

## Recommendations for Improving Polyvinyl Acetate Dispersions in Wood Adhesives

*“Tricks and tips” to solve common problems often encountered during the development of a polyvinyl alcohol stabilized polyvinyl acetate wood adhesive*

### Summary

Polyvinyl acetate dispersions stabilized with polyvinyl alcohol have been used in wood adhesive for over 50 years. The adhesives are divided into four durability classes, D1 to D4, where D1 is the lowest grade and D4 the highest. European Standard EN204 gives the description and the minimal requirements that adhesives must meet in order to classify as a D1 to D4 grade adhesive. In this bulletin we offer some example recipes for D3 and D4-grades and several recommendations for the use of CYLINK® monomers. However we stress that these are guideline recipes and recommendations only as polymerization equipment and therefore end results can differ significantly.

### Recommendations

With these recommendations we will try to improve the following important properties of the wood adhesive:

1. Water resistance
2. Shelf-life
3. Reduction of grit formation when using CYLINK NMA

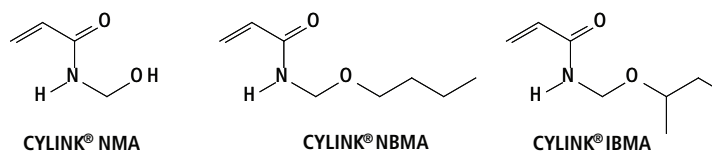
#### 1. Water resistance

Water resistance is usually improved by increasing the number of water resistant bonds. There are several ways to do this:

##### I. Functional cross-linking monomers

Compared to CYLINK NMA (N Methylol Acrylamide), both CYLINK NMBA (N Butoxymethyl Acrylamide) and CYLINK IBMA (Iso Butoxymethyl Acrylamide) have better incorporation into the polymer because of their good solubility in organic solvents and their insolubility in water. CYLINK NMA is however more reactive and therefore works at lower temperatures than either CYLINK NMBA or IBMA. For more in-depth information on the difference between CYLINK NMA, NBMA and IBMA please contact your local sales manager.

Figure 1: Chemical structures of functional crosslinking monomers



### II. Buffering systems

To obtain optimal reaction conditions for incorporation of the functional crosslinking monomers, such as CYLINK NMA, use a buffer such as ammonium hydrogen phosphate to reach a pH of approximately 5 during the reaction. After the adhesive has dried and ammonia has evaporated the ammonium hydrogen phosphate will act like an acid, thus enhancing the crosslinking.

### III. Acid catalysts

Acid catalysts are used in the final dispersion, preferably with a small percentage of a Lewis acid such as aluminium nitrate. This provides good crosslinking but does not cause a significant drop in pH. Catalyzing with 1% PTSA solution or other strong acids will increase the activity but will also significantly reduce the shelf-life.

#### 2. Shelf-life

Shelf-life problems occur when premature crosslinking takes place during storage; predominantly in the water-phase and mainly after catalysis. Water-phase polymerization by-products and grafted or absorbed homopolymers are very prone to premature crosslinking. Increased shelf-life can be achieved in several ways:

### I. Functional cross-linking monomers

With the correct choice of functional crosslinking monomer it is possible to balance crosslinking speed and shelf-life. CYLINK NMA is more reactive and therefore works at lower temperatures than either CYLINK NBMA or IBMA but it is also significantly more sensitive to water-phase polymerization. CYLINK NBMA and IBMA both have better incorporation into the particle and exhibit far less water-phase polymerization thus improving the shelf-life.

### II. Initiator systems

If possible, the use of a redox initiator system is recommended, preferably organic/inorganic such as SFS/t-BHP. The organic/inorganic system moves the initiation from the water-phase more into the organic phase, hence there is less water-phase polymerization and thus the shelf-life is improved. It is also recommended that the reaction temperature be kept as low as possible, the optimum being between 50-55° C. However, this may mean that the reaction time will increase.

### III. Solvents

Solvents such as ethanol, which have chain transfer effects, limit the amount of water-phase polymerization of CYLINK NMA and also reduce the level of grafting at the outside of the particle. Recent studies have shown that isopropyl alcohol (IPA) has a stronger and therefore more pronounced effect, allowing it to be used in lower amounts and therefore ultimately reducing the overall VOC level of the finish product.

### IV. Coalescing Agents

To achieve sufficient flexibility of the dried adhesive the use of a coalescing agent is recommended. Coalescing agents such as butyl glycol also slow down crosslinking reactions during storage and so improve shelf-life.

