# Radiation-Curable Organic-Inorganic Hybrid Nanocomposites

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## ABSTRACT

Research, development and commercialization activities in the nanocomposite area have grown extensively worldwide over the last decade. Nanocomposite materials have the potential to revolutionize traditional material design in various ways. The reduction of grain (particle or phase) size to the nanometer scale has led to unique and interesting physical, and in some cases, chemical properties. Via structural manipulation at the nanoscopic level, the performance of materials can be tailored over a broad spectrum. UCB has been actively involved in developing radiation-curable organic-inorganic hybrid nanocomposite materials for various applications. The performance data of these developed hybrid-nanocomposite materials in Radcure coatings will be presented at this conference.

## Introduction

In the last decade, sol-gel chemistry has been used extensively to produce organic-inorganic nanocomposites. A number of patents and published articles have reported a variety of synthetic routes by using this chemistry and technology for preparation of hybrid nanocomposites. In general, sol-gel derived hybrid nanocomposites can be divided into two basic classes: those where nanoparticles are formed *in situ* or those where nanoparticles are directly employed as starting materials.

In the first class of hybrid nanocomposites, organosilanes and/or other metal alkoxides are employed not only as nanoparticle precursors but also as network formers. Very often, a mixture of several types of precursors is used. In the presence of water, solvent, (i.e. alcohol), and also catalysts (acid or base), simultaneous hydrolysis and condensation of these organosilanes and/or other metal alkoxides take place to form inorganic sols mixed with inorganic/organic networks, therefore, hybrid nanocomposites. Usually, in order to obtain better processability, hybrid systems with highly organic characteristics are desired. To achieve this, organic components, such as monomers, oligomers, or polymers, are incorporated into the precursor solution first, and then hydrolysis, condensation and polymerization/crosslinking reactions are carried out.

However, neither hydrolysis nor condensation reactions can be completed unless high temperature processes are applied (1). As a result, unreacted hydroxyl and alkoxyl groups remain in the products as illustrated in **Figure 1**. Consequently, viscosity stability and hydrolytic resistance are two issues for all produced nanocomposite materials.

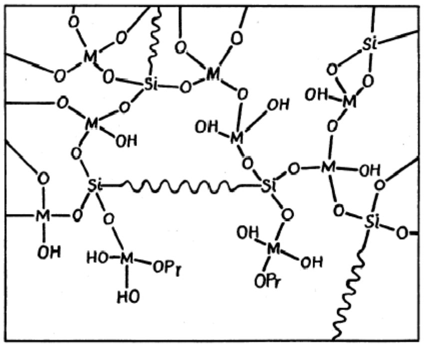


**Figure 1**
**Un-reacted hydroxyl groups remaining in the produced materials**
(US Patent 5,316,855)

In the second class, as described in U.S. patent 4,455,205, U.S. patent 4,478,876, U.S. patent 4,491,508, U.S. patent 6,160,067, and European patent EP 00,736,488, etc., pyrogenic or precipitated nanoparticles (e.g. $SiO_2$, $Al_2O_3$) are used as starting materials. The nanoparticles are first dispersed into organic media, usually hydrophilic solvents such as alcohols. Then organo-functional silane(s) with water and catalysts are added. The grafting reactions take place on the surface of nanoparticles. Finally, the surface modified particles are mixed into the polymeric matrix to form organic-inorganic hybrid nanocomposites.

In surface modification of nanoparticles, trifunctional alkoxysilanes are often utilized as coupling agents. However, often only one of three, sometimes two of three silanol groups of hydrolyzed trialkoxysilanes is/are bonded to the surface of the nanoparticles. This bonding limitation is the result of both the limited reactivity and the steric hindrance of the silanol groups (1). Again, unhydrolyzed alkoxyl and free hydroxyl groups can detract from viscosity and hydrolytical resistance. Moreover, agglomeration of functionalized nanoparticles can also take place through Si-O-Si and/or hydrogen bonds located on the surface of nanoparticles.

In solvent-based systems at low concentration, agglomeration should not be an issue because the solvent dilution inhibits the formation of large particles or networks.

