Halogen-Free, UV-Curable High Refractive Index Materials for Light Management

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CYTEC Functions of Refractive Index

3 Functions of Refractive Index

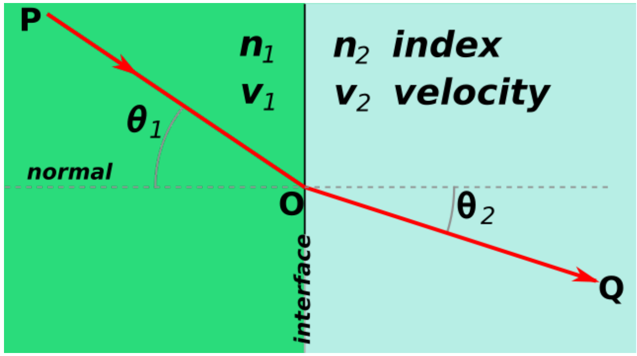
- ***Refraction:*** Light rays change direction when they cross the interface from one material (n_1) to another material (n_2);

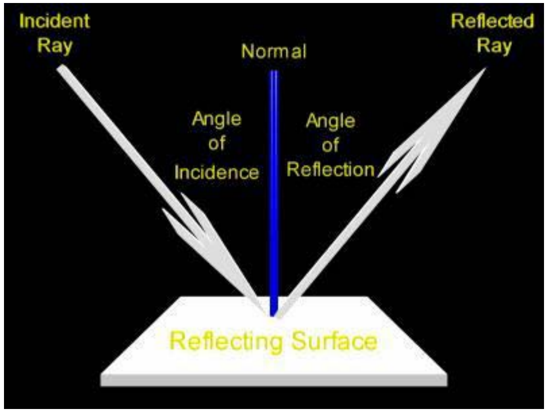
- ***Reflection:*** Light reflects partially from the inter-surfaces of 2 materials that have different refractive index;

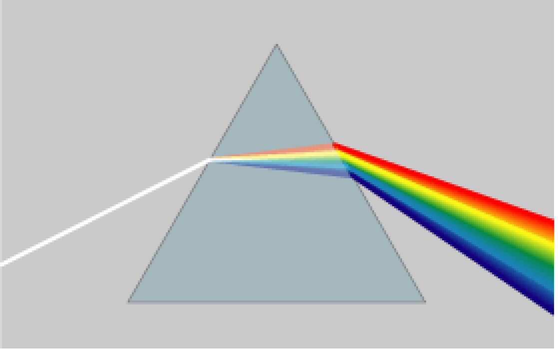
- ***Dispersion:*** Dispersive effect due to the diversity of the wavelengths of the light, the bending effect being frequency dependent.

- **Snell's Law-Refraction**

$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{v_1}{v_2} = \frac{n_2}{n_1}$$





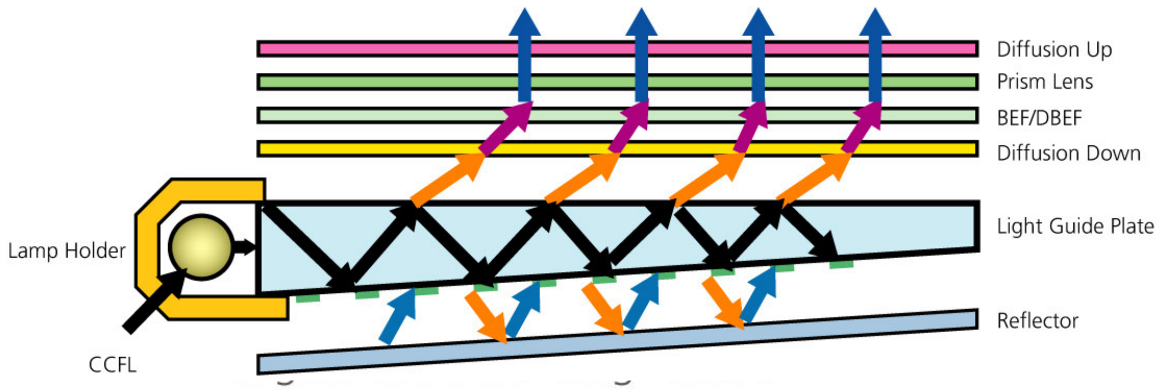


Potential Applications of High RI Materials

- Brightness enhancing films
- Anti-reflective coatings
- High-reflective coatings
- Bragg reflectors
- Optical fiber coatings
- Plastic lenses
- Graded index optical lenses
- Fresnel lenses
- Photonic devices
- Security Coatings

Various applications for high refractive index materials

CYTEC Brightness Enhance Films



Cited from acer

A micro-replicated prism film (made from high RI materials) that is used to increase display brightness by managing the exit angle of light .