## 3. Reduction of grit when using CYLINK NMA

Because of the water soluble properties of CYLINK NMA it is more difficult to incorporate it into the polymer. The first indication of water-phase polymerization will be an increase in viscosity, but when there is too much water-phase polymerization this will eventually fall out as grit or coagulate on the reactor stirrer. Reduction of the grit formation can be achieved by diluting CYLINK NMA to a 10-20% solution and by using a delayed addition technique. With this technique the CYLINK NMA is added after the reaction has started with only the bulk vinyl acetate monomer present.

Solvents with chain transfer effects can also help in reducing grit by decreasing the amount of water-phase polymerization (see above). More background information on preventing homo-polymerization of CYLINK NMA can be obtained from your local sales manager.

### Formaldehyde release

Although formaldehyde is not considered to be as serious an issue in wood adhesives as for example in Nonwovens, a reduction in formaldehyde release can be obtained by using either CYLINK NBMA/IBMA, or combinations of CYLINK NMA/IBMA or NMA/NBMA. However, even when using CYLINK NBMA and IBMA the formaldehyde released will never be zero. Since crosslinking predominately occurs between NMA moieties and hydroxyl functions from the polyvinyl alcohol and the wood, CYLINK NMA-LF is not expected to yield better results but may reduce the crosslinking strength.

### General recommendations

Most of the properties of a polyvinyl acetate dispersion come from the polyvinyl alcohol used. Polyvinyl alcohol provides good machineability, good creep-resistance, good wet-tack, and most of all the rheological properties required. The choice of polyvinyl alcohol sets the base viscosity of the end product. Because some of our recommendations can have a significant effect on the rheological properties of the dispersion, an adjustment of polyvinyl alcohol type may be required.

A small amount of AEROSOL® OT-75 surfactant can be used to give a more uniform particle size distribution which can have an effect on viscosity, water-phase polymerization or grafting.

Rather than using coalescing agents, occasionally small amounts of other monomers such as ethylene, VEOVA or butyl acrylate are included in the polymerization; Cytec Industries recommends the use of Dioctyl Maleate (CYLINK DOM) as a suitable internal plasticizer, to keep the dried adhesive flexible.

These general recommendations may have slightly different effects when used with other recipes and types of polymerization equipment. You will almost certainly need to fine-tune these recommendations to meet your own requirements.

Here are 3 starter recipes for your consideration:

## Example Recipe I (Bo/A/93B)

POLYMERIZATION OF VINYL ACETATE - CYLINK NMA 48% COPOLYMER

Application: Wood Adhesive

### I. Recipe

	parts per weight
A) Kettle charge	
D. water	150
Airvol 540	7.5
Airvol 205	7.5
paracum v 34/8741 d1	1.0
Vinyl acetate	25
B) Monomer charge	
Vinyl acetate	225
C) NMA charge	
D. water	50
CYLINK NMA 48%	10
Ethanol	5
Sodium bicarbonate	0.6
D) Catalyst charges	
1. D. water	30
Ammonium persulphate	0.375
2. D. water	10
Sodium metabisulphite	0.04

### II. Procedure

- A) Preparation of kettle charge  
Add Airvol 540, Airvol 205 and defoamer to deionized water. Heat to 90°C under stirring and hold at this temperature for 30 minutes to dissolve the Airvol, then cool to 65° C. Place 25 parts vinyl acetate aside for initiation.
- B) Preparation of other charges
  1. Place vinyl acetate in an additional vessel.
  2. Dissolve all NMA charge together and place in an additional vessel.
  3. Dissolve both catalyst charges separately and set aside.
- C) Preparation of latex  
When the contents of the polymerization kettle reach 65° C, add 90% of both catalyst charges followed by 25 parts Vinyl acetate. After initiation and maximum exotherm, start addition of the monomer and NMA charges at a rate of 1.2 and 0.3 parts per minute respectively. Maintain reaction temperature at 70° C during addition by correcting addition speeds. Total addition time should require about 3.5-4 hours. After finishing the additions, add the remaining catalyst charges and hold the batch at 70° C for one hour, then cool to room temperature and filtered into a suitable container.