In order to satisfy increasingly rigorous environmental regulations and meet high performance requirements, it is often desirable to use 100% reactive materials, such as radiation curable materials, or high solids products. It is desirable to produce a solvent-free material by removing both water and solvent (alcohol) azeotropically. In contrast to the case of solvent diluted products, the remained alkoxyl and silanol groups have a much higher probability of contact during the solvent stripping process. As a result, the slow hydrolysis and condensation reactions cause a gradual extension of inorganic networks through siloxane, Si-O-Si, bonds and/or hydrogen bonds. Consequently, increasing viscosity, large particle formation and even gel formation can take place. This is a significantly troubling issue for all practical large-scale productions.

In order to address the issues as described above, a new nanocomposite technology has been developed in the R & D laboratories of Surface Specialties Inc. (UCB). This new technology allows UCB to produce thermally stable and gel-free nanocomposite materials with 100% reactive solids content. Here, gel-free refers to stable viscosity within production specifications and no visible gel formation materials throughout the product shelf life. Moreover, unlike those frequently seen in the sol-gel process, no large (sol) particles are visible. 100% reactive refers to solvent-free or very low levels of solvent contained in the product. In traditional sol-gel processes, high solvent content is typical. Another objective of this project is to provide organic-inorganic hybrid nanocomposites materials that are radiation (UV/EB) curable.

**Experimental Section, Test Methods**

1. Pencil Hardness ASTM D 3363 was employed.

2. Abrasion Resistance of Organic Coatings by the Taber Abraser, ASTM D 4060-84—The coating is applied at uniform thickness to a Leneta chart, and, after curing, the surface is abraded by rotating CS-17, 500g weighted wheels. Coatings are subjected to 50 or more cycle intervals of abrading. If after the 50-cycle interval, there is any sign of breakthrough to the substrate, the testing is terminated. Loss in weight at each 50-cycle interval is also calculated.

3. Scratch Resistance The test panel is held firmly in one position and a 4” x 4” eight layered square of steel wool (~1cm thick), covering a two pound ball peen hammer is rubbed back and forth across the coating, counting each back and forth motion as one double rub. The handle of the hammer is held in as close to a horizontal position as possible and no downward pressure is exerted on the hammer. At the first sign of scratching, haze, or breakthrough to the substrate, the counting and test are terminated.

4. Impact Resistance ASTM D 2794 was employed.

5. MEK Resistance (Chemical Resistance by Solvent Rub) — SMT 160-K (the test method Surface Specialties Inc.) The test panel is held firmly in one position and a 4” x 4” eight layered square of cheese cloth, covering a two pound ball peen hammer is soaked with MEK, and the hammer is rubbed back and forth across the coating, counting each back and forth motion as one MEK double rub. The handle of the hammer is held in as close to a horizontal position as possible and no downward pressure is exerted on the hammer. At the first sign of breakthrough to the substrate, the counting and test are terminated.

6. Adhesion ASTM D 3359-95A (Measuring Adhesion by Tape Test) —An area free of blemishes and minor surface imperfections is selected. Two cuts are made in the film, using a multi-tip cutter for coated surfaces. The coated substrate is placed on a firm base, and parallel cuts are made. All cuts are about ¾ in. (20mm) long. The film is cut through to the substrate in one steady motion using just sufficient pressure on the cutting tool to have the cutting edge reach the substrate. After making the required cuts, the film is lightly brushed with a tissue or soft brush to remove any detached flakes or ribbons of coatings. The cut areas are then covered with one-inch wide semitransparent pressure-sensitive tape. The tape is then removed and discarded. The areas are then brushed and inspected for percent of area removed: 5B=0%, 4B=Less than 5%, 3B=5-15%, 2B=15-35%, 1B=35-65%, 0B=Greater than 65%.

7. Cylindrical Mandrel Bend Tests—a conical mandrel test consists of manually bending a coated metal panel over a cone. As described in ASTM Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus (D 522), a conical mandrel tester consists of a metal cone, a rotation panel bending arm, and panel clamps. These items are all mounted on a metal base. The cone is smooth steel 8 in. in length with a diameter of 1/8 in. at one end and a diameter of 1.5 in. at the other end. When a coating is applied on a 1/32-in.-thick cold-rolled steel panel, as specified in ASTM S 522, a bend over the mandrel produces an elongation of 3% at the large end of the cone and of 30% at the small end of the cone. The coated panel is bent $135^o$ around the cone in approximately 1 s to obtain a crack resistance rating under simulated abuse conditions. In this study, the length of cracking was then measured and reported.

