Hybrid Oligomers – Organic/Inorganic Acrylics

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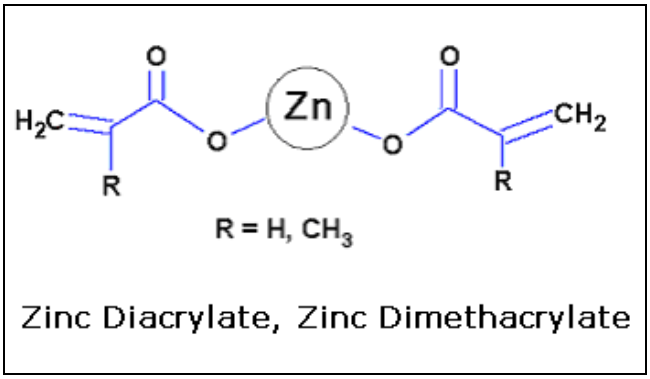
Introduction

Many papers have been written describing metal containing oligomers. [1, 2, 3] Little has been reported on metal containing acrylic oligomers. [4, 5] For years, Sartomer Company has produced zinc diacrylate (ZDA) for use in peroxide cured rubber.

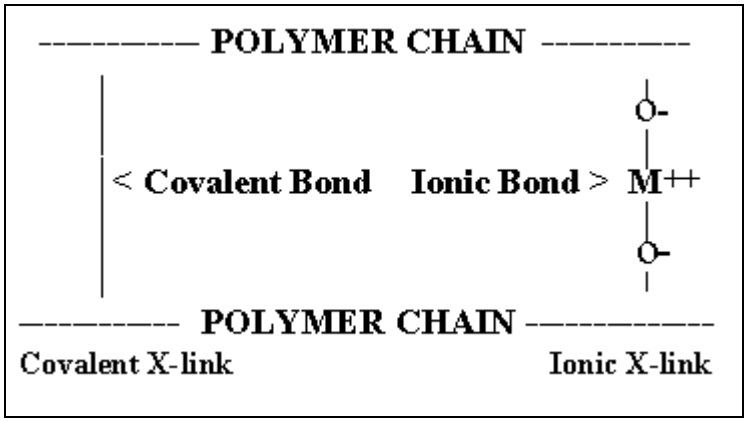
Fig. 1



Metallic Monomers

Polymers crosslinked with ZDA possess ionic crosslinks, which result in different and often enhanced properties when compared to more conventional covalent crosslinks. For example, elastomers crosslinked with ZDA possess low tan δ values comparable to sulfur crosslinked elastomers. Elastomers covalently crosslinked with standard multifunctional acrylates have a significantly higher tan δ. The similarity of metallic and sulfur crosslinks is related to the mobile nature of these bonds compared to crosslinks formed by typical multivalent acrylic monomers

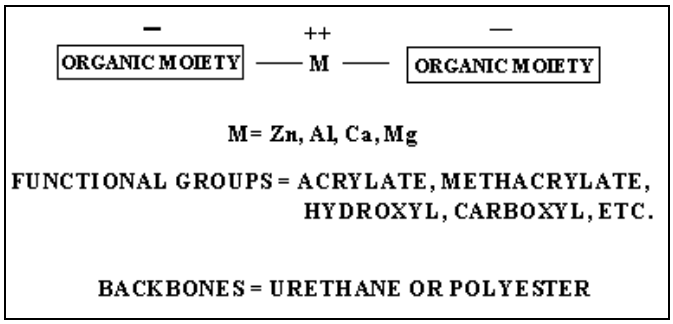
Fig. 2



Metallic Ionic Crosslink

Metal acrylates have not found wide use in UV curing because of their lack of solubility in standard monomer/oligomer formulations. To solve this solubility problem Sartomer has developed a series of organic metal acrylates, which are monomer soluble. [6]

Fig. 3



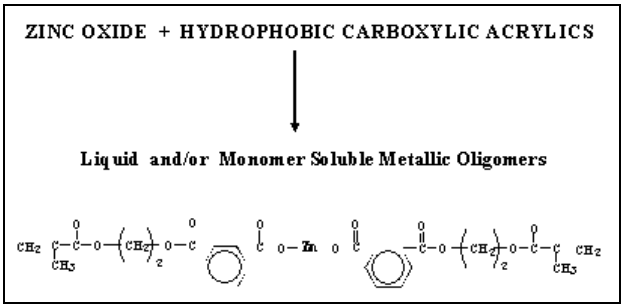
Hybrid Oligomers

These products are soluble in typical monomers such as TPGDA and TMPTA. Because of their hydrophobic nature, these metal-containing oligomers can be used at high levels in standard UV formulations. When formulated with monofunctional acrylates or methacrylates, they produce clear films containing only mobile, reversible ionic crosslinks. These oligomers formulated with monofunctional acrylates permit the production of UV cured hot melt coatings, adhesives and powder coatings that flow at high temperatures and revert to ionically crosslinked films at ambient temperatures.

