Monsanto
Reg'd

# POLYPHENYLENE RESINS

## A High Heat Resistant Resin System

DATA SHEET - DEVELOPMENT PRODUCT

AUGUST, 1968

### Introduction

A technique has been developed by Monsanto for the preparation of polyphenylenes - a thermo-oxidatively stable polymeric system that can be reinforced with fibres to yield useful composites.

This data sheet gives information on the polyphenylene prepolymer 1711 which is the basic component for crosslinking or chain extension and leading to high molecular weight, infusible polyphenylene resin. The method of crosslinking using PP Curing Agent B1 is described along with information on the fabrication of composites from asbestos and high modulus carbon fibre. Properties of laminates made in the laboratory are given.



Monsanto 10-18 Victoria Street London SW1 01-222 5678
1 Place Madou Brussels 3 02-19.11.01
9 Rue d'Argenson Paris (8) 265.65.20

0120924

## PROPERTIES OF POLYPHENYLENE PREPOLYMER 1711
(Typical)

### Physical

| | | |
|---|---|---|
| Description | - | A mixture of low molecular weight polyphenylenes |
| Form | - | Solid (coarse powder) |
| Colour | - | Dark Brown |
| Softening Range | - | 133 - 175°C |
| Boiling Point | - | above 400°C |
| Specific Gravity 25°C | - | 1.17 |
| Solubility (gm/100 ml solvent) | - | |

| Solvent | At Reflux Temp. | At 25°C |
|---|---|---|
| Diphenyl Ether | 150 | 30 |
| Toluene | 140 | 40 |
| Chlorobenzene | 130 | 50 |
| 1, 2 Dichloroethane | 100 | 45 |
| Benzene | 85 | 35 |
| Chloroform | 85 | 50 |
| Dimethyl Formamide | 20 | 5 |
| Water<br>Ethanol<br>Petroleum Ether | ) Insoluble | |

### Functional

The propolymer crosslinks with PP Curing Agent B1 when heated to above 275°C and this may be done in the presence of a fibre support to yield composite structures.

## POLYPHENYLENE/ASBESTOS LAMINATES

The following procedure is recommended when using chrysotile asbestos felts:

### Impregnating Solution

This is prepared from:

| | |
|---|---|
| Polyphenylene Prepolymer 1711 | 260 gm |
| PP Curing Agent B1 | 140 gm |
| PP Catalyst C30 | 0.22 ml |
| Chlorinated aliphatic hydrocarbon solvent | 2000 ml |

With chloroform as solvent, a 17.5% w/v solution is obtained of density 1.45 gm/ml at 25°C. Solution of the prepolymer is readily achieved if the powder is stirred slowly into the warmed solvent.

### Asbestos Composite Fabrication

The asbestos felt contained in a suitable tray is completely saturated with impregnating solution. After lightly rolling, the felt is placed on a stainless steel mesh to dry either at room temperature under vacuum or at 50°C.

### Pre-Pressing

The felts are placed between two sheets of 5 thou aluminium foil that have already been sprayed with PTFE release agent. A pre-press treatment of 500 - 1000 p.s.i. at 130°-140°C for 5 minutes is optional but does assist the processing at the next stage.

### Pressing Stage

Using a well ventilated press and with its platten temperature at 310°C, the impregnated felts are inserted and kept under a slight positive pressure to ensure maximum heat transfer. This condition is maintained for 6 minutes in the case of a 12" x 12" x 1/8" board, during which time dry $SO_2$ and HCl gases are evolved. Then full pressure in the range of 500-1000 p.s.i. is applied. Pressure is released three times at 3 minute intervals. Pressing is complete after 4 hours and the laminate ejected when the temperature drops to 100°C whilst maintaining pressure.

Post-Cure

The following schedule is recommended for post-curing the laminate

| | |
|---|---|
| 275°C | 24 hours |
| 300°C | 24 hours |
| 325°C | 24 hours |

Total loss due to cure volatiles estimated on the original weight of resin solids is approximately 25%.

For other forms of asbestos, e.g. flock, woven fabric the same general procedure will be applicable but the solids level of the impregnating solution may need adjustment.

## PROPERTIES OF THE P. P./ASBESTOS LAMINATE

Using chrysotile asbestos the following laminate properties were obtained in the laboratory. The values quoted are typical.

| | |
|---|---|
| Resin content (w/w%) | 50 ± 2 |
| Specific Gravity | 1.4 - 1.7 |
| Flexural Strength* (psi) | |
| Initial 25°C | 30 - 37,000 |
| 300°C | 25 - 30,000 |
| Flexural Modulus* (psi) | 1.8 - 2.5 x $10^6$ |
| Tensile Strength** (psi) | |
| Initial 25°C | 20 - 27,000 |
| 200°C | 15 - 20,000 |
| 300°C | 10 - 14,000 |

Ageing Life

(Time taken for flex strength to fall below 5,000 p s i)

| | |
|---|---|
| At 200°C | 6 - 12 years (by extrapolation) |
| 240°C | 7000 - 15,000 hours |
| 300°C | 1,000 - 1,500 hrs. |
| 350°C | 200 - 400 hrs. |
| 400°C | 30-150 hrs. |

Chemical Resistance

Initial results have shown good hydrolytic and solvent resistance. (Further work is in progress on more resistant supports).