CYTEC Material Requirements

- Optical Properties
- Mechanical Properties
- Adhesion
- Formulation Capability
- Process-ability
- Cost
- Product Stewardship

Requirements driving need for new materials/technologies

Theory for Making High RI Materials

Higher refractive index (n) is often achieved by increasing polarizability (γ) and / or increasing density (ρ).

1. Aromatic Rings
2. Halogen Atoms (Cl, Br)
3. Hetero Atoms (S, P)
4. Inorganic-Organic Hybrid Nanomaterials

Lorentz - Lorenz Equation

$$n^2 = \frac{\frac{8}{3}\pi N_A \gamma \rho + M}{M - \frac{4}{3}\pi N_A \gamma \rho}$$

$n \equiv$ Refractive Index

$M \equiv$ Repeat Unit MW

$N_A \equiv$ Avogadro's Constant

$\gamma \equiv$ Polarizability

$\rho \equiv$ Density

Polarizability number

A/M	H	C	N	O	F	S	P	Cl	Br	I	Ti	Zr	CH_4	C_6H_6
γ	0.67	1.76	1.10	0.80	0.56	2.90	3.63	2.18	3.05	5.35	14.6	17.9	2.59	10.0

Theory guides our new materials R&D

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Technical Strategy

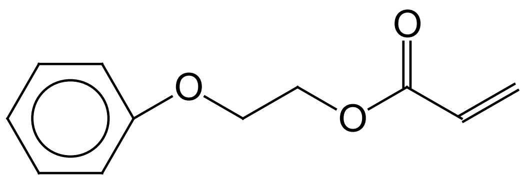
- Traditional Approach - Organic Synthesis/Formulation

- New Approach - Inorganic - Organic Hybrid Nanocomposite – Nanoparticle Dispersion

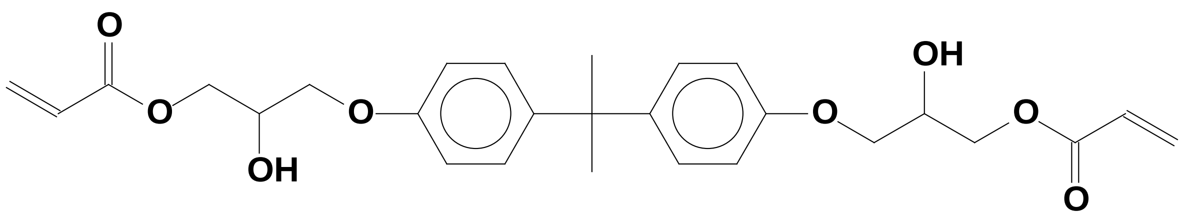
Overall technical strategy for the development of High RI Materials.

Highly Aromatic (Meth)Acrylate Resins

- **2-Phenoxyethyl acrylate**
  - n = 1.51, liquid'
  - Viscosity 20 cPs @ 25°C
  - Aromatic rings = 1



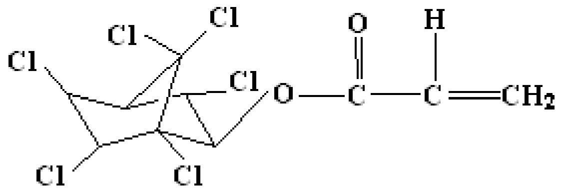
- **Bisphenol-A-epoxy diacrylate**
  - n = 1.55,
  - Viscosity 800,000 cPs @ 25°C
  - Aromatic rings = 2



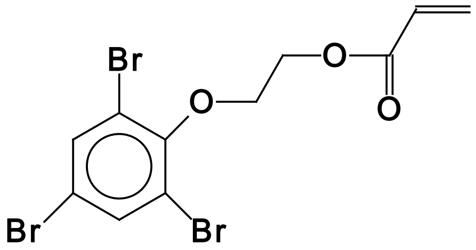
Compromise between refractive index and viscosity