Results and Discussion

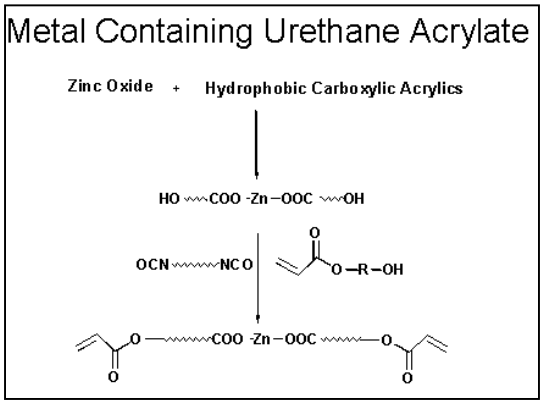
A. Synthesis: Sartomer patents, [7, 8] describe the synthesis of two types of soluble metal oligomers. **Figure 4** presents the reaction scheme for a polyester acrylate type of oligomer and **Figure 5** shows a urethane acrylate synthesis route utilizing zinc oxide to provide the metal content. Sartomer has commercialized several soluble metal-containing oligomers, CN2404 and CN2405. The CN2404 is a polyester acrylate oligomer and the CN2405 is a urethane acrylate oligomer.

Fig. 4



Hybrid Polyester Acrylate Oligomers

Fig. 5



Hybrid Urethane Acrylate Oligomers

B. UV Cure Results: Adhesion to Metal Substrates. **Table 1** shows a base formulation containing standard acrylic monomers, oligomers and a photoinitiator in which we varied the zinc-containing oligomer from 1 to 16 parts.

Table 1 – Base Formulation

Components	Parts
CN966J75	63.5
SR506	31.7
SR238	4.8
SR1135	0.95
Zn Salt Material	0-16 in 4-part increments

These formulations cure to form clear films with varied metal contents. The oligomers evaluated were CN2404 and CN2405.

Figure 6 describes the application and cure conditions for the adhesion experiments.

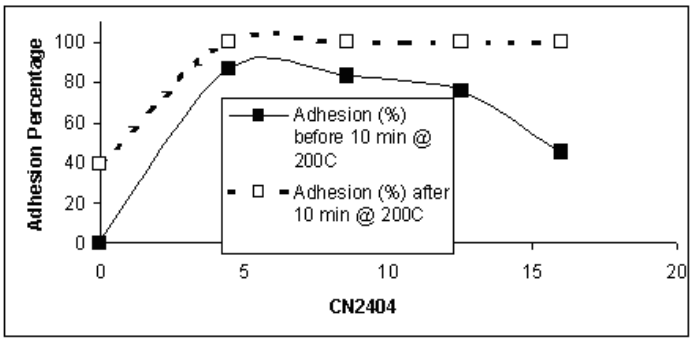
Fig. 6

- Cure Conditions: 4 Passes @ 25 fpm with two 300w/in. Hg. Lamps.
- Film Thickness: 5.0 – 6.0 mils
- Cross Hatch 610 Tape Adhesion before and after baking @ 200°C.

Application & Cure Conditions

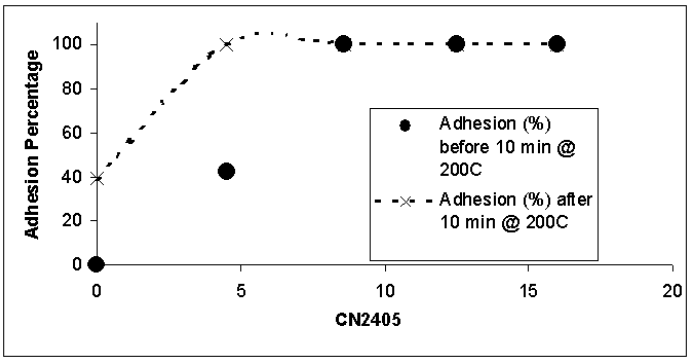
Figures 7 through **11** illustrate the dramatic adhesion enhancement produced by the metal-containing oligomer formulations on aluminum, tin-plated steel, cold rolled steel and glass.

