

Development of a Low Friction Coating
for Heavy Industrial Machinery

SBZ CORPORATION
The major alternative

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Customer Requirements

The customer needed a high performance coating that met the following criteria:

- Low friction.
- Must be able to take up to 250°C temperature for 12 hours per day.
- Adhere to metal (aluminium, copper, steel) substrates.
- Chemical resistant (lubricant oils).
- Flexible to take expansion and contraction.
- Able to withstand wear loads.



Background

Polyamide-imide (PAI) is a high performance polymer that is used as the binder resin for high performance coating systems.

- Aviation coatings for resistance to de-icer fluids, fuels, hydraulic fluids and lubricants.
- Cookware.
- Electrical insulation for turbine rotors and stators.
- Industrial coatings for corrosion protection against acids and alkalis.
- Medical coatings for needles and probes used in brain and spinal cord surgery.

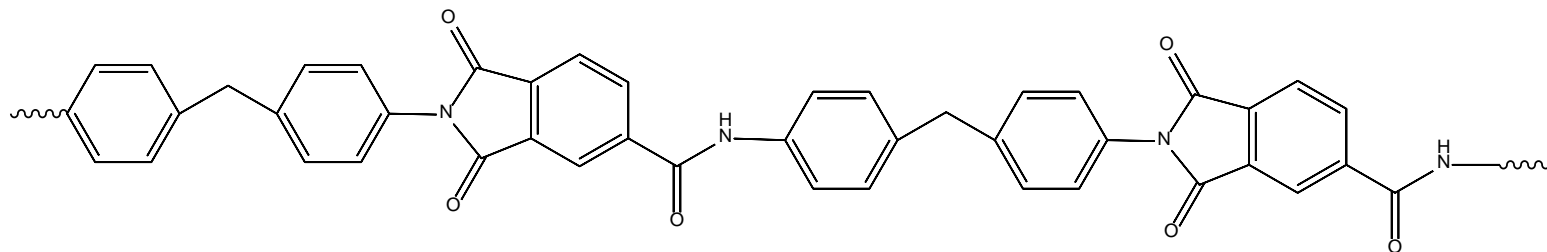


Commercially PAI polymers can be formed one of two routes:

1. Reaction of a diamine with an anhydride-chloride, or
2. Reaction of a diisocyanate with an acid-anhydride.

The second route was the preferred option as it allowed for greater formulation flexibility.

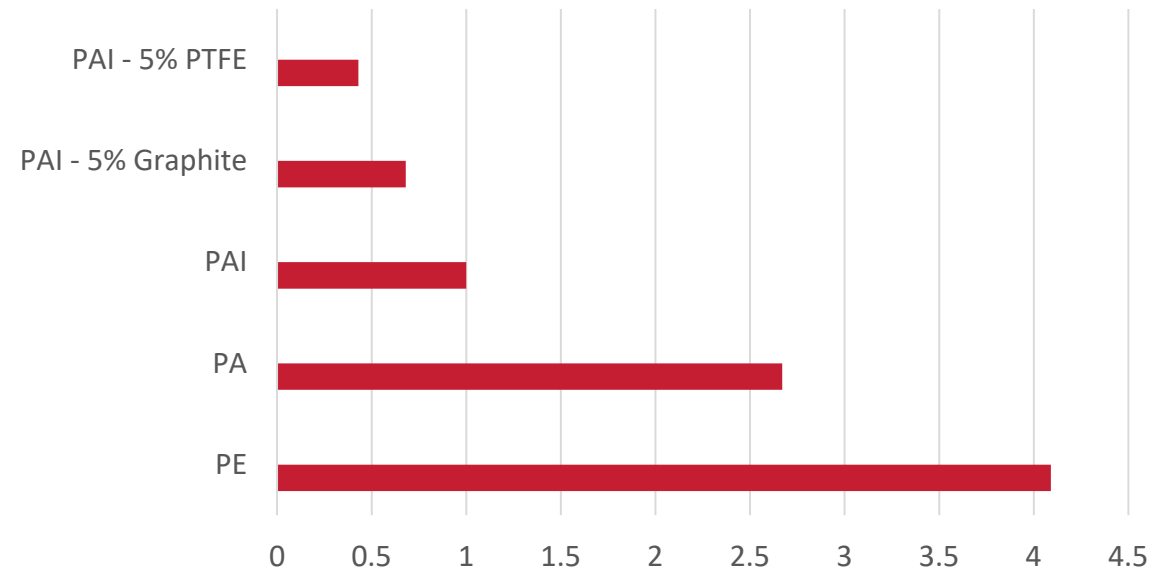
The final polymer is a long chain polymer, with very low branching, hence physically very flexible.