Halogenated Acrylates

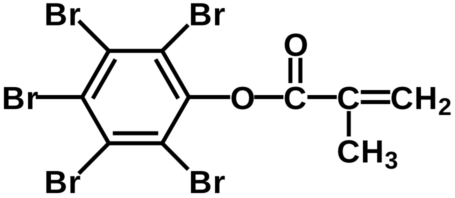
- Chlorinated Isobornyl Acrylate
  n = 1.54, liquid
  Very high concentration of chlorine



- Tribromophenoxyethyl Acrylate
  n = 1.56, solid
  High concentration of bromine



- Pentabromophenyl methacrylate
  n = 1.71, solid
  Very high concentration of bromine



Higher halogenation, higher RI value, but ...

CYTEC New demands from global markets

- Halogen-Free materials are the preferred requirement globally due to growing environmental concerns;

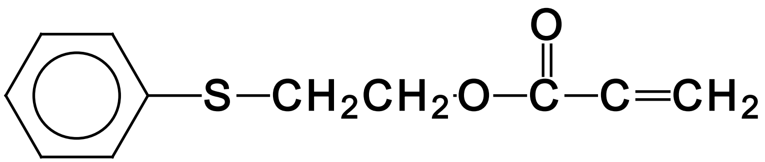
- Higher Refractive Index value – for higher performance;

- Lower viscosity requirement for coat-ability @ room temperature.

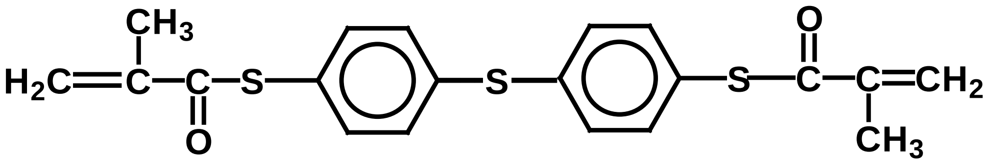
Fast market changes generate many technology challenges

Heteroatom Resins from Organic Synthesis / Formulation

- **Phenylthiolethyl acrylate**
  - n = 1.56, liquid
  - Good diluent,



- **MPSMA Bis(methacryloylthiophenyl)sulfide**
  - n = 1.66, solid



Existing technologies for making halogen-free, high RI materials

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Heteroatom Resins from Organic Synthesis / Formulation

Synthesized Heteroatom Urethane (Meth) acrylates

Properties	Oligomer 1	Oligomer 2
Halogen Free	Yes	Yes
Appearance	Clear liquid	Clear, dark brown, viscous liquid
Color (Gardner)	<1	<12.5
RI (L,), n_D^{20}	1.606	1.639
Molecular Weight (Mn) GPC	560	1,600
Viscosity (cPs @ 60 °C)	1,250	15,000
Density (g/cm^3)	1.18	1.20

Multi-aromatic rings and hetero atom-containing Urethane (Meth)acrylate – New Invented proprietary technology

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Heteroatom Resins from Organic Synthesis / Formulation

Performance Data of 3 Formulations based on heteroatom containing aromatic urethane (meth)acrylate oligomers

Performance	Formulation 1	Formulation 2	Formulation 3
Halogen Free	Yes	Yes	Yes
n_D^{20} (liquid)	1.5653	1.5658	1.5706
RI of Cured film	1.5886	1.5883	1.5906
Viscosity at 25°C	1840	1290	5500
Viscosity at 60°C	149	113	325
Pencil hardness	2H	1H	H
UV-cure Dosage (mJ/cm^2)	880	880	880
Tensile, psi	2700	2039	2337
Elongation, %	59	20	37
Modulus, psi	49508	52798	77719
Toughness, psi	764	279	652
Adhesion to PET film, 5B=100% adhesion	5B	5B	5B

Higher RI provides higher latitude for formulating

Halogen-free, Sulfur-free Resins from Organic Synthesis / Formulation

A new halogen-free and S-free oligomer has been developed.

Oligomer	Properties
Halogen Free, Sulfur-free	Yes
Molecular Weight (Mn) by GPC	2,750
Appearance	Clear, viscous liquid
Color (Gardner)	<1
RI (L, 589 nm @ 20 °C)	1.599
Viscosity (cP @ 60 °C)	117,000
Density (g/cm3)	1.16
Functionality	2 (can be higher)

The viscosity reduction can be achieved with reactive monomer dilution.