8. Viscosity measurements were achieved through use of SMT 013-CC—Surface Specialties Inc. Standard Method of Testing Viscosity by Brookfield DVII+ Viscometer, using spindle #21, giving a shear stress of 245-265 at 50-60% of full scale reflection with a sheer rate between 4-5 $sec^{-1}$ set at 5 RPM. The sample test temperature for Thermosel is controlled electronically. Sample test temperature for Small Cell Adapter is controlled by a circulating water bath. Measurement is accomplished by gauging rotational resistance of a cylindrical spindle immersed in the test fluid against a calibrated spring. Resistance is read directly and converted to viscosity in centipoise by calculation. Sample readings were recorded after allowing chamber temperature to stabilize for 30 minutes, and confirmed after another 5 minutes according to the method of testing.

9. Particle Size and Particle Size Distribution Analysis Nanoparticle samples were analyzed using a Coulter LS230 Particle Size Analyzer. The instrument uses laser light scattering to detect particles in the range of 0.04 to 2,000 micrometers. Samples were fully dispersed in methanol after shaking for three minutes. Particle size data was collected and averaged over 90 seconds for each run. The size calibration of the method was checked using reference standards at 15 and 55 micrometers.

## Nanocomposite Technology Developed in Laboratories of UCB

The new nanocomposite technology developed at UCB involves four features including nanoparticle surface modification, nanocomposite preparation, nanocomposite stabilization, and formulation of radiation (UV/EB) curable organic-inorganic hybrid nanocomposite.

1. Nanoparticle Surface Modification converts commercially available nonreactive nanoparticles to organic compatible and reactive nanoparticles. Commercial nanoparticles are normally inorganic oxides or metal particles. They are nonreactive and incompatible with most organic media. Chemically reactive groups such as vinyl, epoxy, mercapto, acrylate/methacrylate or other groups are bonded to the surface of nanoparticles. Then, the surface-modified nanoparticles can be used in nanocomposite preparation. It is well known that organic silanes, particularly trifunctional; sometimes difunctional alkoxysilanes or other metal alkoxides are often used as coupling agents in the surface modification reactions. However, as described in the introduction, viscosity build up, large particle formation, and in some cases, gelations are serious concerns for large scale production. Moreover, the hydrolytic stability is an issue because of the presence of unhydrolyzed alkoxyl groups or uncondensed hydroxyl groups in the prepared nanocomposites. UCB has developed

technology that utilizes proprietary coupling agents in nanoparticle surface modification reactions. These proprietary coupling agents are hydrolytically stable; therefore, all above concerns can be dismissed.

2. Nanocomposite Preparation There are two classes of commercially available nanoparticles as raw materials to prepare nanocomposites. The 1st class is a colloidal product in which nanoparticles are already homogeneously dispersed in an organic medium, such as solvent. Surface modification of these nanoparticles is a relatively simple process. The 2nd class of commercial nanoparticles is in powder form in which, nanoparticles already agglomerated to form large particles, normally in micrometers, or even millimeters. Normal mechanical agitation or milling can not efficiently reduce particle size to nanoscale, and even when reduced to nanoscale, re-agglomeration often takes place because of their high surface area, and often high surface energy. UCB has developed a proprietary technology to overcome this problem. This proprietary technology can provide an efficient and effective method for producing nanocomposite, particularly, organic-inorganic hybrid nanocomposite materials. The process provides multiple functions including dispersion of particles into organic media, reduction of agglomerated particles to the desired submicron-scale, and rendering the nanoparticle surface available for the following surface modification reactions, diffusing bulky surface modifying agents onto nanoparticle surfaces, and also possibly, activating/accelerating surface modification reactions. In short, UCB's proprietary technology effectively prevents re-agglomeration of nanoparticles.