A pure PAI coating does have a low surface energy compared to standard polyamide (PA) and polyester (PE) coatings, but not enough for it to be classified as low friction.

Normally a suitable filler is added, either graphite, PTFE or molybdenum sulphide, silicone was rejected out right by the customer. Graphite and PTFE were the two preferred options.

Relative Slip Characteristics Compared to PAI



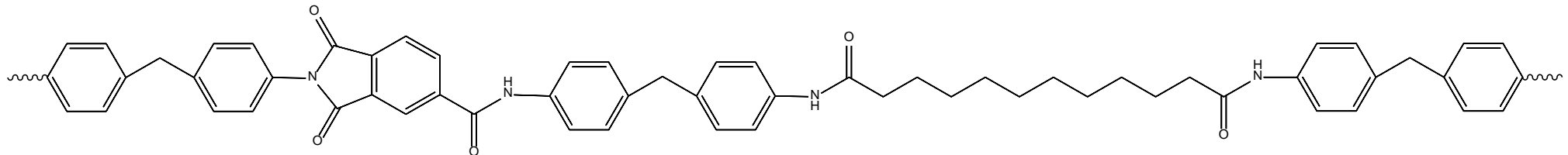
Test panels were prepared with both the 5% PTFE and PAI coatings on to aluminium, mild steel and stainless steel Q-Panels, 2 layers applied 50 microns thick wet, cured for 10 mins at 250°C each time, and a 10 min post-cure at 280°C. This gave an overall cured coating of 33-36 microns.

- Flexibility was tested on mandrel bend (1-10mm diameter bars), and an ISO impact tester.
- Adhesion testing on all substrates.
- Contact immersion testing with H₂SO₄, NaOH and grease.
- Found that the addition of the PTFE reduced the flexibility of coating.
- Particularly on the smaller diameter mandrels (<3mm).

In order to improve the flexibility of the polymer, previous work had shown that the addition of a linear diacid does lead to improvements in flexibility. However, since the acids used are normally aliphatic, this does have an impact upon the chemical resistance of the cured polymer.

Dodecanedioic acid is a cheap long chain acid, that can be added easily into the reaction system. Three different loadings were tried:

1. 2%
2. 5%
3. 10%



Testing

New formulations made up with 5% PTFE and tested.

Polymer	PTFE	2mm Mandrel	1 mm Mandrel	H ₂ SO ₄ (1 hour)	NaOH (1 hour)	Grease (1 week)	Grease (4 weeks)
PAI	0%	Pass	Pass	Pass	Pass	Pass	Pass
PAI	5%	Fail	Fail	Pass	Pass	Pass	Pass
2% DDA	0%	Pass	Pass	Pass	Pass	Pass	Pass
2% DDA	5%	Pass	Pass	Pass	Pass	Pass	Pass
5% DDA	0%	Pass	Pass	Fail	Pass	Pass	Pass
5% DDA	5%	Pass	Pass	Fail	Fail	Pass	Pass
10% DDA	0%	Pass	Pass	Fail	Fail	Pass	Fail
10% DDA	5%	Pass	Pass	Fail	Fail	Pass	Fail

DDA – Dodecanedioic Acid

To obtain an indication of the wear characteristics, samples were coated onto suitable sized sheets (100x100mm) of mild steel with a 33-36 micron film thickness, and then subjected to a wear test using a Taber Abrader.

It was found that after 1000 cycles there was on average a weight loss of 10mg of the PTFE containing coatings when using a CS-10 wheel set. Without the PTFE, the average weight loss was around 6mg for the same test cycle.