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RI of Inorganic Compounds

RI values of some inorganic compounds

Compound	Crystalline Form	Refraction Index, n^D
Al_2O_3	Col. Hex.	1.768, 1.76
Sb_2O_4 or ($Sb_2O_3Sb_2O_5$)	N. Cervantite(W powder), N. Senarmontite(Sb_2O_3,W cub), N. Valentinte (Sb_2O_3, Col rhomb)	2.00, 2.087, 2.18, 2.35,
CdO	Brown Cub	2.490
CaO_2	White tetr.	1.895
Cu_2O	N. Cuprite, red, oct. cub.	2.705
FeO	N. Wuestite, blk. Cub.	2.32
Fe_2O_3	N. Hematite, red-brn to blk trig	2.94-3.01
PbO	Massicot. Yel. Rhomb.	2.51-2.71
$MnOMnO_3$(II,III)	N. Hausmanntite, blk. Tetr(rhomb)	2.15-2.46
SnO_2	N. Cassiterite, white tetr.or hex. or rhomb)	1.997-2.093
TiO_2	N. octahedrite, anatase, br-blk, tetr	2.554-2.493
	N. Brookite, white, rhomb	2.586-2.741
	N. Rutile, Col. tetr	2.616-2.903
ZnO	N. Zincite, white hex.	2.008-2.029
ZnS	N. Sphalerite, col. Cub.	2.368
ZnSe	Yelsh. to redsh. Cub.	2.89
ZnTe	Red cub.	3.56
ZrO_2	N. Baddeleyite, col.-yel-brn monocl.	2.13-2.19-2.20

Targeted inorganic/organic hybrid nanocomposites due to the high refractive index of inorganic compounds

Two Possible Technologies for Preparing Inorganic-Organic Hybrid Nanocomposite Materials

A. Sol-Gel Chemistry and Process:

The process involves the transition of a system from a liquid "sol“ (mostly colloidal) phase into a solid "gel" phase.

B. Nanoparticle Dispersion – Nanocomposite:

Use commercially available nanoparticles as raw materials
--- Surface modify nanoparticles
--- Disperse surface modified nanoparticles into UV resins.

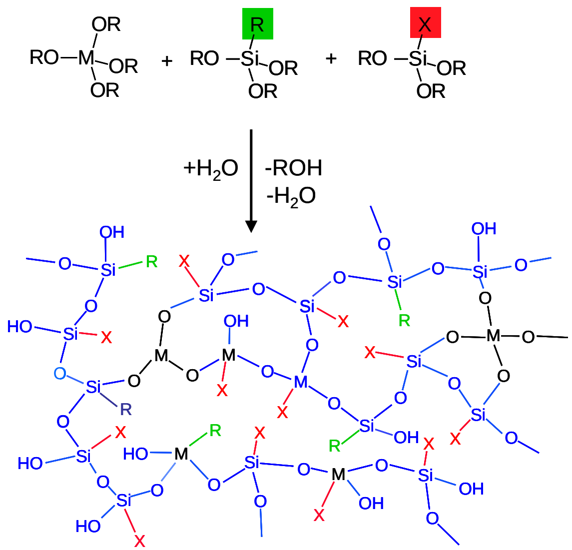
> **Hybrid nanocomposite combines advantages of inorganic and organic phases.**

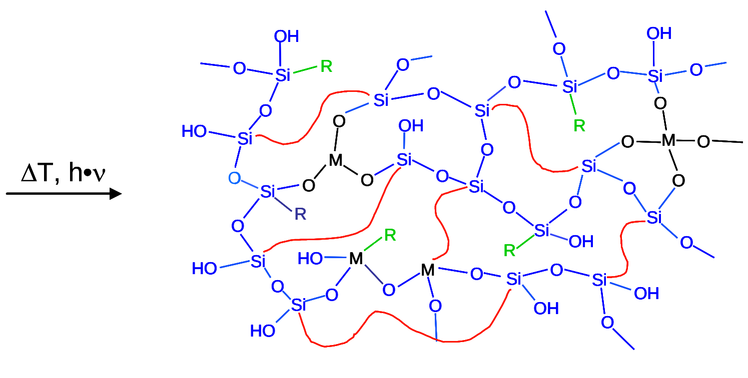
Sol-Gel Process

- Metal alkoxides, chlorides or nitrates are hydrolyzed and condensed
- Low temperature reaction conditions required
- Condensation generates highly crosslinked M-O-M networks with H_2O or ROH as byproducts