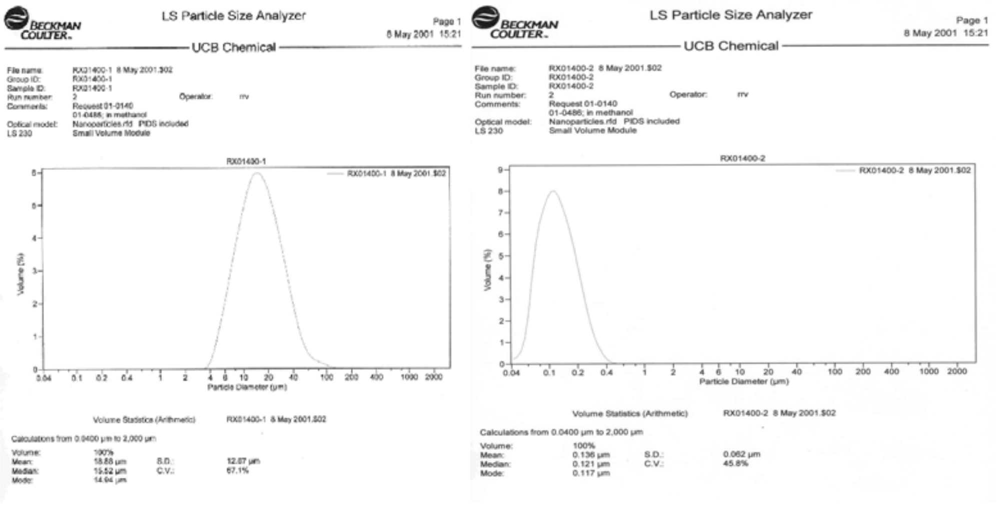
3. Stabilization of Nanocomposite UCB has used proprietary coupling agents in nanoparticle surface modification reactions to avoid thermal stability issues. Often, it is desirable to utilize organic silanes as coupling agents in surface modification reactions because of the popularity of silanes and economic considerations. UCB has also developed proprietary stabilization technology comparable to silane systems. When low levels (often less than 1%) of stabilizing agent are used in silane systems, the increase in viscosity, large particle formation, and final gelation can be significantly reduced.

4. Formulation of Radiation (UV/EB) Curable Organic-Inorganic Hybrid Nanocomposite As inorganic nanoparticles are surface modified with organic groups, particularly as the surfaces of nanoparticles are bonded with epoxy or (meth)acrylate groups, the modified nanoparticles become compatible with various radiation curable monomers and oligomers. As much as 30% by weight of inorganic nanoparticles can be incorporated into radiation curable compositions. After evaporation of solvent(s), various types of inorganic nanoparticles (from silica to aluminum oxide, to zirconium oxide...), a variety of radcure resins (epoxy acrylate to urethane acrylate to polyester acrylate ...), and ultimately, a wide range of radiation curable, inorganic-organic hybrid nanocomposites with high or 100% solids can be prepared.

## Results and Discussion

### Nanoparticle Preparation and Surface Modification

$Al_2O_3$ particles (from various commercial suppliers) in powder form were first mechanically dispersed in organic solvent. A milky white dispersion designated Dispersion Sample 1 was obtained after two hours of mechanical agitation. The stability of this dispersion was low. Precipitation took place 10-15 minutes after the agitation stopped. The $Al_2O_3$ particles size range of Dispersion Sample 1 was 15-20 microns (see Figure 2 and Table 1). In contrast, ultrasonic irradiation and mechanical agitation effectively reduced the $Al_2O_3$ particles to nanoscale. The new dispersion designated Dispersion Sample 2 shows its stability is higher than that of Dispersion Sample 1 (see Figure 2 and Table 1). However, the dispersed Dispersion Sample 2 still reagglomerated, and precipitation was noted after 1-2 days at room temperature. By using UCB's proprietary technology, Dispersion Sample 3 was prepared. Dispersion Sample 3 shows high stability, and no precipitation takes place after one month at room temperature. Notably, the particle size of Dispersion Sample 3 was 123 nm, and remained unchanged throughout this period of time (see Figure 2 and Table 1). As nanoparticle source, Dispersion Sample 3 is ready to use for the preparation of organic-inorganic nanocomposites. After mixing with UV/EB curable resins (monomers and/or oligomers) and other necessary additives including photoinitiators, wetting agents, and etc, UV/EB curable organic-inorganic hybrid nanocomposites can be prepared.



