however, precipitation occurred as a result of acid-induced self-condensation. In contrast, if the sulphite levels were too low, there was insufficient sulphite to effect the opening of the heterocyclic ring structure, which could decrease the molecular weight and result in the solubilising of the phlobaphenes. Twenty percent sulphite was taken as the optimum value since it was the lowest value of sulphite to result in solubilisation without precipitation. A higher value of sulphite was not used despite the fact that 40% sulphite also resulted in complete solubilisation. This, because of the adverse effects excessive sulphite have on the water resistance of adhesives formulated from the redissolved phlobaphenes, as observed during the gelation of the 60% sulphite solution (cf 3.2.4 b). Thus the balance between the solubilising and self-condensing effects of the sulphite was demonstrated to be very delicate.

### 3.2.5 Temperature effects on phlobaphene solubilisation

When small quantities of phlobaphenes were redissolved, the use of reflux conditions did not appear to be disadvantageous (cf 5.10.1). On increasing the mass of phlobaphenes to be redissolved, the use of reflux conditions caused severe precipitation to be incurred. The larger quantity of phlobaphenes was more efficient in retaining the heat applied to the solution. This resulted in an increase in temperature induced auto-condensation. The increased temperature also facilitated the acidic effects of the sulphite in becoming more important resulting in phlobaphene precipitation.

In an attempt to decrease the temperature effect, the temperature for the solubilisation was lowered to 60°C (cf 5.10.6). This was successful in preventing precipitation when the total wet phlobaphene mass did not exceed 200g. Samples of greater mass experienced heat retention effects and precipitation was again incurred. In an attempt to prevent precipitation regardless of sample mass, no heat was applied during the solubilisation process (cf 5.10.6). This was successful in inhibiting phlobaphene precipitation and was the process used for all solubilisation of phlobaphenes for adhesives.

### 3.2.6 Other physical and mechanical effects on phlobaphene solubilisation

a) Stirring

The efficiency of the agitation of the solution was important in the effectiveness of the redissolution process. When small quantities of phlobaphenes were redissolved, magnetic stirring was found to be sufficient. Solubilisation of masses of phlobaphenes greater than 50g required greater stirring, achieved with the use of an overhead stirrer. The maximum speed of this stirrer was 500rpm. This was too slow for quantities greater than 700g of phlobaphenes. Very high speed stirring was found to be efficient in the solubilisation of large quantities of phlobaphenes, where speeds up to 4000rpm were successfully employed.

b) Phlobaphene colour

The colour of the phlobaphenes varied with the amount of hydrochloric acid added to the initial tannin solution. The phlobaphenes varied between pale shades of pink-red and dark black-red. Although it was difficult to establish the exact acid concentration required to achieve a particular colour, it was noted that higher volumes of acid generally resulted in paler phlobaphene precipitates. These phlobaphenes probably consisted of lower molecular weight fractions since a large number of acid molecules would, simultaneously induced auto-condensation and thereafter, phlobaphene precipitation. The lower molecular weight of the fractions would explain the paler colour observed, since fewer chromophores would be found in each molecule.

The darker precipitates were generally formed when a smaller volume of acid or a higher tannin concentration were employed.

In both cases, the precipitates were found to darken during their filtration and pressing. This was due to oxidation of the precipitates and the increase of molecular weight during exposure to air.[28]

### 3.2.7 Phlobaphene solubilisation balance

During the investigations into the redissolution of pine tannin phlobaphenes, it was observed that a fine balance seemed to exist between their solubilisation and precipitation. It appeared that as soon as a small quantity of phlobaphenes precipitated after

redissolution, that a balance or equilibrium had been disturbed. This resulted in more phlobaphenes precipitating than expected.
The balance could be due to the effects of the solubilising hydroxyl groups in opposition to the precipitation effects of the hydrophobic flavan heterocyclic ring.
This can be represented as an equilibrium:

OH vs flavan heterocyclic ring
(water soluble) (water insoluble)
solubility $\rightleftharpoons$ precipitation

If the precipitation of phlobaphenes was induced, the equilibrium shifted in the direction of further precipitation.

solubility $\leftarrow\!\!\dashrightarrow$ precipitation

### 3.2.8 High molecular weight phlobaphene formation

Occasionally and seemingly at random, a very thick, viscous solution of phlobaphenes formed during the solubilisation of the tannin phlobaphenes, using ethanol/water and 20% sodium sulphite (cf 5.10.7). The high molecular weight phlobaphenes formed were generally found in an extremely dilute, pale solution of phlobaphenes. In order to establish that the high molecular weight phlobaphenes were indeed a solution of phlobaphenes and not an agglutinated precipitate, the high molecular weight phlobaphenes were carefully diluted with water. If the high molecular weight phlobaphenes had been a precipitate, on the addition of water, the agglutination would have been decreased and a precipitate would have become noticeable. However, on the addition of water, the high molecular weight phlobaphenes were diluted until a solution similar to a "normal" phlobaphene solution was formed. This indicated that the high molecular weight phlobaphenes were a solution of phlobaphenes which contained the phlobaphenes in a very high percentage solids.