CYTEC Inorganic-Organic Hybrid Nanocomposite

A. Sol-Gel Chemistry and Process





R = $-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NMe_3^+ Cl^-$, C_6H_5
— organic cross-linking
M = Al, Ti, Zr, Fe

R = $-CH_2CH_2(CF_2)_5CF_3$, $-CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NMe_3^+ Cl^-$, C_6H_5
X = reactive group for organic cross-linking
M = Al, Ti, Zr, Si

Functionalized inorganic network (nanosized clusters) in molecular dispersed solution

→

Inorganic-organic hybrid material as cured film (cross-linked)

Challenges/ Issues:

- **Incomplete hydrolysis/condensation**
- **Poor hydrolytic stability**
- **Frequent crack problems for cured films**

Nanocomposite Challenge

- **Overcome Rayleigh Scattering for optical transparency**
  - Designed matrix and nanoparticle to manage refractive index difference (Δn).
  - Dispersed nanomaterial into primary particles to minimize particle size (r).

Rayleigh Scattering Equation

$$P_{scat.} = \frac{128\,\pi^5\,N_A\,r^6}{3\,\lambda^4}\left[\frac{n_p^2 - n_m^2}{n_p^2 + 2n_m^2}\right]$$

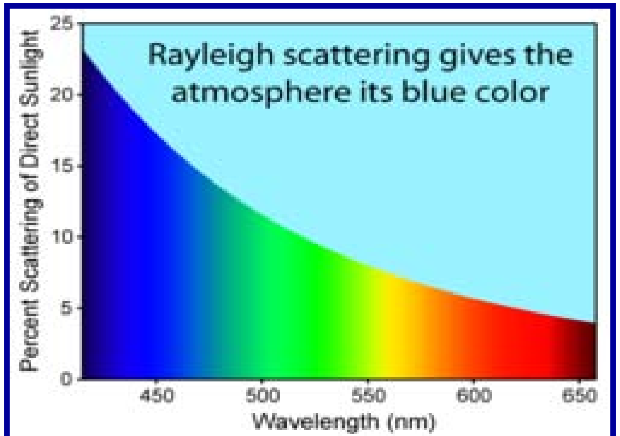
n_p ≡ Refractive Index of particle

n_m ≡ Refractive Index of matrix

r ≡ Particle Radium

N_A ≡ Avogadro's Constant

λ ≡ Wavelength of light



Ref: R. M. Kerker. The Scattering of Light and Other Electromagnetic Radiation. Academic Press 1969, N.Y.

Rayleigh Scattering caused by large and uneven particle size is the major issue.

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Nanoparticle Surface Modification

- Commercial Nanoparticle are usually aqueous dispersions of inorganic oxides or metal particles
- Converts commercially available Nanoparticles that are hydrophilic and non-reactive to Nanoparticles that are hydrophobic and curable
- Modify the surface of the Nanoparticles with organic groups such as those containing UV curable functionality

B. Nanoparticle Dispersion – Nanocomposite:

Inorganic Nanoparticles

Surface functionalization
At 25-60 °C

Functionalized Nanoparticles

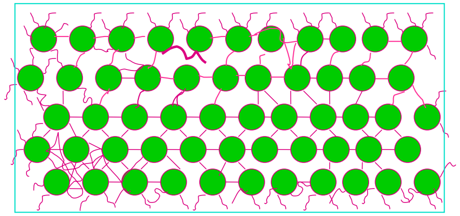
Disperse

Strip off solvents

Homogeneous Nanoparticle Dispersion in UV resins

UV Radiation, PI

Co-polymerize between inorganic/organic phases and particles/particles



The key technical challenge is nanoparticle surface modification

Surface Treatment Achievements

- Surface treatment technology enables inorganic Nanoparticles to be compatible in organic medium without agglomeration

- Surface treatment technology enables low viscosity, even with high Nanoparticle loads;

- Surface treatment technology overcomes Raleigh-Scatter issues for optical transparency

Innovated proprietary nanomaterial surface treatment for dispersion into high refractive index UV resins.