* ASTM D790-66
** ASTM D638-64T

## POLYPHENYLENE/HIGH MODULUS CARBON FIBRE COMPOSITES

For the preparation of carbon fibre composites a mould is used and the time in press before application of pressure is dependent on the size of the mould. The impregnating solution should be 20-25% w/v, but otherwise the procedure for fabrication is essentially that used for asbestos.

Certain properties of the composite are affected by various surface treatments of the fibre, as illustrated in the following table:

### PROPERTIES

| | Untreated Fibre | Treated Fibre |
|---|---|---|
| Resin Content (w/w%) | 30 - 50 | 30 - 50 |
| Specific Gravity | 1.3 - 1.5 | 1.4 - 1.5 |
| Flexural Strength* (psi) | | |
| Initial 25°C | 50 - 80,000 | 80 - 116,000 |
| 240°C | 40 - 55,000 | |
| Flexural Modulus** (psi) | 12 - 13 x $10^6$ | 12 - 17 x $10^6$ (max. value found 23 x $10^6$) |
| Ageing Life | Similar to asbestos | |

* ASTM D790-66

** ASTM D638-64T



Monsanto

0120929

Chemical Resistance

The following results on polyphenylene/carbon fibre (untreated) composites were obtained after 2,000 hours unless otherwise stated.

| Environment | Test Temp. °C | Flexural Strength PSI (Cold) | | Weight Loss % | Dimensional Change % |
|---|---|---|---|---|---|
| | | Initial | Final | | |
| $H_2SO_4$ (Conc.) | R. T. | 67,300 | 70,300 | Nil | Nil |
| | 90°C | 59,700 | 60,900 | Slight increase | Nil |
| $H_2SO_4$ (50% w/w) | R. T. | 67,300 | 63,300 | Nil | Nil |
| | 90°C | 59,700 | 57,700 | Nil | Nil |
| $HNO_3$ (Conc.) | 90°C | 59,700 | Nil | After 696 hrs. sample swollen but had some strength. After 1784 hrs strength less than 3,000 psi. | |
| $HNO_3$ (50% w/w) | R. T. | 67,300 | 62,200 | | Swelling at ends |
| | 90°C | 59,700 | 24,300 | + 12.7 | + 2.6 |
| HCl (Conc.) | 90°C | 59,700 | 58,600 | Nil | Nil |
| HCl (7.5% w/w) | 90°C | 57,800 | 64,800 | Nil | Nil |
| HF (40% w/w) | R. T. | 67,300 | 67,100 | Nil | Nil |
| NaOH (75% w/w) | 90°C | 57,800 | 64,200 | Nil | Nil |
| NaOH (50% w/w) | R. T. | 67,300 | 71,700 | Nil | Nil |
| NaOH (20% w/w) | 90°C | 57,800 | 67,500 | Nil | Nil |
| NaCl (20% w/w) | R. T. | 67,300 | 74,100 | Nil | Nil |
| NaOCl (15.6% w/w) | R. T. | 67,300 | 63,900 | Nil | Nil |
| $H_2O_2$ (100 vol.) | R. T. | 67,300 | 72,700 | Nil | Nil |
| D. M. F. | 90°C | 57,800 | 49,100 | Nil | -1.0 |
| Pyridine | 90°C | 57,800 | 17,000 After 288 hrs. | No change after drying | Very Swollen |

Effect of Steam and Boiling Water

| | | | | | |
|---|---|---|---|---|---|
| Steam | 100°C | 67,300 | 65,000 | Nil | Nil |
| Boiling Water | 100°C | 64,000 | 63,100 | Nil | Nil |

The pure resin shows good resistance to conc. HCl, $H_2SO_4$ and pyridine after 2,000 hrs. at 90°C. Elemental analysis showed that the resin was essentially unchanged. Treatment with conc. $HNO_3$ however results in nitration of the resin.

## Storage and Handling

The impregnating solution made up of Polyphenylene Prepolymer 1171, PP Curing Agent B1 and Catalyst C30 is best stored in a cool place. Storage life can be increased by refrigerated storage. The Prepolymer 1171 is stable in the solid state and in solvent. Curing Agent B1 is stable in the solid state if kept dry, but in solution containing alcohol, it slowly releases HCl. Catalyst C30 contains alcohol solvent and is stable. All solutions should preferably be contained in glass lined vessels especially if long storage times are involved.

When handling this resin system the normal precautions should be taken regarding the use of protective clothing, eye shields, etc. During the curing operation, volatile products are released, and these are dry $SO_2$ and HCl gases plus solvent. Mechanical exhaust ventilation should be associated with the press so as to vent these vapours to the external atmosphere.

## Patents

Monsanto have British Patent No. 1,037,111 and other patents and patent applications covering the polyphenylene resins and their production in the United Kingdom and other countries.