The formation of high molecular weight phlobaphenes seemed to occur at random although they were probably dependent on the formation of phlobaphenes from the acidic tannin solution.

From their appearance, high molecular weight phlobaphenes were thought to have a higher molecular weight than the average phlobaphene solution. This was confirmed during adhesive studies (cf 5.12.5).

In comparison with the ten to twelve week shelf-life of a "normal" phlobaphene solution, the shelf-life of high molecular weight phlobaphenes was established to be approximately four weeks. This time was doubled if approximately 25% phlobaphenes solution (40%), was thoroughly mixed into the solution.

## 3.3 Gelation Time Studies

The reactivity of the phlobaphenes as adhesive components was established with the aid of gelation time studies (cf 5.11).

### 3.3.1 Boiling temperature effect

The time taken for the formaldehyde-phlobaphene mixture to gel is dependent on the temperature of the boiling water bath in which the samples are placed for timing. The boiling temperature of the bath affected the gel time quite markedly.

When the water bath, in a strong extraction cupboard, was boiling gently ($90^oC$), the gel time of a sample of pH=2.72 was 218 seconds. On boiling more rapidly ($92^oC$), the same sample gelled in 192 seconds. Thus, a 12% difference in gel time was experienced for a $2^oC$ temperature change. The low boiling points were due to the lower pressure experienced in the extraction cupboard. From the gel time variation observed over the two degree temperature change it can be deduced that if the samples had been gelled in a $100^oC$ environment, the gel times would have been noticeably shorter than were observed. If the difference between gel times remains constant at 10% for every two degree change, at $100^oC$ the gel time would have been 126 seconds. If the difference between gel times averaged at 5% then at $100^oC$ the gelation time would have been 156 seconds. From these two hypothesised examples it can be seen that at $100^oC$ the gelation time is much shorter than that experienced at $92^oC$. (Table 3.3.1, figure 3.3.1).

### 3.3.2 Effect of pH on the gelation time of phlobaphene samples

The phlobaphene solutions used were initially at an extremely low pH due to their formation from acid-precipitated phlobaphenes. In order to examine the effects of pH on the gelation time, the pH of a solution of phlobaphenes was increased using a concentrated sodium hydroxide solution (40%) (*cf* 5.11).

a) Gel times of a 35% phlobaphene solution

Using a 35% solids phlobaphene solution, the longest gel time or region of lowest reactivity was found to be at approximately pH 1.67, gel time = 134 seconds. (Table 3.3.2, figure 3.3.2) As the pH was further increased, the gel time decreased. This indicated that the phlobaphenes were becoming more reactive with paraformaldehyde. The natural pine tannin pH region is pH=3.5. This generally corresponds to the pH of minimum reactivity of the pine tannins. From this, it could be deduced that the natural pH of the phlobaphenes appeared to be lower than that of pine tannins, in the region of pH=1.7.

b) Gel times of a 40% phlobaphene solution

When a 40% solution of phlobaphenes was used in the gel time studies, different gel times were obtained. (Table 3.3.3, figure 3.3.2). The pH representing the minimum reactivity of phlobaphenes was 2.6. The increase in the pH for the minimum reactivity could possibly be due to variations in the preparation of the different samples of phlobaphenes used in the gelation studies. Another explanation could be the variation in the phlobaphene concentration causing an unexpected internal pH effect. This is likely to be the case, since the 35% and the 40% solutions experienced the same initial pH. At the point of minimum reactivity, the gel time was measured as 131 seconds. This was almost the same as that gel time observed for the 35% solution. An interesting observation was that a second peak

of minimum reactivity existed at pH 3.4 (133 seconds). This pH corresponded to any tannin-like fractions present in the solution, probably formed as a result of the sulphite-cleaving action on the phlobaphenes during their redissolution.
The presence of both points of minimum reactivity allowed the possibility of formulating phlobaphene adhesives in one of two pH regions, namely: 2.6 and 3.5, since both of these regions would allow reasonable pot lives and, under thermosetting conditions, a proper gel time.