### III. Results

Solids (%)	51.5
pH	5.22
PS (nm) 1)	227.( 2%)
2)	1,895. (80%)
3)	10,000. (18%)
Visc (mPa.s, #7,20rpm)	28,000
grit 60 # (g)	-
Reactor coat (g)	< 1
grit 200 # (%)	0.1308

### IV. Water spotting

Time	non-cat	1% pTSA cat
10"	5	10
60"	1	9
150"	1	6
Scratch	dissolves	damages

### V. Catalyzed shelf stability

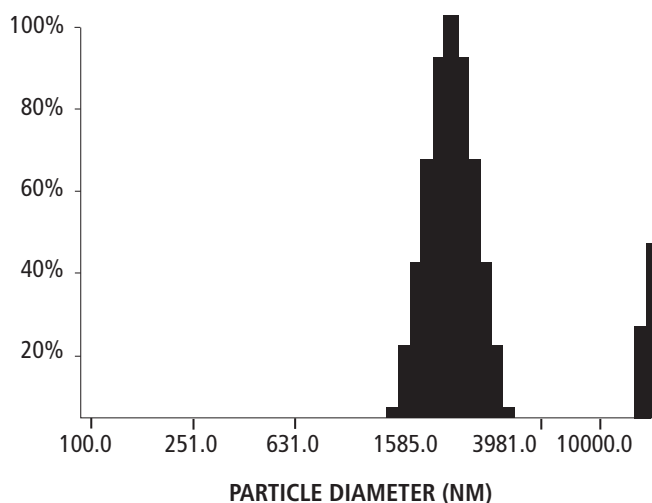
(Latex catalyzed with 5% pTSA)

Time	Viscosity	pH
0 days	8,000	1.4
17 days	90,000	2.1
28 days	106,400	2.4

### VI. Particle Size Distribution

RUN GROUP:	MEAN	S.D.	C.V.(%)	No Runs
MEAN SIZE (NM)	3420	368	11	2
SIZE S.D. (NM)	3850	354	9	2
SIZE C.V. (%)	110	0	0	2
DUST %	8	11	132	2

### SDP DIFFERENTIAL INTENSITY



## Example Recipe II (Bo/A/460)

POLYMERIZATION OF VINYL ACETATE -  
CYLINK IBMA COPOLYMER

Application: Wood Adhesive

### I. Recipe

A) Kettle Charge	Parts per weight
D. water	540
Airvol 205	18
Airvol 540	27
FeCl <sub>3</sub> 1%	2.5
Sodium metabisulphite	1.2
B) Monomer charge	
Vinyl acetate	750
CYLINK IBMA	22.5
C) Catalyst charge	
D. water	195
Ammonium persulphate	1.5
Diammonium phosphate	4.5

### II. Procedure

- Preparation of kettle charge  
Add Airvol 205, Airvol 540, 1% FeCl<sub>3</sub> and sodium metabisulphite to deionized water. Heat to 90° C under stirring and hold at this temperature for 30 minutes to dissolve the Airvol, then cool to 65° C.
- Preparation of monomer charge  
Dissolve CYLINK IBMA in vinyl acetate and place in an addition vessel.
- Preparation of catalyst charge  
Dissolve diammonium phosphate and ammonium persulphate in deionized water and place in an addition vessel.
- Preparation of latex  
When the contents of the polymerization kettle reach 65° C, add 8% of both monomer and catalyst charge. After initiation and maximum exotherm, start addition of the monomer and the catalyst solutions at a rate of 3.2 and 0.8 parts per minute respectively. Maintain 2-3° C exotherm during addition by correcting addition speeds. Total addition time should require about 4 hours. After additions hold at 68° C for half an hour, then cool to room temperature and filter into a suitable container.

### III. Results

Solids (%)	52.9
Theoretical solids (%)	52.8
pH	5.58
PS (nm)	1,836
Visc (mPa.s, #2,20rpm)	36,200
grit 60 # (g)	--
Reactor coat (g)	< 0.5
grit 200 # (%)	< 0.001