Fig. 7



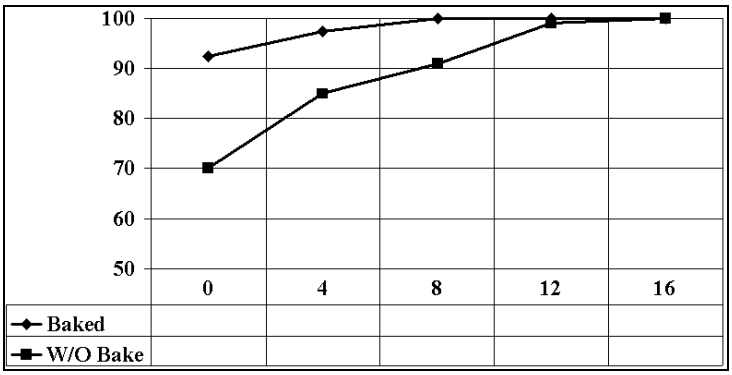
Adhesion on Aluminum – CN2404

Fig. 8



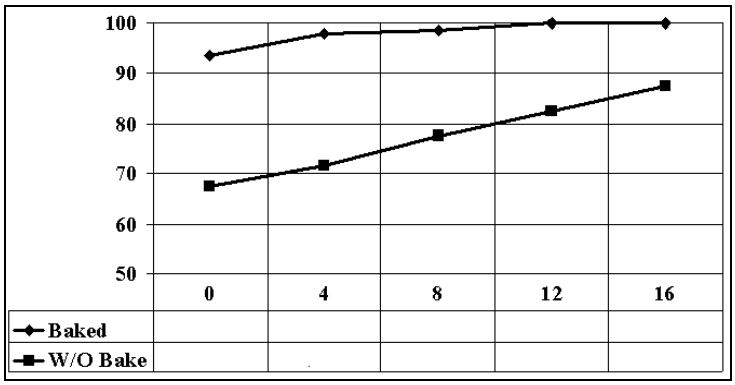
Adhesion on Aluminum – CN2405

Fig. 9



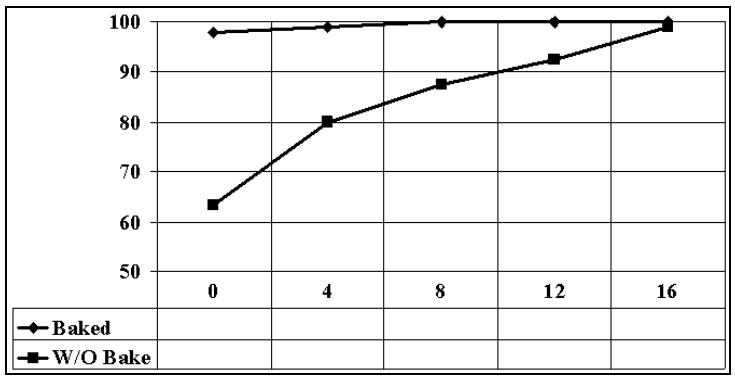
Adhesion to Tin Plated Steel,
% Adhesion, CN2405

Fig. 10



**Adhesion to Cold Rolled Steel,
% Adhesion, CN2405**

Fig. 11



**Adhesion to Glass,
% Adhesion, CN2405**

As expected, adhesion is significantly improved with baking. In all cases water resistance of the cured films was excellent. Full adhesion was maintained after water submersion for 24 hours with room temperature tap water.

Summary and Conclusions

The use of metal-containing oligomers in UV cure formulations has been made possible with a series of hydrophobic acrylate oligomers that are soluble in standard acrylate monomers. These oligomers, shown to promote adhesion to metal and glass substrates, may have many uses in coatings, adhesives, ink and electronic applications. Our initial activity has involved zinc ions but further work is underway studying various other metals. Products derived from metal-containing acrylic oligomers may show utility in providing useful application properties including conductivity, antibacterial and anti-fungal properties, high refractive index and catalysis.

When formulated with monofunctional monomers the hybrid metal-containing oligomers can provide reversible crosslinking for UV hot melt adhesives, powder coatings and hot melt coating applications.

These products represent a new raw material type for UV formulations to create improved properties for various applications. Indeed, we have taken nanotechnology one step further by incorporating metal oxide moieties into organic films at the molecular level.

References

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