

A21M-001

## CAPROLACTONE IN ACRYLIC RESINS

$\epsilon$ -caprolactone is a high boiling liquid capable of reacting with resins containing hydroxyl groups, such as polyesters, epoxies and acrylics.

Resins modified in this way can be used to prepare surface coatings, for stoving applications, which offer an outstanding combination of hardness and flexibility.

In addition, Caprolactone modified resins normally offer lower solution viscosities than unmodified resins of similar molecular weight, allowing formulation of systems with higher solids content at any given viscosity.

This data sheet briefly outlines four methods of preparing Caprolactone modified acrylic resins.

It must be emphasised that the methods given are purely based on laboratory experience, and no guarantees are given or implied that they will be effective, without modification, on an industrial scale.

It is for the individual operator of such processes to satisfy himself that the method chosen is suitable for use with his specific resin and in his particular plant.

### 1. INTRODUCTION

$\epsilon$ -Caprolactone is a 7-membered aliphatic ring compound and is the internal ester of hydroxy caproic acid. The product, as supplied by Solvay Interlox Ltd, has the following typical properties:

Boiling point	:	232°C with decomposition
Melting point	:	-1°C
Viscosity	:	6.67 cps at 20°C
Specific gravity	:	1.079 at 20°C
Flash point	:	230°C – 240°C (closed cup)
Refractive index $n_{20}^D$	:	1.4629
Purity	:	99% minimum
Water content	:	0.1% maximum
Acid value	:	<1.0 mg KOH/g

The product is supplied in 200 kg nett drums, or in bulk tankers.

Since the product is hygroscopic and slowly hydrolyses in the presence of water, it should be stored in sealed containers at all times.

## 2. BASIC CHEMISTRY

$\epsilon$ -caprolactone will react with primary or secondary hydroxyl groups, by a ring opening mechanism, to form polyester chains. These polyester chains are always terminated by a primary hydroxyl group and the length of the chain is determined by the ratio of Caprolactone to the hydroxyl groups.

Caprolactone can be used as a partial or complete replacement for the soft Monomer normally used in the manufacture of acrylic resins.

In order to prevent the formation of long Caprolactone chains when modifying resins containing more than one hydroxyl group per mole. IT IS ESSENTIAL TO EMPLOY REACTION TIMES OF GREATER THAN FIVE HOURS.

It should be noted that Caprolactone chains of greater than about three Caprolactone units in length will tend to lead to problems of side chain crystallisation, particularly in common paint solvents and hence lead to poor formulation stability and inferior paint film performance.

It is also essential that all the reactants are dry and that the reaction mixture is free from hydroxylic solvents to prevent side reactions, such as the formation of low molecular weight Caprolactone 'homopolymers'.

Caprolactone Monomer remaining unreacted in the finished resin should be as low as possible and certainly no more than 0.2%, since unreacted Monomer in the applied paint films will lead to poor hydrolysis resistance in the coating.

Resins produced in this way, since they contain primary hydroxyl groups, may be cross-linked with amino resins, such as melamines, benzoguanamine etc. and with isocyanates. The resulting coatings offer an outstanding combination of hardness and flexibility.

These outstanding properties are believed to be due to the very high cross-link density achieved through the primary hydroxyl groups, all of which are on the end of inherently flexible Caprolactone chains.

### 3. PREPARATION OF CAPROLACTONE MODIFIED HYDROXY ACRYLIC RESINS

Four methods of producing Caprolactone modified hydroxy-acrylic resins are described in the following pages. The methods are given in the form of laboratory experiments and are the result of actual experiments carried out in the Solvay Interlox laboratories.

These four methods may be classified as follows:

1. Modification of a preformed styrene-acrylic copolymer, at high temperature (145-150°C).
2. One-stage preparation of a Caprolactone modified styrene-acrylic copolymer.
3. Medium temperature modification of a preformed hydroxy-acrylic resin (125-135°C).
4. Low temperature Caprolactone modification of a preformed hydroxy-acrylic resin (50-60°C).