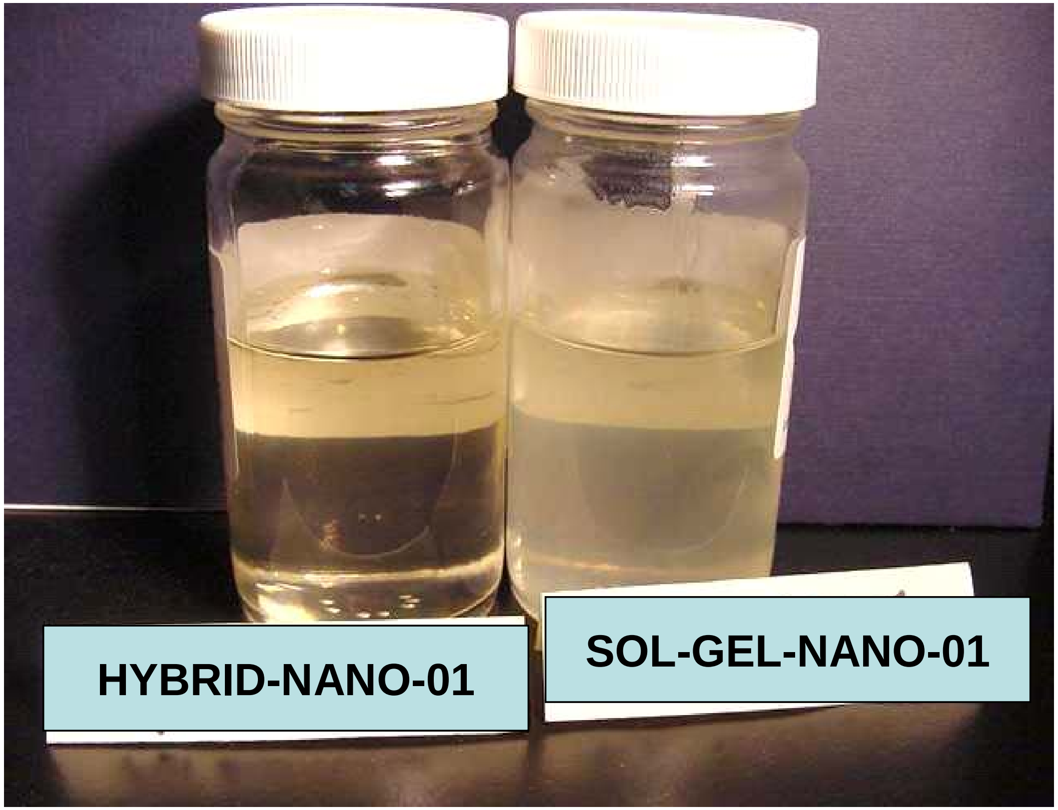
Acrylated Nanocomposites

Inorganic-Organic Hybrid Nanocomposite Material

High optical transparence indicates no Rayleigh Scattering issue.

