silane Coupling Agents



- Hydrolyzable group reacts with inorganic surfaces
  - Many metals and most inorganic materials have hydroxyl groups or tightly bound water on their surface. The silane will form bonds with these hydroxyl groups, by either covalent or hydrogen bonding.
  - The usual reactive group on the silane that promote adhesion are hydrolyzable organic groups, like alkoxy or acetoxy silanes.
  - R group is typically a reactive group that the silicone adhesive will react or interact with.

Silane Coupling Agents

Structure	Recommended Cure System
	Addition Cure Peroxide Cure Condensation Cure
	Condensation Cure Peroxide Cure
	Addition Cure Peroxide Cure

Primers & Adhesion: Silicone Primers

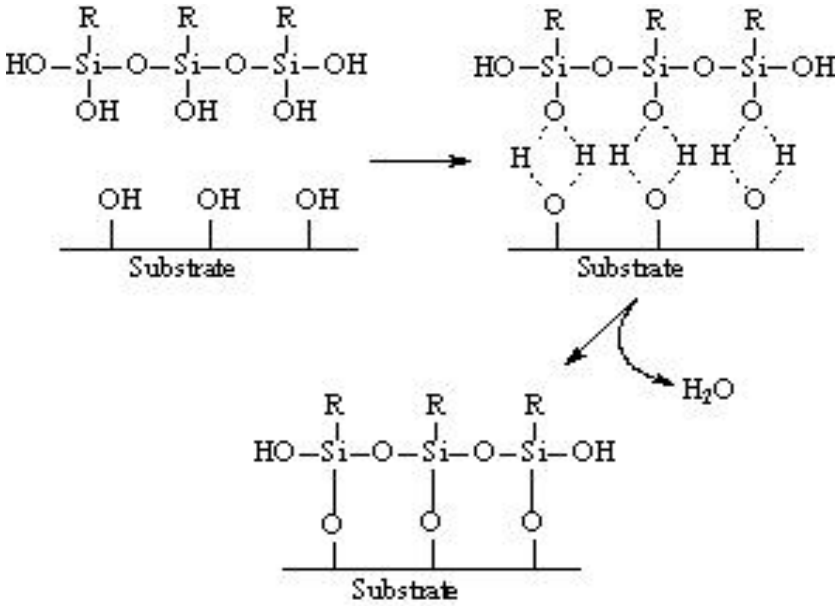
- Primer consists of:
  - Reactive silane coupling agent
  - Condensation catalyst
  - Solvent
- Reactive compounds are between 5 - 20% by weight
- Some primers are engineered to work with platinum.
- Others with condensation cure silicones.

Ideal Silane Primer Reaction

First; Hydrolyze silane

$$R\text{-}Si(OR')_3 + 3H_2O \longrightarrow R\text{-}Si(OH)_3 + 3HOR'$$

Second ; Silanols react with substrate



- The above reaction is reversible so there is a dynamic equilibrium and helps relieve any internal stresses between substrate and adhesive. This is a valuable feature; stresses caused by curing, thermal expansion or other forces can be relieved, helping to maintain the adhesive bond.

Factors Affecting Bonding

- **Primers:**
  - Change surface of substrate to relatively organic surface to allow the adhesive to allow better wetting and potential covalent bonding between substrate and adhesive.
  - The adhesive must completely wet the primer boundary layer in order to exclude voids. These are substrate and cure related.
  - Restrict the entrance of water or chemicals that can cause bond failure over time.
  - The primer boundary layer must maintain contact with the inorganic substrate and the silane interface. Because the silane/ inorganic phase is in dynamic equilibrium, the boundary layer must be rigid enough to maintain physical proximity of the silane/ substrate.

Adhesion Promoters

- **Primerless adhesive**
- **Substrate dependent**
- **Reactive silicones or silane coupling agents added to the Part A or Part B by the manufacturer.**
- **Can affect rheology, shelf life, etc.**

Failure Modes

- Adhesive failure
  - The bond failed from the adhesive to the substrate. If it's a primed surface, that means either the substrate to primer bond failed or the primer to adhesive bond failed.
- Cohesive failure
  - The bond failed through the adhesive/silicone, leaving a coating of silicone on either side of the substrates (test panels). Generally speaking, cohesive failure is the better failure mode. This means the adhesive bond is stronger than the silicone and, provided the silicone properties are consistent, the adhesive bond will not fail before the adhesive.