LS Particle Size Analyzer
Page 1
8 May 2001 15:21
UCB Chemical

File name: RX01400-1 8 May 2001.$02
Group ID: RX01400-1
Sample ID: RX01400-1
Run number: 2 Operator: rrv
Comments: Request 01-0140
01-0486; in methanol
Optical model: Nanoparticles.rfd PIDS included
LS 230 Small Volume Module

Volume Statistics (Arithmetic) RX01400-1 8 May 2001.$02

Calculations from 0.0400 µm to 2,000 µm

Volume: 100%
Mean: 18.88 µm S.D.: 12.07 µm
Median: 15.52 µm C.V.: 67.1%
Mode: 14.94 µm

**Dispersion Sample 1**

LS Particle Size Analyzer
Page 1
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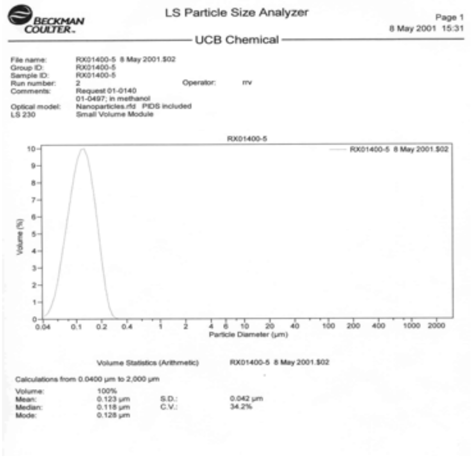
File name: RX01400-2 8 May 2001.$02
Group ID: RX01400-2
Sample ID: RX01400-2
Run number: 2 Operator: rrv
Comments: Request 01-0140
01-0486; in methanol
Optical model: Nanoparticles.rfd PIDS included
LS 230 Small Volume Module

Volume Statistics (Arithmetic) RX01400-2 8 May 2001.$02

Calculations from 0.0400 µm to 2,000 µm

Volume: 100%
Mean: 0.136 µm S.D.: 0.062 µm
Median: 0.121 µm C.V.: 45.8%
Mode: 0.117 µm

**Dispersion Sample 2**



LS Particle Size Analyzer
Page 1
8 May 2001 15:31
UCB Chemical

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Sample ID: RX01400-5
Run number: 2 Operator: rrv
Comments: Request 01-0140
01-0497; in methanol
Optical model: Nanoparticles.rfd PIDS included
LS 230 Small Volume Module

Volume Statistics (Arithmetic) RX01400-5 8 May 2001.$02

Calculations from 0.0400 µm to 2,000 µm

Volume: 100%
Mean: 0.123 µm S.D.: 0.042 µm
Median: 0.118 µm C.V.: 34.2%
Mode: 0.128 µm

**Dispersion Sample 3**

**Figure 2**
**Particle size and Particle size distribution for dispersed particles**

**Table 1**
**Properties of Three Dispersions Prepared by Different Process**

| Sample | Dispersion Sample 1 | Dispersion Sample 2 | Dispersion Sample 3 |
|---|---|---|---|
| **Dispersion Technology** | mechanical agitation | mechanical agitation +Ultrasonic irradiation | UCB's proprietary technology |
| **Average(nm) Particle Size** | 19,000 | 136 | 123 |
| **Stability of Dispersion** | 15 minutes,<br>precipitation took place | 2 days,<br>precipitation took place | >30 days<br>particle size not changed, no precipitation |

Thermal Stability

1. Thermal Stability at Room Temperature

For comparative purposes, a benchmark hybrid nanocomposite sample, named SOL-GEL-NANO-01 in **Figure 3**, was prepared by classic sol-gel processes. The process solvent was methanol. The silane, such as 3-Methyacryloxypropyltrimethoxysilane, was hydrolyzed in a mixture of water and methanol at 40°C. Reaction time was 2 hours. The hydrolyzed silane was formulated with 60% by weight UV-curable oligomer. After the sample was mixed well, was then evaporated under 100 millibar vacuum and at 40°C. 99.2% solids of reactive nanocomposite formula were obtained.