#### 3.1 Addition of Caprolactone to a preformed styrene-acrylic copolymer (high temperature method)

A 10:1 styrene:2-hydroxy ethyl acrylate copolymer was prepared by the classical route, using xylene as solvent, to give a product with the following characteristics:

Solids content	:	45.8%
Hydroxyl value (on solid resin)	:	48.5 mg KOH/g
Viscosity (40% solution)	:	300 cps at 20°C

Caprolactone was reacted with this polymer, at a level of 3.125 moles of Caprolactone per mole of hydroxyl group, by the following method:

##### Total reactants used:

Copolymer solution (45.8% solids)	:	150g
Xylene	:	17g
$\Sigma$ -caprolactone	:	21.17g
Di-butyl tin dilaurate (DBTL)	:	0.06g

The copolymer solution and xylene were charged to a reactor fitted with a stirrer, thermometer, reflux condenser and nitrogen feed.

The mixture was heated to boiling and the Caprolactone and DBTL added.

This mixture was maintained at reflux, about 145°C, until the free Caprolactone content had fallen to below 0.1%, as determined by gas-liquid chromatography.

The total reaction time required was about 10 hours. The product was a clear yellow solution with the following characteristics:

Solids content	:	47.8%
Hydroxyl value (on solids)	:	37.1 mg KOH/g
Viscosity (40% solution)	:	225 cps at 20°C

A quicker and more controlled reaction could be achieved by replacing the di-butyl tin dilaurate catalyst by stannous octoate, at a level of 50-100 ppm on resin solids. Also, the presence of some acid functionality in the resin tends to have a synergistic effect on catalyst activity and hence increase reaction rate.

Whichever catalyst system is chosen, care must be taken to ensure that the level used is not great enough to reduce reaction times below five hours.

Reaction times in excess of five hours are required to promote even distribution of the Caprolactone amongst the available hydroxyl groups.

### **3.2 Preparation of a Caprolactone-styrene-acrylic copolymer in a one stage reaction**

In this preparation, an acrylic resin similar to that prepared by method 3.1 was prepared by a one stage reaction, in which the acrylic polymerisation and the Caprolactone addition are carried out in a single operation.

The resin produced had properties very similar to those of the resin obtained by the two stage process.

The formulation used was designed to give a resin with a Caprolactone content of 3.125 moles per mole of hydroxyl group and the method was as follows:

#### **Total reactants used:**

Styrene	:	340.7g (3.28 mols)
2-hydroxy ethyl acrylate (HEA)	:	38.2g 0.33 mols)
Xylene	:	500.0g
2:2 azo bis 2-methyl propionitrile (AIBN)	:	1.7g
Stannous octoate (10% in xylene )	:	1.0g
$\epsilon$ -caprolactone	:	122.9g (1.08 mols)

A two litre flask, equipped with a stirrer, thermometer, reflux condenser and nitrogen feed was initially charged 34.1g of styrene, 3.8g HEA and 163.8g xylene.

This mixture was brought to reflux, about 145°C, and 0.66g of AIBN in 18.8g xylene added over 10 minutes, followed by 1g of stannous octoate solution.

The remainder of the Monomer, 306g styrene, 34.4g HEA and 122.9g Caprolactone, were mixed together in 222.8g xylene and 0.66g AIBN added.

This solution was pumped into the reactor, maintaining constant reflux over six hours.

At the end of this addition, a further 0.38g AIBN in 93.9g xylene was added over 15 minutes.

The reaction was continued until the free Caprolactone content, determined by gas-liquid chromatography, had fallen below 0.2%. Total reaction time was 16 hours.

### 3.3 Modification of a preformed acrylic resin at medium temperature

In this method, stannous octoate was used as catalyst, allowing a reaction temperature of 130°C to be used. The starting point acrylic resin had the following properties after having been dried by azeotropic distillation:

Solids content (in xylene/butyl acetate)	:	60%
Hydroxyl value (on resin solids)	:	110 mg KOH/g
Acid value (on resin solids)	:	14.5 mg KOH/g

The level of Caprolactone used in this preparation was 1.35 mols per mole of hydroxyl group.