c) Gel times of a 48% phlobaphene solution

The use of a more concentrated phlobaphene solution, 48%, resulted in slight variations in the gel times experienced. The first pH of minimum reactivity, 2.3, corresponded to the phlobaphenes when the three experiments were compared (figure 3.3.2). A lower gel time of 99 seconds was noted. (Table 3.3.4, figure 3.3.2). The shorter gel time may have been due to the higher concentration of phlobaphenes per solution volume, since the rate equation for adhesion generally follows the equation:

$$r = k*[\text{phenolic groups}].$$

This was further validated by the gelling of the phlobaphene - paraformaldehyde system at room temperature above pH 3.6. This implied that the phlobaphenes were sufficiently reactive and in a high enough concentration at this pH to gel spontaneously. On the addition of heat, the phlobaphene gel melted and a boiling point gel time was also obtained.

A second peak of minimum reactivity was noted at pH 3, corresponding to the pine tannin region. Both pH values for the minimum reactivity were slight variations on those obtained for the 40% solution. This could be attributed to variations in the preparation of the phlobaphene solution or to slight variations in the concentrations of sodium hydroxide employed. In addition, the effect of the boiling temperature on the gel time may have contributed to the variations in the gel times and pHs noted (cf 3.3.1).

The pH influences on the gel times and the positions of minimum reactivity, in each case, seemed to indicate that the pH influenced the phlobaphene structure. The variations in structure were possibly related to reactions between the hydroxyl groups and the surrounding aqueous medium. In addition, the pH would have caused variations in the chemical form of the hydroxyl groups from the acidic $-H_3O^+$ to the more alkaline deprotonated $-O^-$[15]. The presence of these variants would have caused effects similar to the acid and alkaline induced condensations although it is likely that these effects would not be experienced by every molecule within the solution and that the extent of the changes would be small. This was noted in the relatively small variations in gel times between the three different phlobaphene concentrations.
The pH of minimum reactivity for the phlobaphenes was lower than for natural pine tannins. This could be attributed to at least one of several factors. The increased molecular weight of the phlobaphenes would

allow them to gel quickly in the presence of formaldehyde, since a small number of methylene cross-links formed with the formaldehyde would cause them to gel. At low pH, the sulphite effect in modifying the structure, would cause the phlobaphenes to remain more soluble and therefore require a longer time to gel. This then could explain the lower pH at which the minimum reactivity was experienced. Another possibility is that at the high temperatures used in gelling, the interflavonoid bond may be cleaved[33]. This cleavage would result in new pH dependent compounds which would affect the gelation time at a particular pH.

## 3.4 Thermosetting Adhesives Tested on Beech Strips

In order to reduce the variable effects of the beech strip preparation, gluing and oven moisture content and temperature variations, a control series of beech strips was prepared with each series tested. The control consisted of beech strips glued with an exterior wattle adhesive (commercially prepared) and 15% (by mass of glue solids) paraformaldehyde (cf 5.12.3, 5.12.1). The tensile strengths (cf 5.12.2) obtained for the wattle-glued strips from each series were averaged. This average value was used to standardise the tensile strengths obtained for each gluing series. These standardised values are compared and discussed below.
Despite the lack of accepted SABS tensile strength standards for thermosetting adhesives on beech strips, beech strips were used because they allowed rapid scanning of potential exterior grade particle board

adhesives. The selection of acceptably strong glues was made by comparing the values obtained with the known exterior grade commercial wattle adhesive which was had been tested on beech strips.

### 3.4.1 Adhesives prepared with no fortifier

The average tensile strength obtained for the commercially available exterior grade wattle adhesive was 2710N (40% wood failure) when the beech strips were tested dry and after they had cooled to room temperature. This strength was used throughout as a comparative value to which the other adhesives were compared. (table 3.4.2)

a) Phlobaphenes at pH = 0

In the first series, the pH of the phlobaphenes was unaltered (pH=0) (cf 5.12.4, table 3.4.1, 1.2). From the dry tensile strength (750N), this was seen to be substantially weaker than the wattle control. (table 3.4.2, 1.1 and 1.2). This weakness could be attributed to the extremely low pH, which was unlikely to be encountered industrially due to the method of preparing the phlobaphenes. Another reason for the weakness of the phlobaphene adhesive may be attributed to the high percentage of sulphite present in the phlobaphenes, as required for their redissolution. This was more noticeable from the water based tensile tests of boiling the strips for six hours or soaking them for twenty-four hours (cf 5.12.2). The strength of the strips after boiling was 540 N compared with the control

value of 1566N. Similarly, the soaked strips only had a strength of 620N compared with 1904N for the wattle control. (table 3.4.2, 1.1 and 1.2).
The low strengths after the water tests confirmed that the high presence of sulphite did cause tremendous weakening of the adhesive. This occurred due to the hydrophilicity of the sulphite groups, which having attracted the water then dissolved in it resulting in a weakened glueline.