The freshly produced nanocomposite was a clear and viscous liquid. However, the sample became cloudy after 12 hours at room temperature (see **Figure 3**). Either large particle formation or micron-phase separation has occurred. The clouding appeared to be the result of continued hydrolysis and condensation reaction. The liquid gelled two months after the sample was prepared.

With UCB's proprietary technology, the organic-inorganic hybrid nanocomposite, designated HYBRID-NANO-01 in **Figure 3**, was prepared. It should be noted that HYBRID-NANO-01 has a composition similar to SOL-GEL-NANO-01 (see **Table 2**). Organic solvent was evaporated by following the same procedures as in the preparation of SOL-GEL-NANO-01. A clear and viscous liquid with 99.8% solids content was obtained.

**Table 2**
**Composition of Hybrid Nanocomposites**

| Composition | SOL-GEL-NANO-01 (% by weight) | HYBRID-NANO-01 (% by weight) |
|---|---|---|
| Organic Silanes | 30.0-40.0 | 30.0-40.0 |
| Catalyst, additives, | 0.10-1.0 | 0.1-0.8 |
| Proprietary agents | absent | 0.1-1.0 |
| Aliphatic Urethane Acrylate oligomer | 60.0-70.0 | 60.0-70.0 |
| Total | 100.0 | 100.0 |

In contrast to SOL-GEL-NANO-01, HYBRID-NANO-01 remained clear, and the viscosity remained unchanged for 6 months at room temperature (see **Figure 3**). This phenomenon indicates that the proprietary stabilizing agents effectively stopped, or at least inhibited the condensation of unreacted silanol functionality.

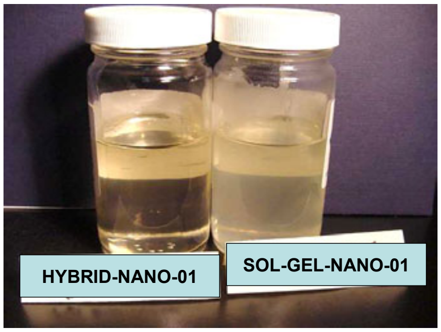

**Figure 3**
**The picture of two nanocomposite samples was taken after 12 hours the samples were collected.**

2. Thermal Stability at Elevated Temperature (60 °C)

**Figure 4** compares the preparation of a nanocomposite via nanoparticle surface modification by using silane, designated SOL-GEL-NANO-02, and the preparation of a nanocomposite via nanoparticle surface modification with the same silane, but stabilized with UCB's proprietary technology, designated HYBRID-NANO-02. After solvent evaporation, both final products contained >98% solids.

Both SOL-GEL-NANO-02 and HYBRID-NANO-02 samples were transferred to clear glass bottles and were placed in a 60°C oven. **Figure 4** depicts the viscosity-time profile of SOL-GEL-NANO-02 and HYBRID-NANO-02. It can be seen that the viscosity of HYBRID-NANO-02 did not significantly increase. In contrast, the viscosity of SOL-GEL-NANO-02 continuously increased, and finally gelled after aging for 4 weeks. HYBRID-NANO-02 can be considered thermally stable at 60°C.

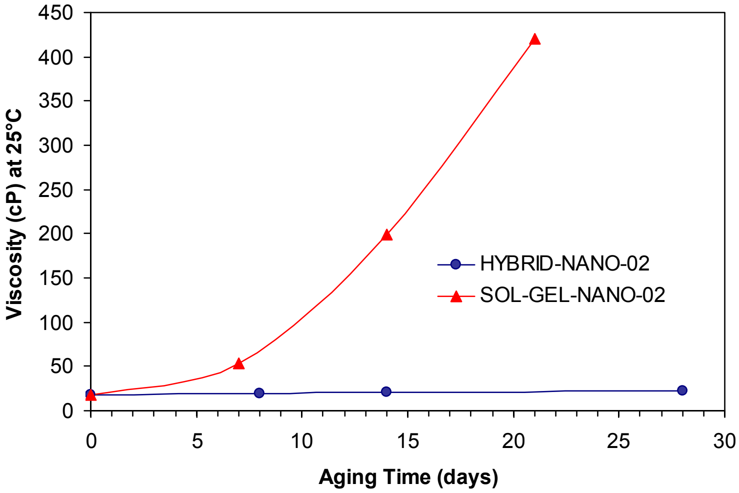

**Figure 4**
**Viscosity changes of SOL-GEL-NANO-02 and HYBRID-NANO-02 during thermal stability experiments.** (SOL-GEL-NANO-02 gelled after aging for 4 weeks.)