The method used was as follows:

#### Total reactants used:

Acrylic resin (60% solution)	:	425g
Σ-caprolactone	:	76.95g
Stannous octoate (10% in xylene)	:	0.20g

The reactants were charged to the flask and the temperature raised to 130 °C. This temperature was maintained, with constant stirring, for 5½ hours. By the end of this period, the free Caprolactone content measured by gas-liquid chromatography, had fallen to 0.2%. The resin produced had the following properties:

Solids content	:	66%
Acid value (on resin solids)	:	11.95 mg KOH/g
Hydroxyl value (on resin solids)	:	84.5 mg KOH/g

### 3.4 Modification of a preformed acrylic resin at low temperature

In this method, p-toluene sulphonic acid was used as catalyst, allowing a temperature of 50°C to be used in the reaction.

The resin used was that described in section 3.3.

#### Total reactants used:

Acrylic resin (60% solution)	:	425g
ε-caprolactone	:	76.95g
p-toluene sulphonic acid monohydrate	:	0.1g

The method used was as follows:

The reactants were charged to a reaction flask, equipped with a stirrer, thermometer, reflux condenser and nitrogen inlet.

The mixture was heated to 50°C and maintained at this temperature, with constant stirring, until the free Caprolactone content had fallen below 0.2% as determined by gas-liquid chromatography.

The reaction time required in this case was 6½ hours. The resin produced had the following properties:

Solids content	:	66%
Hydroxyl value (on resin solids)	:	84.5 mg KOH/g
Acid value (on resin solids)	:	15.6 mg KOH/g

It should be noted that the presence of the acid functionality in the resin used in examples 3.3 and 3.4 has a synergistic effect on the catalyst. It would probably not be possible to carry out Caprolactone modifications using the conditions described if the resins used lacked some level of acid functionality.

#### 4. **PROPERTIES OF PAINT FILMS FROM CAPROLACTONE MODIFIED ACRYLIC RESINS**

The changes in properties which may be obtained by modifying acrylic resins with Caprolactone are illustrated by the following figures.

These were obtained from paint films produced from systems produced from the basic styrene acrylic resin described in section 3.1 and from the Caprolactone modified resin produced from it.

Paints were produced from these two resins to the following general formula:

Acrylic resin solution (40% solids)	:	58.2 parts
Hexa methoxy methyl melamine	:	9.9 parts
Titanium dioxide (Tiona RH 472)	:	26.6 parts
Xylene	:	4.1 parts
Catalyst solution*	:	1.2 parts

\*20% p-toluene sulphonic acid in iso propyl alcohol.

The systems as used for the preparation of the test panels had the following characteristics:

Solids content	:	60%
Pigment to binder ratio	:	0.8:1
Acrylic to melamine ratio	:	7:3

The paints were applied, using a standard doctor blade, to give 75 $\mu$  wet films.

The following substrates were used:

Glass, for hardness and gloss measurements.

Polished aluminium, for the mandrel bend test.

Bonderised steel, for reverse impact, chemical and stain resistance tests.

All films were cured at 130°C for 30 minutes. The results obtained were as shown in the following table.

Test	Unmodified resin	Modified resin
Rocker hardness (Sward)	53	48
60° gloss, per cent	110	105
Mandrel bend, inches	3/4	1/16
Reverse impact, inch lbs.	2	160
Chemical resistance:		
5% acetic acid, 24 hours at 25°C	10	9
5% sodium hydroxide, 100 hours at 25°C	10	10
Petrol, 24 hours at 25°C	4	8
Stain resistance:		
Kiwi ox blood polish, 24 hours contact	-	5
Red lipstick, 24 hours contact	-	10

**For further information please contact:**

Perstorp UK Limited  
 Baronet Road  
 Warrington  
 Cheshire WA4 6HB  
 United Kingdom

Telephone: +44 (0) 1925 643210  
 Fax: +44 (0) 1925 232207  
 E-mail: [contact.capa@perstorp.com](mailto:contact.capa@perstorp.com)  
 Website: [www.perstorpcaprolactones.com](http://www.perstorpcaprolactones.com)

The information given in this data sheet is given as a general guide and should not be taken to cover all cases. Each customer should ensure that the product concerned is suitable for the specific purpose and the manner in which it is intended to be used. The information given must not be taken in any way to form a specification. This data sheet does not form part of the Conditions of Sale of our products and is of a general nature.

**FREEDOM FROM PATENT RESTRICTIONS SHOULD NOT BE ASSUMED**