b) Phlobaphenes at pH = 3.5
The pH of the phlobaphenes was increased to 3.5 to observe the effects of increasing the pH on the adhesive properties of the phlobaphenes. A problem encountered was that on increasing the pH, agglutination of the phlobaphenes was observed. This agglutination appeared to occur as a result of too rapid addition of the sodium hydroxide, inefficient stirring of the solution to minimise localised pH changes and a temperature increase experienced. Eventually, these effects were identified and minimised by overhead stirring, dropwise addition of the base and placing the phlobaphene solution in an ice-bath to minimise temperature increases.
The phlobaphene solution used in the preparation of the adhesive at pH 3.5 was slightly agglutinated (*cf* 5.12.4, table 3.4.1). The dry strength of the strips was 941N, 35% of the strength obtained with the wattle adhesive. (table 3.4.2, 1.3). However, this was 25% higher than the value obtained at the lower pH. The higher pH was used preferentially in further tests since

this was thought to be the more likely region of natural phlobaphenes (cf 3.3.2). The six hour boil revealed that the sulphite present in the phobaphenes had resulted in extreme bond weakening since the strength decreased to 398N. This was lower than the strength obtained using the lower pH phlobaphenes. This decrease in strength could be attributed to the effect of the agglutination of the phlobaphenes. Agglutination of the phlobaphenes apparently caused a form of polymerisation or cross linking between the phlobaphenes. This led to a probable increase in molecular weight probably causing an increase in the glue strength. However, the increased molecular weight of the phlobaphenes would also imply a lower degree of paraformaldehyde induced cross-linking. This so, since the exponential increase in weight with cross-linking would cause more rapid precipitation of the cross-linked phlobaphenes before sufficient strength had been obtained. Thus, whilst the glue may have appeared reasonably strong whilst dry, under the wet conditions of boiling and soaking the adhesive would be noticeably weaker than expected. This was observed in the decreased strength after boiling (398N) and after twenty-four hours soaking in cold water (544N) (cf table 3.4.2, 1.3).

c) Higher molecular weight phlobaphene glue

A high molecular weight solution of phlobaphenes was tested in the same adhesive formulation as the normal phlobaphenes. The pH of the higher molecular weight phlobaphenes was carefully

increased to 3.2 before the preparation of the formulation (cf 5.12.5, table 3.4.1). The dry strength of the higher molecular weight phlobaphenes was 2434N. . This increase in the strength was mainly attributed to the natural and unforced increase in the molecular weight during the solubilisation of the phlobaphenes and not as a result of the addition of the sodium hydroxide. It appeared that the sulphitation effects in the higher molecular weight phlobaphenes were less noticeable since, despite the same redissolution conditions as the standard phlobaphenes, the water effects on the adhesive were less marked. Tensile strengths of 1210N (boil) and 1245N (soak) were obtained (table 3.4.2, 1.4). In addition, the wood failure was noticeable, if slight, compared with a lack of wood failure in the standard phlobaphenes at a similar pH. This indicated that the adhesive formulated from the high molecular weight phlobaphenes had greater adhesion than that composed from the standard phlobaphenes. Thus, the use of higher molecular weight phlobaphenes with no fortification appeared to give adhesives of acceptable strength. The only problem foreseen was the erratic and ill-defined conditions under which higher molecular weight phlobaphenes formed in preference to normal phlobaphenes.
Since the formation of higher molecular weight phlobaphenes could not be depended upon, fortification of the standard phlobaphene mixture was investigated.

d) Pine tannin adhesives without fortifiers

A pine tannin adhesive was prepared using the same formulation as used for the higher molecular weight phlobaphenes, phlobaphene and control adhesives (cf 5.12.6, table 3.4.1). The strength of the pine tannin adhesive was lower than that obtained using the wattle control, as well as being lower than the higher molecular weight phlobaphenes glue. (table 3.4.2, 1.5). A dry tensile strength of 1297N was obtained whilst values of 747N (boil) and 635N (soak) were also obtained. The lower value for the dry strength of the pine tannin compared with that of the higher molecular weight phlobaphenes could be attributed to the higher molecular weight of the latter. In the case of the weathering tests, the pine tannin adhesive favoured less well compared with the higher molecular weight phlobaphenes. This so since the pine tannin used was the "sulphited" pine tannin which contained approximately 5% sodium sulphite, possibly more sulphite than that retained in the solution during the formation of the high molecular weight phlobaphenes. The presence of the sulphite caused an increase in the water attack susceptibility of the cured pine tannin adhesive and, thereby, an increased potential for water attack on the various cross-linking bonds in the adhesive.

