V-Pyrol™
vinylpyrrolidone

V-Cap™
vinylcaprolactam




Intermediates
Solvents
Monomers
Polymers
Specialty Chemicals

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Reactive Diluents for Free Radical Radiation Curable Systems

V-Pyrol™/RC (N-vinyl-2-pyrrolidone)[a] and V-Cap™/RC (N-vinyl-2-caprolactam)[b] are versatile reactive diluents for free radical radiation curable coatings, inks, and adhesives for use on a wide variety of substrates including:

- flooring
- paper
- wood
- particle board
- plastics
- textiles
- vinyl

Both monomers provide unique benefits as reactive diluents.[1] Key advantages include:

- low viscosity
- increased cure speed
- improved adhesion
- enhanced hardness
- increased tensile strength

The physical properties of the V-Pyrol and V-Cap reactive diluents are shown in Table 1. Both monomers are cyclic lactams and differ only in ring size. V-Cap/RC diluents have a lower vapor pressure, reduced water solubility, and a higher melting point compared to V-Pyrol/RC diluents. These properties give the formulator additional options when preparing UV and EB formulations.

[a] CAS Registry No. 88-12-0
[b] CAS Registry No. 2235-00-9

Overview

The emergence of radiation curable systems was a reaction to a changing industrial environment. Concern over an energy shortage, pollution, and increasing costs of petrochemical solvents was the catalyst in the development of this new technology that offers the following features:

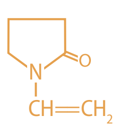
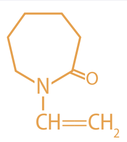
- conforms to
  emission standards
  performance requirements
- decreases
  energy consumption
  original capital equipment cost
  space requirements
- increases
  productivity (line speed)
  substrate selection
  raw material efficiency
  quality

Free radical radiation curing economically combines photochemistry and polymer science in a 100%-reactive system. It is simply a free radical polymerization initiated by a high energy source, i.e. ultraviolet (UV) or electron beam (EB) radiation. Production equipment is available from several suppliers and the process is a commercial reality for wood products, metal decoration, plastics, electronics, printing, and flooring.

Summary of EB vs. UV Free Radical Systems

Issue	EB	UV
Energy Consumption	lower	higher
Initiator	no	yes
Capital Expenditure	higher	lower
Maintenance Cost	lower	higher
Operational Efficiency	higher	lower
Productivity	higher	lower
Substrate Selection	higher	lower

Table 1 – Physical Properties of N-Vinyl Lactams[c]

Name	V-Pyrol/RC diluent	V-Cap/RC diluent
Structure		
Molecular Weight	111	139
Assay (%)	98.5	98.0
Physical Form	liquid	solid
Appearance	clear	crystalline
Specific Gravity	1.04° (4°C)	1.01° (40°C)
Melting Point	17°C	35°C
Boiling Point	193°C @ 400mm	116°C @ 10mm
Viscosity (cps)	2.07 (25°C)	3.51 (40°C)
Vapor Pressure @ 20°C	<0.1mm	<0.1mm
Vapor Pressure @ 70°C	3.4mm	1.2mm

[c] These data are typical of production but are not necessarily specifications. Current specifications are available on request.

Radiation Curable Systems

The simplest formulation consists of an oligomer and a reactive diluent, with a photoinitiator necessary for UV systems. Additives, such as surfactants, adhesion promoters, pigments, fillers, and flattening agents also may be included to modify the final coating properties.

Oligomers

These low-molecular-weight unsaturated polymers act as the backbone of the system and essentially determine the final properties. The unsaturation is usually ethylenic or allylic and the compounds are characteristically highly viscous. Acrylated urethanes, polyesters and epoxies are the most frequently used oligomers. Polythiols also have some applications.

Photoinitiators for UV Systems

In UV systems, photoinitiators are the counterparts to catalysts in thermal systems. Their effectiveness is dependent on the formulation. The choice of a photoinitiator also depends on the atmosphere for curing — air versus nitrogen.