Application of Primers

- **Application of the primer should be in as thin a film as possible.**
  - A too thick layer of highly crosslinked silanes gives a chalky appearance.
  - A dye can be included in the primer to see the coating.
- **Any application of primer should result in a smoothly wetted surface.**
  - As the solvent evaporates, the film should stay uniform without any pooling.
  - On low surface energy substrates, 1 - 5% of a high boiling solvent can be included to keep the reactive species in a film and give them time to react as the low boiling solvent evaporates.
- **Primers require a period of time to hydrolyze and form a film and should be exposed to atmospheric moisture for about a half hour at 30% relative humidity.**
- **Heat accelerated curing is possible but some experiments should be done before proceeding.**

Handling Primers and Adhesion Promoters

- **Primer**
  - Exposure to atmospheric moisture should be minimized and any long term storage should have an inert atmosphere blanket.
  - Applicators should be changed regularly to prevent hydrolyzed silane build-up. Any spraying equipment should be regularly inspected for clogging.
- **Silicones with Adhesion Promoters**
  - Because they are formulated by the manufacturer, there are no special handling procedures.
  - Follow manufacturers instructions.

Adhering to Difficult Substrates with Silicone Adhesives

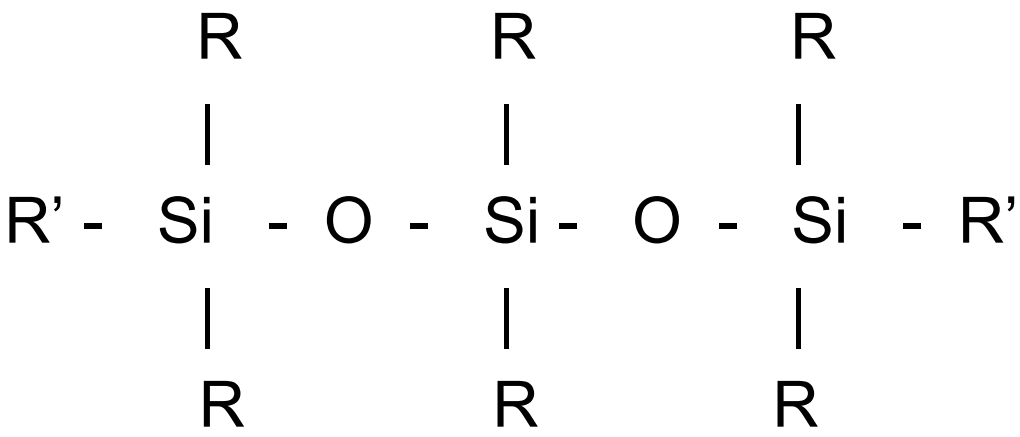
- Why a Silicone Adhesive?
- Main Section
  - Substrates
  - Materials
  - Testing Parameters
- Conclusion
- Future Studies

Why a Silicone Adhesive?

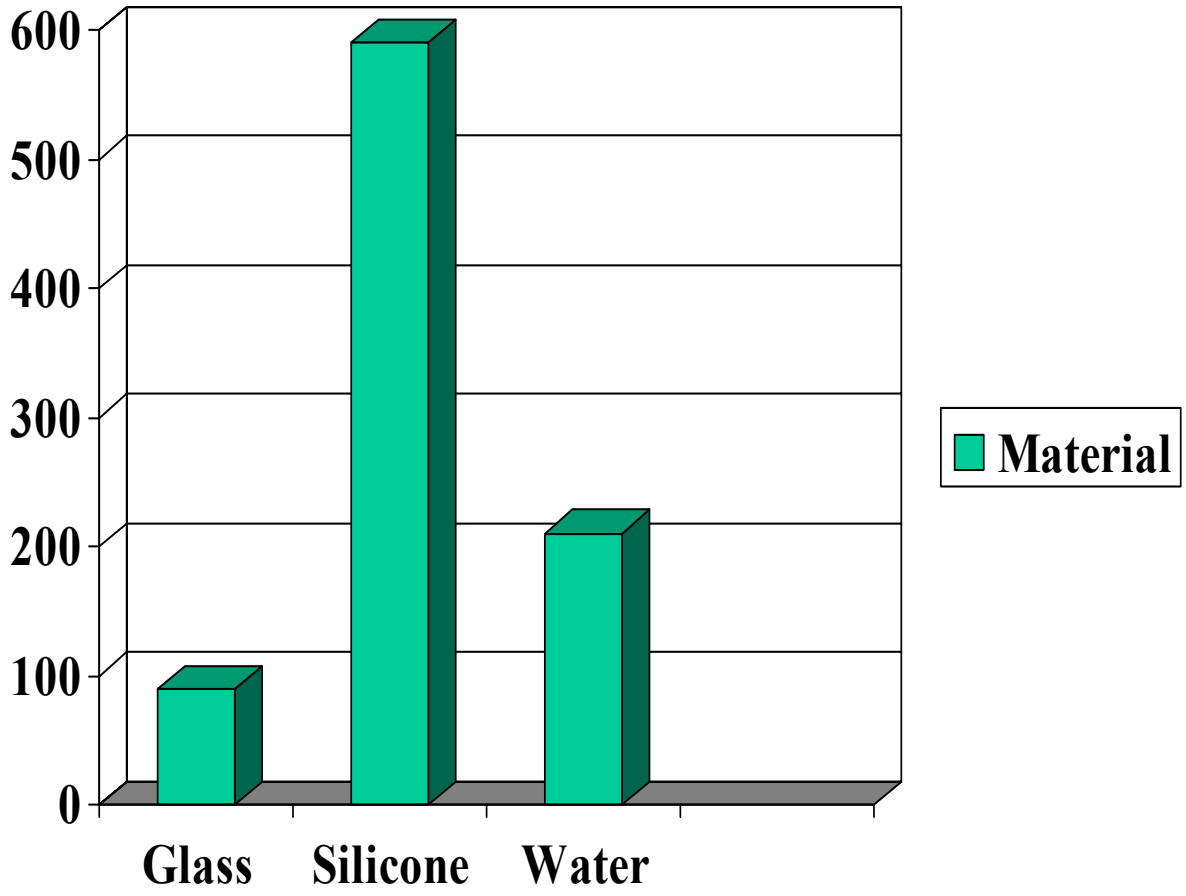
- Excellent elastomeric properties at a wide temperature range, -115-260ºC
- Fuel Resistance
- Optical Clarity-Refractive Index up to 1.57.
- Low Shrinkage-2%
- Low Shear Stress
- Vibration resistance, from –50-65°C
- Low out-gassed, NASA E-595
- Dielectric Strength of 500 V/mil