In all the comparisons with the wattle control adhesive it must be remembered that the wattle adhesive had been fully optimised prior to commercialisation. In contrast, the formulations based on phlobaphenes were scanning formulations with the aim of establishing the most likely successful exterior formulation. The phlobaphene formulations have not, as yet, been optimised.

### 3.4.2 Phlobaphene adhesive formulations using a fortifier - polymeric 4,4' diphenylmethane diisocyanate (MDI)

Fortification of the phlobaphene adhesives was seen to be essential after the low tensile strengths of the non-fortified adhesives were observed. A diisocyanate was selected as the fortifier for the phlobaphene adhesives. In particular, polymeric MDI or 4,4'-diphenylmethane diisocyanate was used. This was added to the formulation in an emulsified form for ease of application, since MDI is a solid.

The possible reactions in which the MDI partook are several. In general, diisocyanates react with polyols forming polyurethanes.

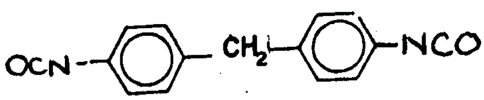


Figure 3.2 Diagrammatic representation of the structure of MDI

The reactions can be represented as:

| | | | | |
|---|---|---|---|---|
| MDI | + | polyol | = | polyurethane |
| OCN-R-NCO | + | R'-OH | = | OCN-R-NH-CO-OR' |

In the case of phlobaphenes, these can be considered to be the polyols since they contain numerous reactive alcoholic functionalities on both the phenolic rings and on the heterocyclic ring.

MDI also reacts with water, forming polyureas and carbon dioxide. This reaction could be observed to be occurring by the foaming or bubbling of the adhesive formulations after reaction at $90^{o}C$ at 12% emc (equilibrium moisture content).

| | | | | |
|---|---|---|---|---|
| MDI | + | water | = | polyureas |
| 2*OCN-R-NCO | + | $H_2O$ | = | OCN-$[R\text{-}NH\text{-}CO\text{-}NH\text{-}]_n$R-N CO+ $nCO_2$ |

In addition, the diisocyanate could react with the -OH functional groups of the carbohydrates and lignin present on the surface of the wood itself. This reaction is depicted below:

| | | | | |
|---|---|---|---|---|
| wood-]-OH | + | MDI | = | wood-]-O-CO-NH-R-NCO |

Further reaction would see the diisocyanate link the two wood surfaces to each other in the formation of a cross-link.

The reactions of the diisocyanate with the various components of the glue-mix would occur in conjunction with the reaction between the paraformaldehyde and the phlobaphenes themselves. The increase in the number of cross-linking reactions would result in increased gelling of the adhesive and thereby, an increase in the physical strength of the glue.

a) <u>30:70 MDI:phlobaphene glue-mix</u>

Using a 30:70 ratio of the MDI to phlobaphenes (*cf* 5.12.4, table 3.4.1, 2.1), a great increase in strength was observed. The dry tensile strength increased by 69% to 1590N. (Table 3.4.2, 2.1). This increase in strength was directly attributable to the presence of the MDI. This demonstrated that the polyurethane formation was important in effectively increasing the adhesive strength. The effect of water on decreasing the adhesion was also minimised. After boiling, the strength had decreased by 33% compared with the wattle control, to 1076N. This, in comparison with the 58% decrease in strength on boiling when no MDI was present.

This demonstrated that the MDI bonded strongly with the phlobaphenes by cross-linking them further. This probably resulted in smaller intermolecular spaces in addition to the increased bond-strength. Both of these could explain the decrease in the observable sulphite-water effect. After soaking the beech strips, the tensile strength had only decreased by 30% to 1114N. Once again, the effect of the MDI in minimising the bond breakage due to water effects, was highly noticeable.

b) <u>20:80 MDI:phlobaphene formulation</u>

The effects of decreasing the proportion of MDI in the formulation were examined by decreasing the percentage of MDI by 40% (*cf* 5.12.4, table 3.4.1, 2.2). The dry tensile strength decreased slightly as the MDI was decreased. A value of 1297N was obtained, 18% less than that obtained with the 30:70 formulation. (Table 3.4.2, 2.2). This decrease in strength continued in the case of the boil and soak tests. In the case of the six hour boil, a tensile strength of 746N was obtained. This was 30% less than the strength obtained using the 30:70 formulation. The decreased strength was due to the increasing effect of the sulphite being exerted during the weathering tests. A similar decrease in strength of 33% was noted after the twenty-four hour soak, where the strength was 743N for the 20:80 formulation compared with 1114N for the 30:70 mix. From the two accelerated weathering tests, the effect of decreasing the MDI could be seen to effect a decreased adhesive strength.