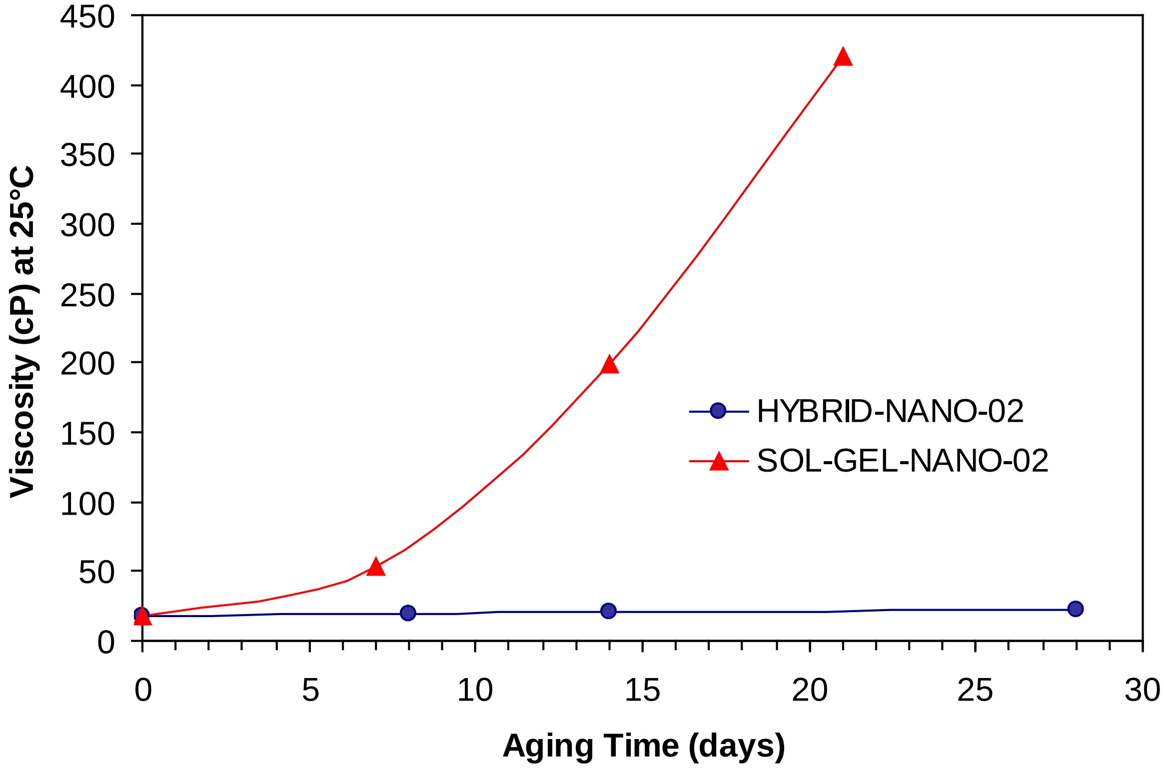
Stability Comparison

- Sol-Gel-Nano-01: normal Sol-Gel process
- Hybrid-Nano-01: Nanoparticle dispersion with new surface treatment



Viscosity-Time Profile

- Samples aged at 60°



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Acrylated Nanocomposites

Properties of Nanoparticle Dispersions

High RI Nanoparticle Dispersion	Properties
Halogen Free	Yes
Organic Medium	UV-resin
Appearance	Very light yellow, clear liquid
Color (Gardner)	<1
RI (L, 589 nm @ 25 °C)	1.56 -1.59
Viscosity (cP @ 25 °C)	1,500 – 15,000
Density (g/cm3)	1.20- 1.26

Good stability @ 60°C for a week, @ room temperature for at least 6 month, no agglomeration, no significant increase in viscosity.

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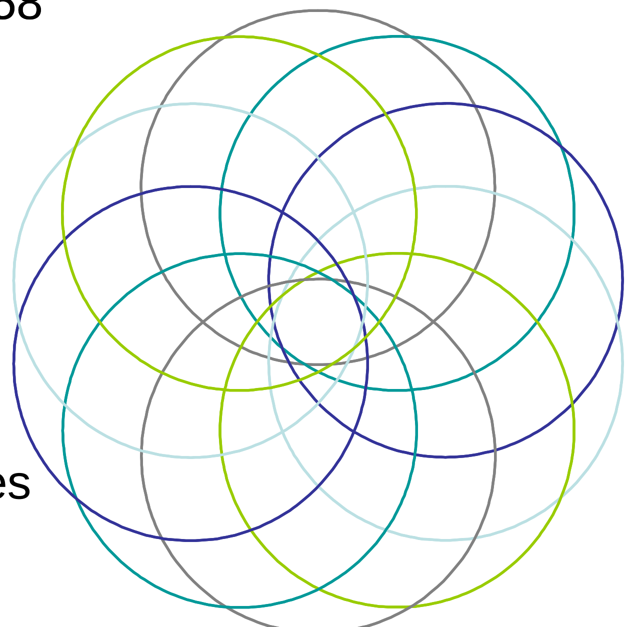
Acrylated Nanocomposites