Why a Silicone Adhesive?

Polyorganosiloxane



Thermal Expansion Properties of a Typical Silicone



Fuel Resistance

	JP-5	Hydrol	Skydrol
20 mole% Fluoro	28% Swell	43% Swell	4% Swell
50 mole % Fluoro	6% Swell	28% Swell	3% Swell
100 mole % Fluoro	1.6% swell	5% Swell	6% Swell

Substrates

- Low Surface Energy
- Metals

Low Surface Engery

- Polycarbonate
- Polyetherimides (PEI)
- Polyamide
- Polyurethane
- Polymethylmethacrylate (PMMA)
- Polysulphone
- Polyimide

Aircraft Applications

Aircraft cockpit showing Polyamide flight controls, PMMA displays, and polycarbonate & PEI flight consoles. Silicone adhesives can be used to seal the various components.

PMMA aircraft windshields are chosen for their excellent clarity and non-yellowing properties in outdoor environments. Silicones can be used to provide a seal around the windshield.

Metals

- Titanium
- Stainless Steel
- Aluminum

Aircraft Applications

Titanium turbine blades during processing and fabrication.

Aircraft Applications

Aluminum used in brakes and gears.

Materials

- Primer SP-270
- Silicone Adhesive R31-2186

Primer SP-270

- What are primers and why are they used?