c) 10:90 MDI:phlobaphene formulation

A further decrease in the quantity of MDI in the glue-mix was expected to afford a further decrease in the strength of the adhesion. However, this was not observed. When the proportion of MDI was decreased to a 10:90 ratio with the phlobaphenes (cf 5.12.4, 3.4.1, 2.3), the strength observed was remarkably similar to the strengths observed with the 20:80 formulation. The dry tensile strength increased slightly, to 1359N. (Table 3.4.2, 2.3). This was equivalent to a 5% increase in the tensile strength. This increase was however, not significant since 5% variations could be attributable to experimental errors. These could include the preparation of the adhesive, its spreading on the beech strips and variations in

the clamping pressure. The strength obtained after boiling was equivalent in the two formulations, whilst a 30% increase in the strength after soaking was experienced in the 10:90 formulation. A value of 969N was obtained, compared with 743N for the 20:80 formulation.
The increase in strength on decreasing the MDI could be due to experimental errors. However, it appeared possible that a plateau region existed at the start of the use of MDI where the strength was increased from the non-fortified situation quite markedly, (by approximately 40%), but remained almost constant until the MDI had reached a certain concentration. At this point, which from the experiments was in the region of the 30:70 ratio, the strength of both the dry and weathered strips increased.

d) 35:65 MDI:phlobaphene formulation

On increasing the ratio of MDI slightly further (cf 5.12.4, table 3.4.1, 2.6), the tensile strength was similar to that obtained when a 10:90 ratio was employed (table 3.4.2, 2.6). This seemed to indicate that an optimum of MDI of around 30:70 was observed with decreases in strength noted when the MDI was either increased or decreased.
On increasing the MDI to 35:65, the phlobaphenes became supersaturated with the MDI and the strength decreased. It was noted, that whilst the dry tensile strength decreased to 1351N from the optimal strength of 1590N, the weathering tests yielded smaller decreases in strength, especially

when compared with the decline in strength noted for the water-based tests for the 10:90 and 20:80 formulations. The higher values of 1138N (boil) and 1168N (soak) indicated that although beyond the optimal quantity of MDI, the high percentage of MDI minimises the water-induced strength loss due to the sulphite groups.

e) <u>Non-granulated phlobaphene / MDI formulation</u>

In each of the phlobaphene formulations studied thus far, the phlobaphenes at a pH of between 3.0 and 3.5 had been slightly granulated due to the addition of the sodium hydroxide causing alkaline induced condensation. In one case, (<u>cf</u> 5.12.4, table 3.4.1, 2.7), the pH was increased with extreme caution and care was taken to prevent any temperature increases on the addition of the base. This resulted in phlobaphenes in which absolutely no agglutination was noted. In a 30:70 formulation with MDI, these non-agglutinated phlobaphenes proved very strong in comparison with the agglutinated phlobaphenes. The dry tensile strength was measured at 2040N (table 3.4.2, 2.7), almost 30% higher than the strength obtained for the same formulation where agglutinated phlobaphenes had been used. This indicated that whilst increasing the pH, any temperature increase caused agglutination. This agglutination reduced the phenolic groups present in the molecules, thereby decreasing the potential reaction between the phlobaphenes and the MDI. The care taken to minimise the temperature rise, thereby minimising the reactivity of the base induced agglutination, resulted in greater potential points for reaction with the MDI and resulted in greater strength of the formulation. After experiencing a six hour boil, the tensile strength had dropped to 1200N. This represented a 12% increase compared with the agglutinated phlobaphenes. Similarly, the strength after soaking had increased by 55% to 1717N. Both of these results indicated that the non-agglutinated phlobaphenes allowed the formulation of stronger adhesives. As a result of this experiment, all phlobaphenes undergoing pH alterations were maintained at a constant low temperature for the duration of the addition of the base.