Typical Photoinitiators Include:

- benzophenone/amine
- benzoin ethers
- acetophenone derivatives
- thioxanthones
- phosphine oxides

Reactive Diluents

These are monomers that become part of the film and modify the final properties. Their main functions are to modify the viscosities and the crosslink densities of the formulations. The diluents may be monofunctional or multifunctional and are usually vinyl or acrylic monomers. The preferred characteristics are innocuousness, diluent efficiency, reactivity, and low volatility.

Common commercially available reactive diluents include:

Monofunctional Diluents

- V-Pyrol™/RC diluents
- V-Cap™/RC diluents
- ethoxyethoxyethyl acrylate (EEEA)
- 2-ethylhexyl acrylate (EHA)
- styrene

Multifunctional Diluents

- tripropyleneglycol diacrylate (TRPGDA)
- hexanediol diacrylate (HDDA)
- trimethylolpropane triacrylate (TMPTA)

Summary of Properties and Applications of Various Types of Commercial Oligomers

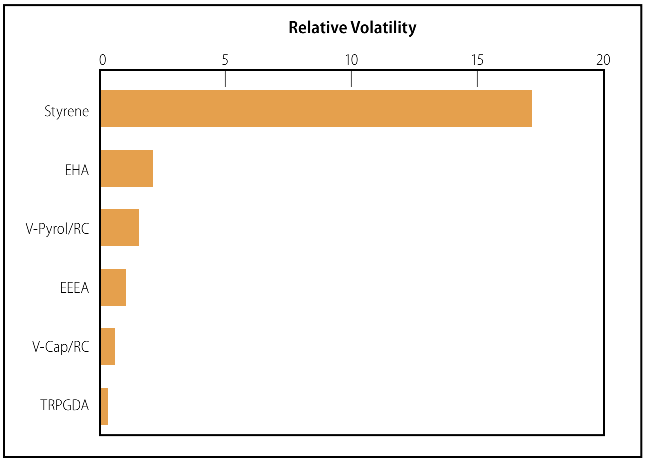
Oligomers	Properties		Applications	
Urethane Acrylates	Hardness Toughness Flexibility Chemical Resistance	(or) Softness Flexibility	Decorative Wood Plywood Particle Board	Flooring Plastic Optical Fibers Glass
Polyester Acrylates	Economy Low Viscosity Toughness	Abrasion Resistance Excellent Wetting and Flow	Wood Paper	Paperboard Lithographic Inks
Epoxy Acrylates	Adhesion Penetration	Chemical Resistance Hardness	Metal Decorative	Wood Overprint Varnish

Volatility

Both V-Pyrol™ and V-Cap™ reactive diluents are relatively nonvolatile. This is important because it prevents loss of monomer due to evaporation and reduces pollution and safety concerns. The physical form (solid), higher molecular weight, and lower vapor pressure of V-Cap/RC diluents all contribute to especially low volatility.

As shown in Figure 1, V-Cap/RC diluent is less volatile than V-Pyrol/RC diluent and, in fact, has the lowest volatility of any of the monofunctional diluents tested.[13]

Figure 1: Volatility

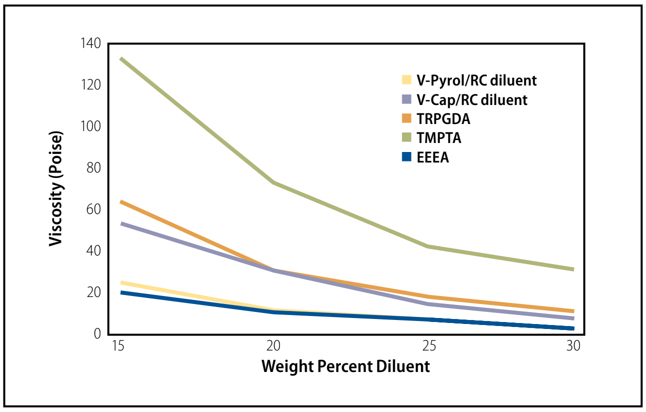


Viscosity

The V-Pyrol/RC and V-Cap/RC reactive diluents are very effective at reducing the viscosity of acrylate oligomers. Although the V-Cap monomer is a crystalline solid at room temperature (melting point = 35°C), at temperatures above its melt point it is a low viscosity liquid (3.51 cps @ 40°C) which can be readily handled and easily incorporated into formulations. Once a formulation is completely homogeneous, V-Cap diluent is unlikely to crystallize from solution.