$CH^2=CHSi(OCH^3)^3$

$H^2NCH^2CH^2CH^2Si(OCH^2CH^3)^3$

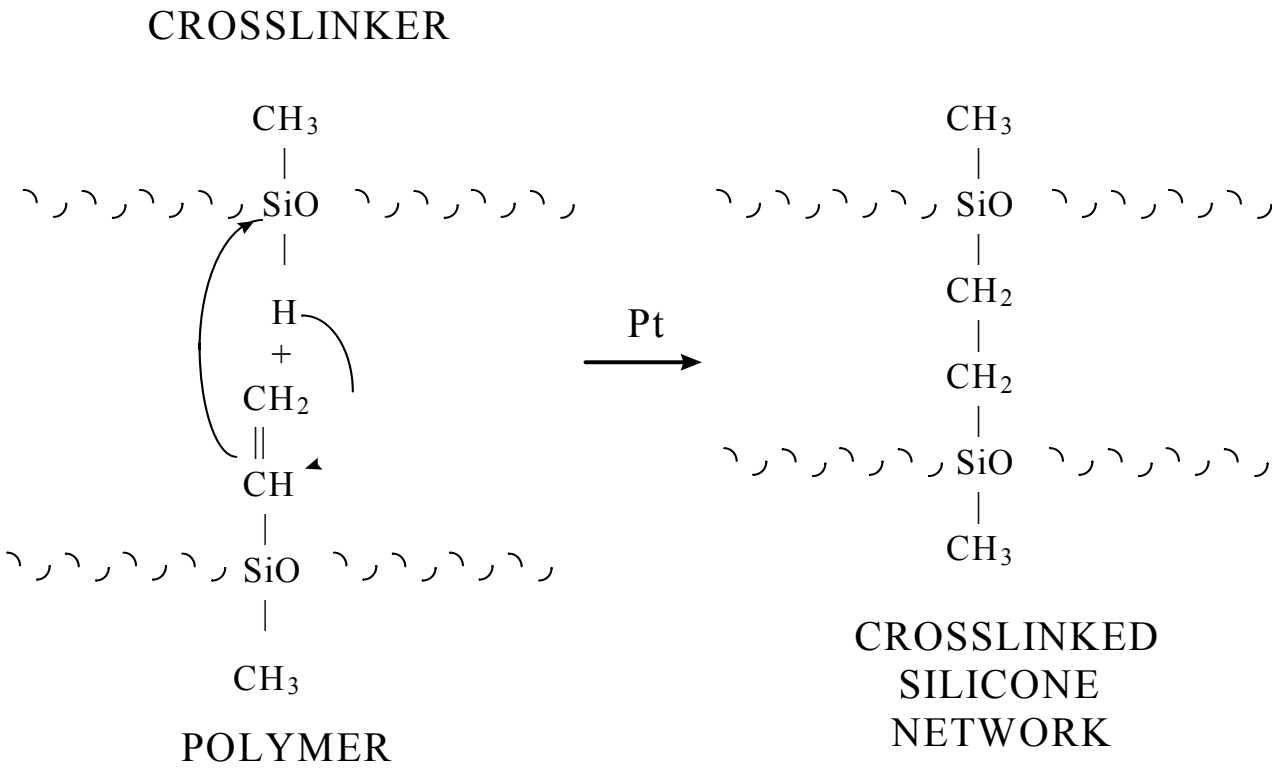
$CH^2=C(CH^3)CO^2CH^2CH^2CH^2Si(OCH^3)^3$

Silicone Adhesive R31-2186

- Viscosity, cP, 25C 80,000
- Work Time, hours, 25C 2
- CURED-15 minutes@150C Mix Ratio 1:1
  - Specific Gravity 1.10
  - Durometer, Type A 30
  - Tensile, psi 900
    - Elongation, % 600
  - Tear, ppi 70

50ml Cartridge Unit

Cure Mechanism



Testing Parameters

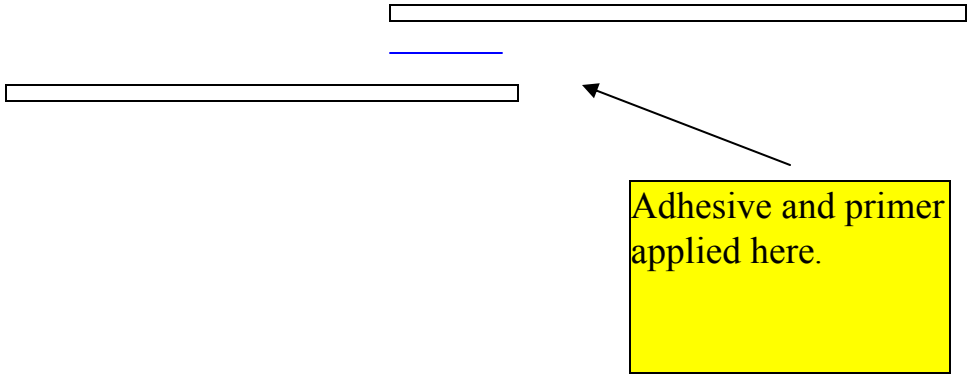
- Lap Shear-ASTM D-1002
- Preparation of Substrates
- Equipment
- Flame Treatment

Lap Shear ASTM D-1002

- Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading.
- Approved by the Department of Defense.

Preparation of Substrates

Lap joint



Equipment

. Instron 5500 Series Tabletop models for 450 lb to 11,250 lb capacities. New model updating the 1011.