f) <u>30:70 MDI:higher molecular weight phlobaphenes formulation</u>

Having established that a ratio of 30:70 of MDI to phlobaphenes was optimal and that higher molecular weight phlobaphenes glued more strongly than standard phlobaphenes, it was decided to investigate the tensile strengths of an MDI/higher molecular weight phlobaphenes formulation on beech strips (*cf* 5.12.5, table 3.4.1, 2.4). The results were unexpected. (Table 3.4.2, 2.4). Instead of yielding greater strength than the formulation containing no MDI, the strengths of the glued beech strips were lower in the case of the dry strength, where 1870N as opposed to 2434N was obtained. However, in the case of the six hour boil, the strength increased from 1210N to 1395N and after the twenty-four hour soak, a rise in strength from 1245N to 1399N was observed. The decrease in strength for the dry tests was probably due to the fact that the two samples of higher molecular weight phlobaphenes were not identical. The higher molecular weight phlobaphenes used in conjunction with the MDI was likely to have been composed of molecules of lower molecular weight, indicated by the drop in strength. By contrast, the MDI was seen to effectively overcome the hydrophilic effects of the sulphite, preventing excessive water-induced bond weakening. From these experiments, the effect of the MDI could be further indicated.

g) <u>Acidic phlobaphene / MDI formulation</u>

The effectiveness of the MDI in strengthening adhesives formulated using acidic phlobaphenes was demonstrated (<u>cf</u> 5.12.4, table 3.4.1, 2.5). The investigations using phlobaphenes at pH=0 had proved that, particularly under artificial weathering conditions, the formulation was extremely weak. On the addition of a large quantity of MDI, (almost 48%), the strength of the formulation was increased (table 3.4.2, 2.5). The increased tensile strength was particularly noticeable during the weathering tests, where the strength increased from 540N to 887N in the case of the six hour boil. An increase in strength from 544N to 935N was experienced during the soak. Once again, although less effectively, the MDI had minimised the water-induced bond cleavage, resulting in stronger adhesion of the formulation.

### 3.4.3 MDI dependence on pH in phlobaphene formulations

Having established that the natural pH for phlobaphenes formed under natural conditions was approximately pH=2 (cf 2.5), the MDI series of formulations was repeated at this lower pH. This allowed any variations in the effect of the MDI at the lower pH to be established (Table 3.4.1, 3.1, 3.2, 3.3).

As the MDI ratio was decreased from 30% to 20%, the strength followed suit (Table 3.4.2, 3.1, 3.2). The strength was, in both cases lower than that observed at the higher pH. At 30% MDI, the strength was 900N (dry), 376N (boil) and 738N (soak). The dry strength was approximately 58% of that obtained at pH 3. The decrease in the weathering strengths was also marked, with the boil strength having decreased by 65% whilst the soak strength had dropped by 34%. These decreases indicated that a pH of 2 was less than optimal with respect to the strength of the adhesive, despite being the natural phlobaphene pH.

Using 20% MDI (table 3.4.2, 3.2), the strengths decreased both with respect to the 30% formulation and when compared with the higher pH example. An average decrease in strength of 58% was observed in the dry and boil tests whilst the soak strength had decreased by 44%. Once again, these demonstrated that the optimal pH was toward a higher pH region.

When the MDI was reduced to 10% (table 3.4.2, 3.3), an unusual observation was made. The strength of the formulation increased with respect to the 20% formulation. The increased strength was particularly noticeable for the dry strength which increased by 28% to 703N. This value was, however, still less than the strength observed when the MDI was added to the phlobaphenes at a higher pH. The increase in strength for the boil and soak tests was slight and averaged at 10%.

From the experiments using the phlobaphenes at a lower pH, the strength decreased quite noticeably, implying that the MDI had a pH dependent region of optimal reactivity.

This effect of pH was further reinforced, when a phlobaphene / MDI formulation was prepared at pH=6 (cf 5.12.4, table 3.4.1, 3.4). Once again the strength was found to be lower than that obtained at pH=3 (table 3.4.2,3.4). The dry strength was 828N, lower than the strength at both pH=2 and 3. After boiling, the strength was higher than that obtained at pH 2 but lower than at pH 3. The variation in the soak strength was similar to that noted for the dry strength.

### 3.4.4 Influence of the addition of pine tannin to the phlobaphene formulation

In an attempt to increase the strength of the phlobaphene formulations and to decrease the weathering effects experienced, sulphited pine tannin was added to the formulations as a second fortifier (cf 5.12.6). The quantity added was varied to establish the optimum addition.

a) <u>1:1 ratio of pine tannin and phlobaphenes</u>

Equal quantities of 40% solutions of pine tannin and phlobaphenes were combined. The adhesive formulation employed also contained 30% MDI, for added strength (table 3.4.1, 4.1). After pressing, the dry tensile strength of the beech strips was found to average at 1549N. (Table 3.4.2, 4.1). This was almost identical to the strength observed when no pine tannin was added, viz. 1590N. Having been boiled for six hours, the strips showed a strength of 1040N. This was very similar to 1076N, the strength observed when no pine tannin was used as fortifier. The cold water soak test resulted in a strength of 1027N, also similar to 1114N obtained when no pine tannin was present.