Performance of UV-Curable Inorganic-Organic Hybrid Nanocomposite Formulation

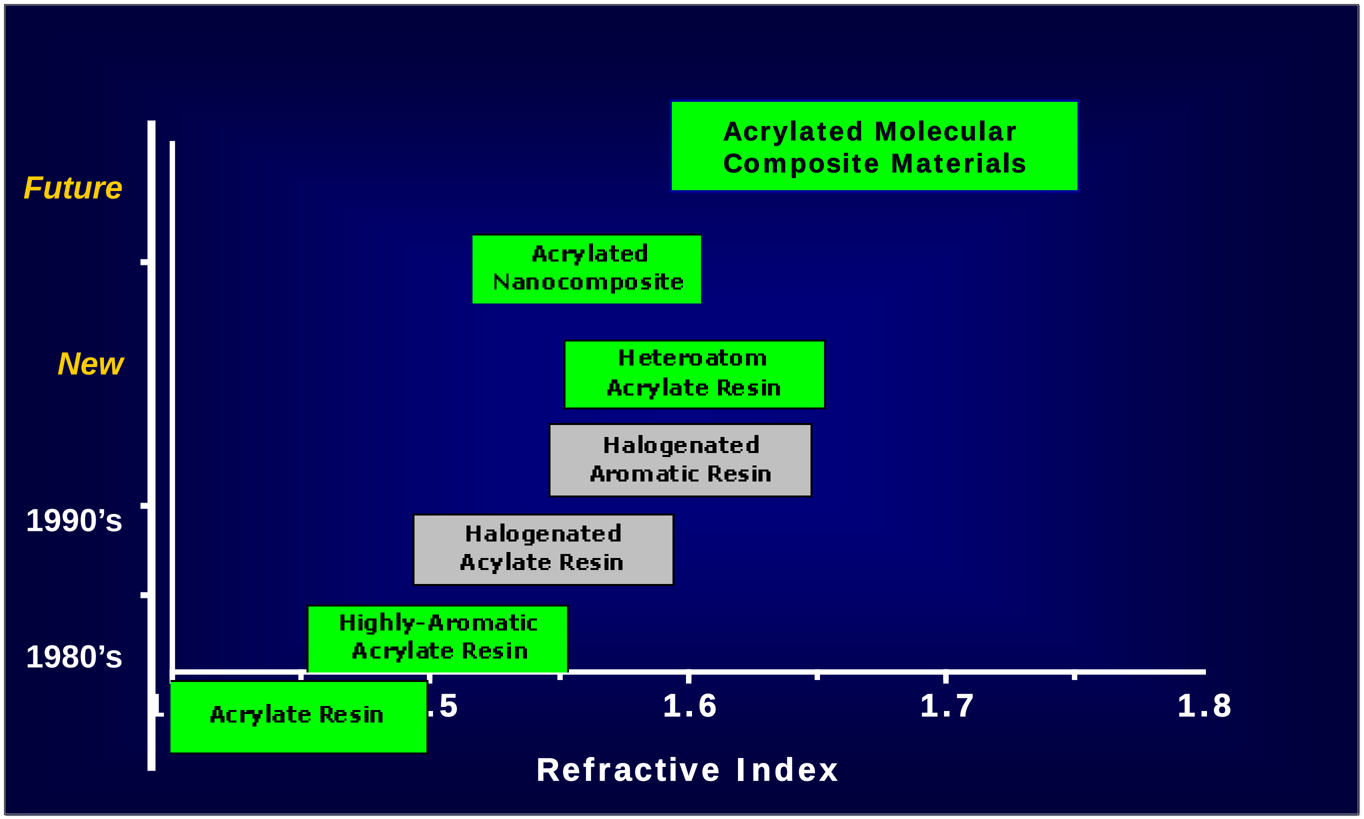
Performance	Value
Halogen Free	Yes
Appearance	Clear liquid with yellow color
Color (Gardner)	<1
Density (g/cm^3)	1.24
n_D^{20} (liquid)	1.55
RI of Cured film	1.58
Viscosity at 25°C	2,500
Viscosity at 60°C	100
Pencil hardness	5H
UV-cure Dosage (mJ/cm^2)	880
Tensile, psi	4,000
Elongation, %	4.5
Tg °C (tan delta)	70
Toughness, psi	100
Adhesion to PET film, 5B=100%	5B

Easy to be formulated, advanced performance in comparing to neat organic resins.

It’s not only high RI



CYTEC Technology Roadmap



Color Key:

Halogen-Free

Halogenated

Long term research efforts focus on higher refractive index, better performance, more environment friendly technologies

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Conclusions

- Based on a broad understanding of the refractive index, new technologies have now been developed to address multi-challenges from fast growing global markets.

- Multi- aromatic rings and heteroatom containing urethane acrylates were developed to have a high RI (>1.60) while halogen-free.

- Newly developed surface chemistry leads to new Nanoparticle dispersion (Nanocomposite) products that overcome Rayleigh scattering. (Halogen-free, low viscosity material with 1.59+ RI).

Acknowledgements

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