As shown in Figure 2, the diluency of V-Pyrol/RC diluent is comparable to the commonly used diluent ethoxyethoxyethyl acrylate (EEEA) while V-Cap/RC diluent is similar to tripropyleneglycol diacrylate (TRPGDA). Both monomers can also be used in conjunction with other diluents to further optimize formulation viscosity.

Figure 2: Viscosity of Oligomer/Diluent Blends

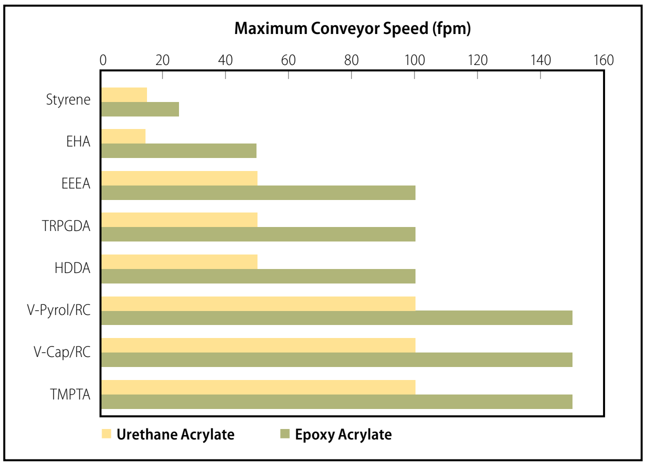


Cure Speed

UV and EB formulations based on V-Pyrol™/RC and V-Cap™/RC diluents cure more rapidly than formulations based on other monofunctional diluents.[2-5] The reactivity of acrylate oligomer/reactive diluent blends (80 parts/20 parts), each containing 3 parts of a free radical photoinitiator, was determined using both an epoxy acrylate and a urethane acrylate oligomer. Cure speed was deter mined by measuring solvent resistance, hardness, abrasion resistance, and surface feel as a function of UV conveyor speed. Results demonstrate extremely rapid cure speeds for both N-vinyllactams. The cure rate was superior to the other monofunctional diluents tested.

N-vinyllactams used as reactive diluents in UV and EB formulations exhibit a high degree of conversion to polymer which results in improved long-term performance. To insure complete conversion of monomer, the level of N-vinyllactam in a formula should not exceed 20 to 25 weight percent.

Figure 3: Cure Speed of Oligomer/Diluent Blends



Cured Film Properties

A. Tensile Properties

Both V-Pyrol/RC and V-Cap/RC reactive diluents provide high Tg homopolymers (Tg = 175 and 135°C respectively). Therefore, when formulated with acrylate oligomers, they increase the hardness and tensile strength of the cured films.[2,6,7] This is a distinct advantage, since most monofunctional diluents give low Tg homopolymers and seriously soften the cured film.

The tensile properties of prototype UV-cured coating formulations containing vinyllactams were compared to similar formulations containing other reactive diluents. Results clearly demonstrate that, unlike the acrylates, the presence of V-Pyrol/RC or V-Cap/RC reactive diluents increases tensile strength and Young's modulus while reducing elongation.

Table 2 - Tensile Properties

Composition	A	B	C	D	E
V-Cap/RC diluents	14.0	—	—	—	—
V-Pyrol/RC diluents	—	14.0	—	—	—
EHA	—	—	14.0	—	7.0
HDDA	—	—	—	14.0	7.0
EBECRYL* 8800-20R[a]	50.0	50.0	50.0	50.0	50.0
EBECRYL 7100[b]	10.0	10.0	10.0	10.0	10.0
TMPTA	18.0	18.0	18.0	18.0	18.0
TRPDGA	8.0	5.0	8.0	8.0	8.0
Ingacure* 184[c]	5.0		5.0	5.0	5.0
Performance					
Tensile strength (psi)	3208	3474	1250	2280	1711
% Elongation	3.4	3.3	6.0	3.5	5.3
Young's Modulus (kpsi)	149	162	45	105	74

[a] Aliphatic Urethane Acrylate/TRPGDA blend from Cytec or equivalents
[b] Acrylated Amine Oligomer from Cytec or equivalents
[c] BASF or equivalents

B. Adhesion

Both V-Pyrol™/RC and V-Cap™/RC[4, 8, 11] diluents provide outstanding adhesion to a wide variety of difficult substrates including vinyl. This gives formulations extra utility in terms of the substrates on which they can be applied. Increased adhesion is most likely caused by the outstanding solvency of the lactam ring.