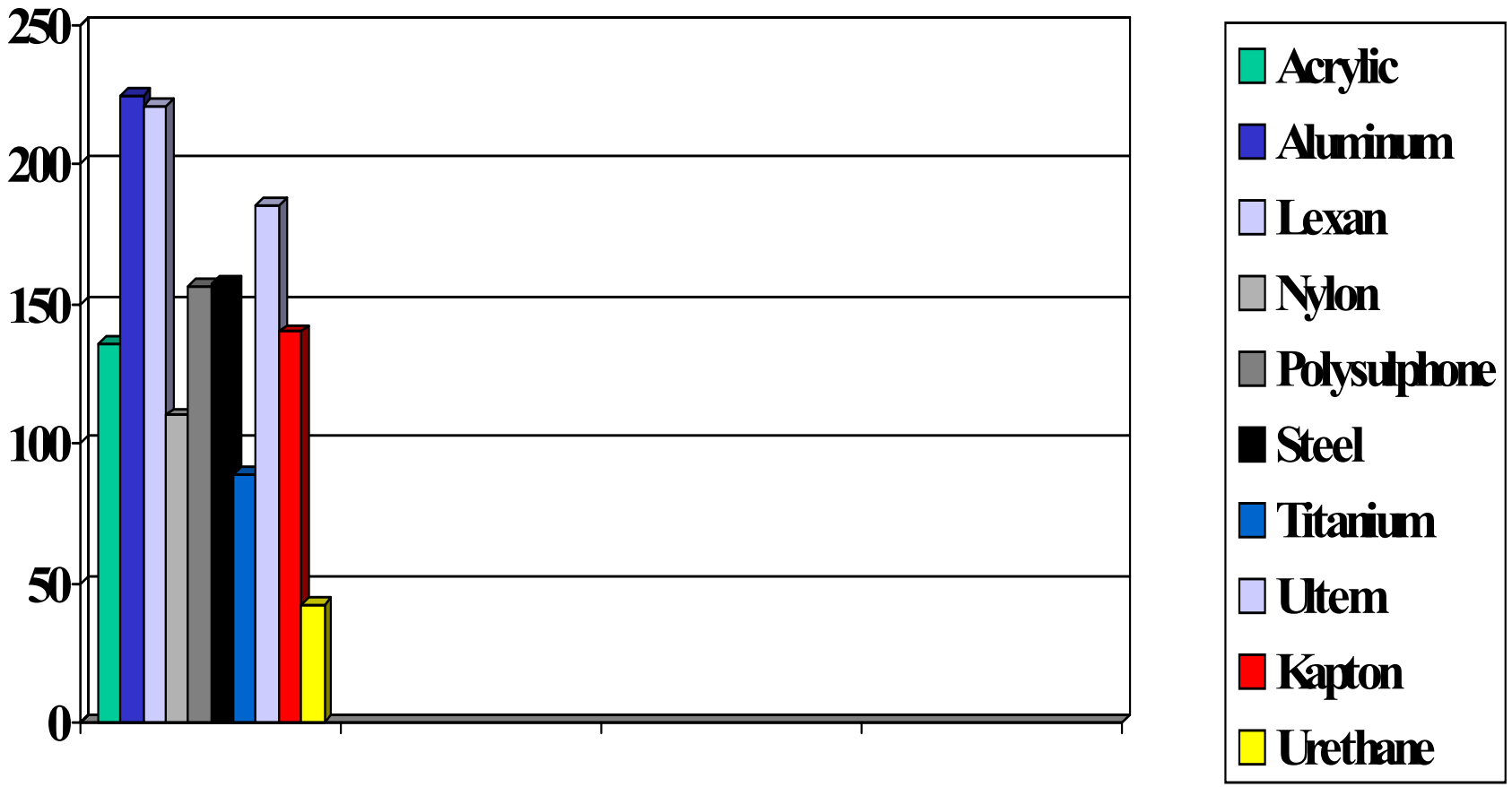
Flame Treatment

Results

substrates	*low*	*medium*	*high*	*mean*	*median*	*st. dev. (s)*	*st.dev. (p)*	*c.o.v.*
Acrylic	101	147	161	136	147	31	26	23.02
Aluminum	156	256	262	225	256	60	49	26.5
Lexan Ж	185	223	254	221	223	35	28	15.66
Nylon	69	111	151	110	111	41	33	37.16
Poly-sulphoneЖ	154	155	158	156	155	2	2	1.34
Stainless steel	82	168	220	157	168	70	57	44.49
Titanium	82	88	96	89	88	7	6	7.92
UltemЖ	153	165	237	185	165	45	37	24.56
Kapton Ж	79	170	171	140	170	53	43	37.74
Urethane	28	30	69	42	30	23	19	54.6

Figure 9. All 100% cohesive failure. Flamed treated substrates denoted by the symbol Ж

Mean Lap Shear Results



Conclusion

- R31-2186 primed with SP-270 would be a great first choice for adhering a silicone adhesive to a substrate.
- This technology can be used to develop different types of adhesives for specific applications.
  - Healthcare Class VI
  - Low out gassed Electronic or Space Grade
  - Optically clear
  - Fuel resistant

Future Studies

- Plasma Treatment
- Other substrates
- Primerless