Speaking to the customer, they requested a lower weight loss, of 5mg per 1000 cycles. It was thought that adding a mineral filler to the lower coating would improve the toughness of the coating. Calcium carbonate, dolomite, fumed silica, precipitated calcium carbonate and silica were all tried at 25% and 50% loading rates. The fumed silica was only tried at 5% as the viscosity of the resultant formulation was unworkable at higher loading rates.

Testing

Filler	Loading	500 Cycles	700 Cycles	1000 Cycles	1mm Mandrel
None		2.1 mg	4.7 mg	6.1 mg	Pass
CaCO	25%	0.9 mg	2.1 mg	4.1 mg	Pass
CaCO	50%	0.8 mg	1.5 mg	3.6 mg	Pass
Dolomite	25%	1.2 mg	3.7 mg	5.2 mg	Pass
Dolomite	50%	0.9 mg	3.1 mg	4.6 mg	Fail
Fumed Silica	5%	3.9 mg	5.1 mg	8.3 mg	Pass
Precp. CaCO	25%	0.8 mg	2.0 mg	3.9 mg	Pass
Precp. CaCO	50%	0.8 mg	1.6 mg	3.4 mg	Pass
Silica	25%	0.6 mg	1.8 mg	3.8 mg	Pass
Silica	50%	0.5 mg	1.1 mg	3.1 mg	Fail

Sent to the customer the following formulations for them to try in their process, all made up on 25kg capacity laboratory equipment.

- Pure PAI
- PAI with 5% PTFE
- PAI with 25% calcium carbonate
- PAI with 50% calcium carbonate
- PAI with 50% calcium carbonate and 5% PTFE
- PAI with 25% precipitated calcium carbonate
- PAI with 50% precipitated calcium carbonate
- PAI with 50% precipitated calcium carbonate and 5% PTFE

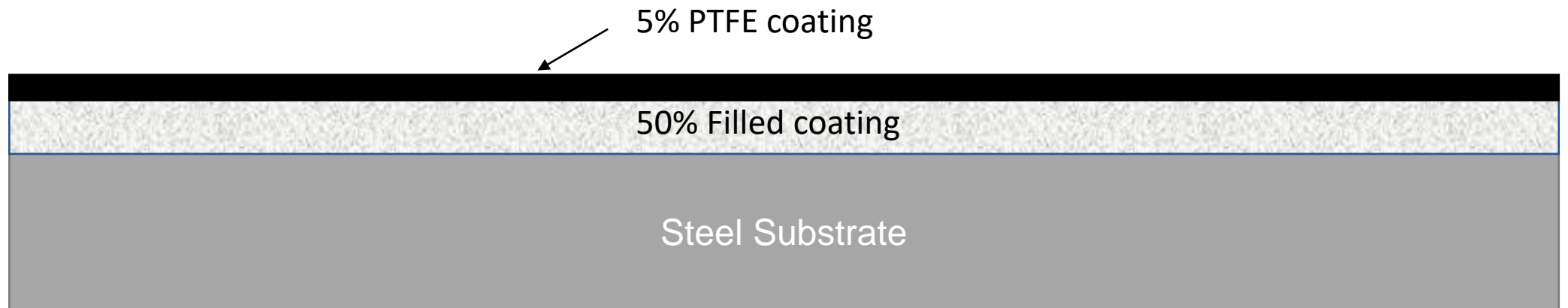
The original intention was to apply the system in a single layer.

However due to the thickness required (~35 micron when cured) too many bubbles appeared in the film due to solvent entrapment. So a two layer system was tried, which gave good results, but was costly due to the high loading of the PTFE. Switched to 50% calcium carbonate for the base layer, and a thin 5% PTFE as a top coat. This met the requirements for the flexibility and the low friction.