Table 3 - Adhesion to Vinyl and Polyester

Composition	A	B	C
V-Cap diluents	25.0	—	—
V-Pyrol diluents	—	25.0	—
EHA	—	—	25.0
EBECRYL* 6700[a]	75.0	75.0	75.0
DC-193[b]	0.5	0.5	0.5
Ingacure* 184[c]	3.0	3.0	3.0
Performance			
Adhesion (%)			
Polyester	100	100	100
Vinyl	100	100	68

[a] Aromatic Urethane Oligomer from Cytec or equivalents
[b] DOW or equivalents
[c] BASF or equivalents

C. Water Resistance

The low water solubility of V-Cap/RC diluent is apparent in the cured film. This property is readily demonstrated by measuring the contact angle of a water droplet on the cured surface. A high contact angle is seen using V-Cap/RC diluent indicating a hydrophobic coating. Thus V-Cap/RC diluent based formulations are expected to show increased water resistance.

Table 4 - Water Resistance

Composition	A	B
V-Pyrol diluents	25.0	—
V-Cap diluents	—	25.0
EBECRYL 8000[a]	45.0	45.0
TMPTA	30.0	30.0
Surfynol* 104H[b]	1.5	1.5
Ingacure 184[c]	2.0	2.0
Performance		
Contact Angle (DI Water)	52.0	65.0

[a] Aliphatic Urethane Acrylate from Cytec or equivalents
[b] Air Products or equivalents
[c] BASF or equivalents

Stability

The V-Pyrol/RC and V-Cap/RC monomers, like most reactive diluents, should be stored under ambient conditions and used within six months of purchase. When formulated with acrylates, stability is generally excellent but decreases with increasing acidity. Thus, it is best to formulate with acrylate monomers and oligomers having low levels of residual acrylic acid (low acid number). V-Pyrol and V-Cap diluent formulations containing high levels of acid will turn pink providing an early warning sign of instability.

Special Handling Requirements

Please note that V-Cap diluent has a freezing point of 95°F (34°C) and is normally a solid at room temperature. However, it readily supercools and thus will often remain a liquid for extended periods of time at room temperature. The supercooled liquid will spontaneously crystallize if seeded by a frozen crystal or may crystallize with mild agitation. The crystallization process is exothermic, the temperature rapidly reaching, but never exceeding the freezing point (34°C).

Melting Instructions

During the freezing process, some stratification of the stabilizer may occur, therefore, to insure product quality and consistency, it should be melted and thoroughly mixed prior to use. V-Cap diluent may be safely melted by placing the container in a constant temperature water bath or heated room, no warmer than 120°F (49°C).

Melting in drums is expected to require several days. Steam or electrical heating systems, which generate localized hot spots, should never be used to melt this product. Material being melted should be agitated at regular intervals to assure redistribution of the polymerization inhibitor and oxygen.

Prolonged storage at elevated temperatures will cause yellowing and polymer formation and should be avoided. This result emphasizes the importance of storing V-Cap and V-Pyrol diluents at room temperature. Repeated freezing and thawing of V-Cap diluent is not expected to cause stability problems if care is taken to redistribute the stabilizer during melting. V-Cap subjected to 24 freeze/thaw cycles shows no decrease in GC purity and no polymer formation.