<u>Performance of UV–Cured Films/Coatings prepared from Organic-Inorganic Hybrid Nanocomposites</u>

HYBRID-NANO-03 is an organic-inorganic hybrid nanocomposite composition based on Ebecryl® 1290 and 10% of surface modified silica nanoparticles. Ebecryl® 1290 is a hexa-functional aliphatic acrylated urethane oligomer that imparts high surface hardness and surface scratch resistance. However, Eb 1290 in its cured form is extremely brittle. The performance targeted by HYBRID-NANO-03 is increased flexibility without the loss of properties such as hardness and scratch resistance.

Approximately 0.5-0.6 mil coatings were drawn down on Parker Bonderite 40 steel panels. The panels then were cured in air with 300 watt/inch mercury vapor electrodeless H lamps at the maximum belt speed that gave tack-free (cured) coatings. The properties of the cured films/coatings from HYBRID-NANO-03 were then tested according to the methods described above. For comparison, Eb 1290 was formulated, cured, and tested as the control sample.

The performance data of both the control sample and HYBRID-NANO-03 in **Table 3** indicate improvements in flexibility as reflected in the impact resistance. Adhesion also increased. The abrasion resistance of HYBRID-NANO-03 increased from 100 cycles to greater than 20,000 cycles without failure versus the Eb 1290 control composition. At the same time, HYBRID-NANO-03 still preserved the desirable properties of Eb 1290.

**Table 3**

**Property Comparison of HYBRID-NANO-03 and Formulated Eb 1290**

| **PROPERTY** | Eb 1290 (Control sample) | HYBRID-NANO-03 |
|---|---|---|
| **APPEARANCE** | Newtonian, viscous liquid at 60°C | Viscous liquid, pseudoplastic at 25°C |
| **ENERGY DENSITY ($J/cm^2$)** | 0.6 | 0.6 |
| **SURFACE PENCIL HARDNESS** | >9H | >9H |
| **MEK RESISTANCE** | >200 | >200 |
| **ABRASION RESISTANCE** | 100 cycles failed | 20,000 cycles without failure |
| **SCRATCH RESISTANCE (steel Wool double rubs)** | >200 | >200 |
| **IMPACT RESISTANCE (lb-inch)** | 8 | 16 |
| **ADHESION ON STEEL PANEL** | 3B | 4B-5B |
| **Conical Bend** | 4 inch failed | 4 inch failed |

**Table 5** presents more details regarding improvements in abrasion resistance. In addition, the weight lost per abrading cycle for HYBRID-NANO-03 significantly decreases.

**Table 5**

**Abrasion Resistance Test Results**

| **Sample** | **CS-17 Test Results (failed-broken through, weight lost: $\mu$g/cycle) Coating thickness: ~ 0.5 mil** | | | |
|---|---|---|---|---|
| **Control Sample Eb 1290** | 100 cycles,<br>Failed,<br>66.0 | | | |
| **HYBRID-NANO-03** | 100 cycles,<br>Passed,<br>0.0 | 1,000 cycles,<br>Passed,<br>3.6 | 10,000 cycles,<br>Passed,<br>2.2 | 20,000 cycles,<br>Passed,<br>2.0 |

## Conclusion

The nanocomposite technology developed at UCB comprises four features including nanoparticle surface modification, nanocomposite preparation, stabilization of nanocomposites, and formulation of radiation (UV/EB) curable organic-inorganic hybrid nanocomposite. The technology allows UCB to produce thermally stable, organic-inorganic hybrid nanocomposite materials with 100% reactive solids content. The organic-inorganic hybrid nanocomposite compositions are radiation (UV/EB) curable, and the properties of material can be tailored by selection of inorganic nanoparticles (size/properties) or by selection of organic resin and diluents.

## References:

1. G. Jeffrey Brinker, George W. Scherer "Sol-Gel Science, The Physics and Chemistry of Sol-gel Processing" pp 108-206, Academic Press Inc. 1990