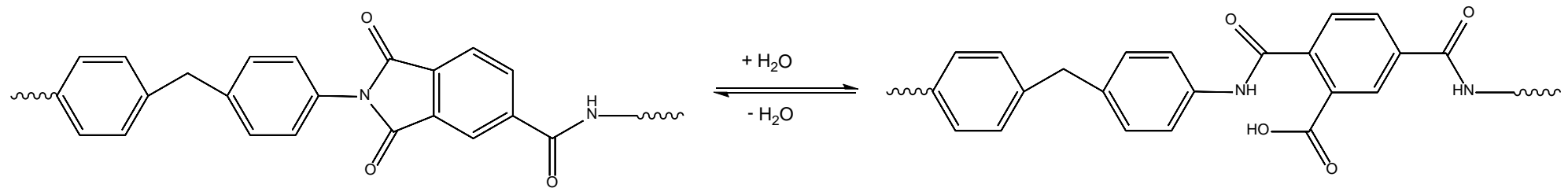
However the customer wanted to have a system suitable for them to mix in the PTFE and the calcium carbonate fillers in-house.

The only way to do this was to convert the PAI base polymer from solvent based (NMP) to water dispersible since PTFE is not stable in solvents.

Typical coating setup



PAI is not water soluble, however it is possible to make it water dispersible by hydrolysing the polymer to convert the imide group to amic acid.



This can be achieved by mixing the PAI with water under basic conditions (pH >8.5). The reaction is reversible, and at high temperatures (>110°C) ring closure takes place to reform the imide ring. The polymer only needs to have 25% of the imide groups to be converted to amic acid in order for the polymer to be water dispersible.

Scale Up

PAI was supplied as 35% solids in NMP and naphtha solvent blend. Needed to switch to 50% solids and then to dilute down with water and amine to make a water dispersed product.

On a lab scale (25lt) the process was to make 20kg of 50% PAI in NMP. In a separate vessel distilled water was mixed with a tertiary amine under a nitrogen blanket. The water/amine mix was heated to 70-80°C and then the 50% PAI resin was slowly poured in over the course of an hour, keeping the temperature between 75-80°C with an anchor stirrer going at 20 rpm. The mix was left stirring for 1 hour, then cooled to 40°C before sampling for QC checks and discharge.



Scale Up Plan

25 kg
Lab



600 kg
Production
Pilot



4000kg
Production

- Full manual control.
- Single point temperature monitoring.
- Heating fluid temperature control.

- Part computer control.
- Two point temperature monitoring.
- Hot oil bleed valve and heating jacket temperature monitoring.
- Cooling coil in heating jacket and water jacket.

- Full computer control.
- Three point temperature monitoring.
- Hot oil bleed valve.
- Glycol chilled coil in heating jacket.

Issues found with production pilot trials:

Control of PAI polymer into vessel

- Initially relied on drum pump to dose material into vessel.
- Needed a heated jacket around the container to keep the material warm to keep the viscosity low.

Speed of stirrer

- Fixed speed.
- As the PAI polymer was charged into the vessel, the stream of material would get wrapped around the shaft.

Issues found upon scaling up to 4000 kg batch sizes:

Control of temperature in the vessel

- Needed to keep the heating oil around the vessel about 5°C higher than the desired vessel temperature to prevent exotherms, particularly the start of the process.

Amine leaking from the vessel at >60°C

- Seals needed to be replaced with Viton as standard seals were not amine resistant.

Feed rate of PAI into the vessel

- PAI pumped from reactor.
- Subsurface feed solved problems with material around the stirrer shaft.

Filtration of finished product

- If the stirrer speed was too fast or too slow, then the final product was not homogenous.



The addition of the fillers was done at the customer, but trial work done by both parties.

Initial blending of material was done using a Silverson high shear mixer, for lab batches.

For the pilot batches, an inline Silverson high shear mixer was used fitted on a recirculation line. The filler and polymer mixture was pumped in as a slurry, then processed to form a homogenous mixture.

For full production, the customer switched to using 3 roll mills.
Can cope with very high viscosity material.

Control of particle size

- 1 micron particle size to allow for spray application.

Control of temperature

- 35-40°C to minimise amine loss and to maintain a working viscosity.

Replaced calcium carbonate with precipitated grade

- Tighter particle size distribution.

Two separate machines used to prevent contamination.

A green rectangular road sign with a white border and four silver mounting bolts. The sign is mounted on two grey poles. The text on the sign is in white, bold, sans-serif capital letters.

ANY
QUESTIONS ?



SBZ CORPORATION

The major alternative