Prototype Floor Tile Formulation

Composition	A	B
V-Pyrol™/RC diluents	10.0	—
V-Cap™/RC diluents	—	10.0
EBECRYL* 6700[a]	48.0	48.0
TMPTA	22.0	22.0
TRPGDA	15.0	15.0
Ingacure* 184[b]	5.0	5.0
Performance		
Viscosity (cps @ 25°C)	1055	1580
Min. Dose (mJ/cm2)	340	340
Hardness	H	H
% Adhesion	96	96
MEK Double Rubs	200	200
Water Resistance[c]	pass	pass
Stain Resistance[d]		
Shoe Polish	0	0
Mustard	3	3
Iodine	2	1
2% KMnO4	4	4
Tensile Strength (psi)	5120	5980
% Elongation	3.6	3.6
Young's Modulus (kpsi)	335	219
Stability @ 50°C	> 4 weeks	> 4 weeks

[a] Aromatic Urethane Acrylate from Cytec or equivalents
[b] From BASF or equivalents
[c] Tile submerged for 16 hours shows no blistering or peeling
[d] ASTM D-1308, 16 hours @ 50°C. 0 = no stain, 5 = severe stain

Prototype Solder Mask Formulation

Composition	E	F
V-Pyrol/RC diluents	13.2	—
V-Cap/RC diluents	—	13.2
Photomer* 4072[a]	13.2	13.2
EBECRYL 3600[b]	42.1	42.1
NYTAL* 300[c]	27.8	27.8
Benzophenone	3.7	3.7
Performance		
Viscosity (cps)	2375	4400
Min. Dose (mJ/cm2)	175	175
% Adhesion		
Copper[d]	100	100
Printed Wire Board	100	100
MEK Double Rubs	> 200	> 200
Solvent Resistance[e]		
MEK	> 8	> 8
Toluene	> 8	> 8
Water	> 8	> 8
Decomposition Temp. (°C)	352	352
Low Temp Stability[f]	pass	pass
High Temp Stability[g]	pass	pass

[a] Propoxylated Trimethylolpropane Triacrylate from IGM resins or equivalents
[b] Epoxy acrylate oligomer from Cytec or equivalents
[c] Talc from RT Vanderbuilt or equivalents
[d] Requires annealing for 10 minutes at 400°F
[e] ASTM D-1308:hours to attack @ 25°C. 0 =no stain, 5 =severe stain
[f] Panel submerged in liquid nitrogen for 10 seconds shows no blistering or peeling
[g] Panel placed in a 550°F oven for 20 seconds shows no blistering or peeling

Prototype Polyester Coating

Composition	C	D
V-Pyrol™/RC diluents	14.0	—
V-Cap™/RC diluents	—	14.0
EBECRYL* 8800-20R[a]	50.0	50.0
EBECRYL 7100[b]	10.0	10.0
TMPTA	18.0	18.0
TRPGDA	8.0	8.0
Ingacure* 184[c]	5.0	5.0
Performance		
Viscosity (cps @ 25°C)	800	1175
Min. Dose (mJ/cm2)	150	150
Hardness	3H	3H
% Adhesion	100	100
Mandrel Bend (in.)	0.125	0.125
MEK Double Rubs	200	200
Stain Resistance[d]		
Iodine	3	3
2% KMnO4	4	4
Tensile Strength (psi)	3473	3208
% Elongation	3.3	3.4
Young's Modulus (kpsi)	162	149
Stability @ 50°C	> 4 weeks	> 4 weeks

[a] Aliphatic Urethane Acrylate/TRGDA blend fromCytec or equivalents
[b] Acrylated Amini Oligomer from Cytec or equivalents
[c] From BASF or equivalents
[d] ASTM D-1308, 16 hours@ 50°C.
0 =no stain, 5 =severe stain

Prototype UV Wood Coating

Composition	G	H
V-Pyrol/RC diluents	25.0	—
V-Cap/RC diluents	—	25.0
EBECRYL 8800[a]	45.0	45.0
TMPTA	30.0	30.0
Surfynol* 104H	1.5	1.5
Irgacure 184	2.0	2.0
Performance		
Viscosity (cps @ 25°C)	844	1631
Min. Dose (mJ/cm2)	850	850
Hardness	3H	3H
% Adhesion	100	100
MEK Double Rubs	200	200
Stain Resistance[b]		
Iodine	3	3
2% KMnO4	5	5
Shoe Polish	1	
Mustard	4	4
Contact Angle (DI Water)	52.0	65.0
Stability @ 50°C	> 4 weeks	> 4 weeks

[a] Aliphatic Urethane Acrylate from Cytec or equivalents
[b] ASTM D-1308: 16 hours @ 25°C.
0 =no stain, 5 =severe stain

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