Metallic Monomers for Metal Adhesion

Introduction
Metallic monomers are multifunctional acrylates and methacrylates that can be used to create strong adhesive bonds to metal surfaces in a variety of applications such as:

- Rubber products
- Alkyd coatings
- Polymer concrete
- PVC plastisols
- Water based adhesives
- Water based systems
- Epoxy sealants
- Epoxy coatings

These metallic monomers are currently offered by Cray Valley Company in the form of diacrylates, dimethacrylates and a monomethacrylate, namely:

- SR633 - Metallic Diacrylate with scorch retarder
- SR705 - Metallic Diacrylate
- SR708 - Metallic Dimethacrylate
- SR709 - Metallic Monoacrylate

Curing Methods
Like most acrylates and methacrylates, metallic monomers can be cured by both free radical and Michael addition reactions. The most common methods of initiating cure are:

- Peroxide or azo decomposition
- UV radiation
- Polyamine addition

By selecting the appropriate curing method, metallic monomers can be used in aqueous or organic media and cured at either ambient or elevated temperatures.

Each of the application areas in which these products can be used to promote adhesion are discussed.

Rubber Products
SR633 is a coagent for peroxide-cured rubbers that produces extremely strong rubber-to-metal adhesion without the use of external adhesives. Strong rubber-to-metal bonding can be obtained with a variety of rubbers as illustrated in Figure 1 for silicone rubber, EPDM, natural rubber and hypalon. NBR, HNBR, neoprene and SBR also bond strongly to metals when cured with SR633.

Figure 1

Rubber-To-Steel Adhesion

The rubber to metal or rubber to rubber bonding can be achieved in two ways. SR633 can be compounded into the rubber and the rubber pressed against the appropriate substrate and cured. SR633 can also be compounded into a rubber and the rubber calendared into a thin tape. This tape can then be applied between rubber surfaces or between rubber and metal surfaces as an adhesive bonding layer and then cured.
The use of pressure and plasticizers (monomers) is generally helpful to insure good wetting and bonding of the two surfaces to be adhered.

**Alkyd Coatings**
Metallic monomers also increase the adhesion of alkyd coatings to metal substrates. When acrylic monomers are used in polyester alkyd coatings as reactive diluents, a loss in adhesion normally occurs due to shrinkage. By using SR705 or SR708 in combination with acrylic monomers, adhesion is restored as shown in Table 1 for aluminum.

**Table 1: Alkyd Coatings Adhesion to Aluminum**

<table>
<thead>
<tr>
<th>DILUENT</th>
<th>CROSS HATCH % RETAINED</th>
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<tbody>
<tr>
<td>SOLVENT</td>
<td>100</td>
</tr>
<tr>
<td>SR239</td>
<td>50</td>
</tr>
<tr>
<td>SR239/SR705</td>
<td>92</td>
</tr>
<tr>
<td>SR239/SR708</td>
<td>100</td>
</tr>
</tbody>
</table>

SR239 = HEXANEDIOL DIMETHACRYLATE  
SR705 = METALLIC DIACYRlicate  
SR708 = METALLIC DIMETHACRYLATE

**Polymer Concrete**
Polymer concrete is a composite material formed by polymerizing a liquid monomer such as dicyclopentenyloxyethyl acrylate in an admixture containing various aggregates.

When SR705 is part of the monomer system, adhesion between the concrete and reinforcing materials is greatly increased. This is shown for galvanized steel and cold rolled steel in Figure 2.

**Figure 2**

**PVC Plastisols**
Acrylic monomers are used to modify PVC plastisols in automotive coatings to obtain improved chip resistance. SR705 can be used in combination with monomers such as trimethylolpropane trimethacrylate or with epoxies to increase adhesion to conventional automotive substrates. This is illustrated for SR705 with various substrates in Figure 3.

**Epoxy Coatings**
SR705 also functions as a “reactive filler” in conventional epoxy coatings to increase adhesion to a variety of substrates. An example of this is shown in Table 2 for a 15 mil pigmented epoxy coating bonded to cold-rolled steel. As the data show, the conventional coating suffered complete adhesive failure, while the coating containing SR705 experienced only 40% coating loss in cross hatch adhesion.

**Table 2: Epoxy Coatings Adhesion to Steel**

<table>
<thead>
<tr>
<th>SR705</th>
<th>CROSS HATCH % RETAINED</th>
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<tbody>
<tr>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>5%</td>
<td>60</td>
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PART A: EPON 828/TiO2 (W & W/O SR705)  
PART B: TRIETHYLENE TETRAAMINE
Epoxy Sealants
Acrylic monomers are used as reactive diluents in amine cure epoxy formulations to reduce viscosity and to increase cure speed. The increased crosslink density that occurs with the acrylic monomers often leads to a reduction in adhesion. SR705 can be added to the formulation as a “reactive filler” to increase adhesion without adversely affecting viscosity or cure speed. This is illustrated in Figure 5 with a 2-part epoxy sealant containing SR238 (hexanediol diacrylate) as diluent. SR705, when added at a concentration of 5%, significantly increased the lap shear adhesion to both aluminum and galvanized steel.

Conclusions
In summary, metallic monomers offer:

- rubber-to-metal adhesion without the use of external adhesives
- improved adhesion in solvent-free coatings and adhesives
- improved metal adhesion in water-based systems
- increased mechanical properties