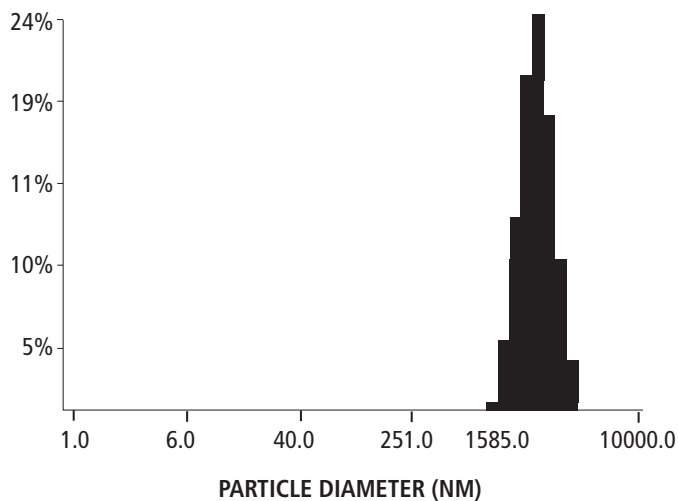
### IV. Water spotting

Time	non-cat	1% pTSA cat
10"	9	10
60"	7	9
150"	5	8
Quality	3	9

### V. Particle Size Distribution

RUN GROUP: 460ang	MEAN	S.D.	C.V.(%)	No RUNS
SDP INTENSITY RESULTS WITH 1 PEAKS				
MEAN SIZE (NM)	1836	184	10	5
SIZE S.D. (NM)	644	388	60	5
SIZE C.V.(%)	34	17	49	5
DUST %	12	12	107	5

### SDP DIFFERENTIAL INTENSITY



## Example Recipe III: (Bo/A/474)

POLYMERIZATION OF VINYL ACETATE -  
CYLINK NMA - CYLINK IBMA TERPOLYMER

Application: Wood Adhesive

### I. Recipe

A) Kettle Charge	Parts per weight
D. water	570
Airvol 325	36.3
AEROSOL OT-75	2.31
FeCl <sub>3</sub> 1%	2.82
SFS	0.825
B) Monomer charge	
Vinyl acetate	825
t-butylhydro peroxide (85%)	2.4
CYLINK IBMA	12.3
C) NMA charge	
D. water	150
Ethanol	16.5
CYLINK NMA 48%	16.5
SFS	2.0
Diammonium phosphate	5.1

### II. Glass Transition Temperature

T<sub>g</sub> is calculated as 31.1° C.

### III. Procedure

- Preparation of kettle charge  
Add Airvol 325, AEROSOL OT-75, 1% FeCl<sub>3</sub> and SFS (Sodium formaldehyde sulphoxylate) to deionized water. Heat to 90° C under stirring and hold at this temperature for 30 minutes to dissolve the Airvol, then cool to 65° C.
- Preparation of monomer charge  
Dissolve t-butyl hydroperoxide and CYLINK IBMA in vinyl acetate and place in an addition vessel.
- Preparation of NMA charge  
Dissolve all in deionized water and place in an addition vessel.
- Preparation of latex  
When the contents of the polymerization kettle reach 65° C, add 8% of both monomer and NMA charge. After initiation and maximum exotherm, start addition of the monomer and the NMA charges at a rate of 3.8 and 0.8 parts per minute respectively. Maintain 2-3° C exotherm during addition by correcting addition speeds. Total addition time should require about 4 hours. After finishing of the additions hold the latex at 68° C for half an hour, then cool to room temperature and filter into a suitable container.

### IV. Results

Solids (%)	53.8
pH	5.73
PS (nm)	1,017
Visc	11,700
(mPa.s, #2,20rpm) grit 60 # (g)	-
Reactor coat (g)	< 0.1
grit 200 # (%)	< 0.01

### V. Water spotting

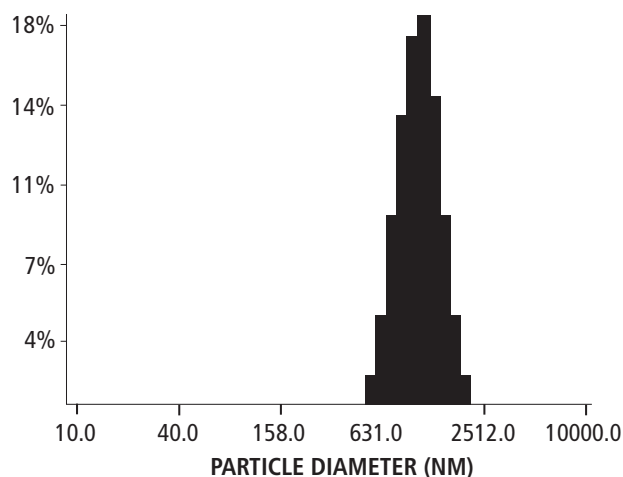
Time	non-cat	1% pTSA cat
10"	9	10
60"	5	10
150"	3	9
Quality:	5	9

(duplicate run)

### VI. Particle Size Distribution

RUN GROUP: 474	MEAN	S.D.	C.V. (%)	No RUNS
MEAN SIZE (NM)	1017	54	5	8
SIZE S.D. (NM)	345	104	30	8
SIZE C.V. (%)	34	8	25	8
DUST %	2	2	76	8

### SDP DIFFERENTIAL INTENSITY



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PRT-823