From this, no advantages from the presence of pine tannin could be observed.

b) <u>2:1 ratio of phlobaphenes and pine tannin</u>

Twice as many phlobaphenes as pine tannin were added in the second formulation (table 3.4.1, 4.2). The strength of this formulation was poor in comparison with the strength obtained with no pine tannin present. The tensile strength of the dry strips was 1407N, (table 3.4.2, 4.2), 22% less than that obtained when no pine tannin was used. The weathering tests also provided low strengths. 676N (boil) and 1062N (soak), were observed. The decrease in strength may have been attributed to the interactions between the pine tannin and the MDI, minimising those between the phlobaphenes and the MDI. In addition, the pH of the formulation was 3.84, lower than the 3.91 of the 1:1 formulation. The pH may have resulted in the variation observed.

c) <u>1:2 ratio of phlobaphenes and pine tannin</u>
When the quantity of pine tannin was increased in relation to the phlobaphenes (table 3.4.1, 4.3), the strength of the formulation increased. The dry strength increased by 10% with respect to the formulation containing no pine tannin, to a value of 1742N. (Table 3.4.2, 4.3). However, both the weathering tests demonstrated a weakening in the formulation despite the presence of the MDI. Strengths of 916N (boil) and 1120N (soak) were observed compared with the boil value of 1076N and the soak value of 1114N obtained with no added pine tannin. The weakening experienced during the weathering tests was probably due to the increased sulphite present in the formulation due to the fact that sulphited pine tannin was used as the fortifier.

From the results obtained using pine tannin as an added fortifier, it was clear that the addition of pine tannin did not markedly improve the strength of the formulation.
Thus, having scanned various formulations, it was established that the most effective formulation with respect to both strength and water resistance, was the phlobaphene/MDI (70:30) formulation. For this reason, it was decided to employ a 30:70 ratio of MDI and phlobaphenes in a formulation for particle board.

## 3.5 Particle Board Thermosetting Adhesives

Particle board adhesives were prepared using redissolved phlobaphenes according to the formulations scanned with the aid of beech strips.

### 3.5.1 General comments on particle board preparation

Standard conditions are generally used during particle board research to allow relatively accurate comparisons of boards to be made, despite variations in their adhesive formulations.

In general, single layer boards with an expected density of $0.680 g/cm^3$ and 12mm thick are pressed at $195^{\circ}$-$200^{\circ}C$ and a pressure of $30 kg/mm^2$. A pressing time of 7.5 minutes is generally employed. Of this, the first two minutes are taken to reach the maximum pressure which is maintained for two and a half minutes before being slowly released over the following three minutes.

Several deviations from the standard were inadvertently made (cf 5.13.3). Three layer boards were pressed, having an average density of approximately $0.620 g/cm^3$. This may have induced errors in the strength of the boards, since three layer boards are often stronger than their equivalent core-only boards. In addition, the boards had an average thickness of 17.5mm. This, too, would probably result in an effectively stronger board, since a thicker board, under stress can disperse the stress over a larger area and thereby apparently be less affected. The pressing time employed for the boards was only four and a half minutes. However,

approximately half a minute extra was used to increase the pressure prior to the timing of the pressing. The decreased pressing time may have resulted in incompletely reacted adhesives in the particle board, and therefore, in a weaker board than expected.
Despite the variations from the generally accepted standards, the boards pressed proved to be strong and are discussed as such.

### 3.5.2 Effect of varying the paraformaldehyde content in a phlobaphene formulation

Having established that the strongest adhesives containing phlobaphenes were those formulations containing 30% MDI (*cf* 3.4.4), they were used, without modification in particle board. (*cf* 5.13.1)

a) Variation in the core paraformaldehyde added

A particle board containing 15% paraformaldehyde was prepared initially (table 3.5.1, 1). The formaldehyde released from this board was excessive, 264.2mg/100g dry board, in comparison with a more acceptable value of 30mg/100g obtained from urea-formaldehyde boards. For this reason, the paraformaldehyde was decreased to 10% and then 5% in the core (table 3.5.1, 2, 3).

The pH of the three boards was fairly similar ranging from 3.8 for the 10% paraformaldehyde (table 3.5.1, 2), to 3.9 for the 15% paraformaldehyde (table 3.5.1, 1), to 4.1 for the 5% paraformaldehyde formulation (table 3.5.1, 3).

In each case, the core contained a ratio of 30:70 MDI and phlobaphenes, whilst the surfaces contained 7% MDI in the case of the two boards with the higher formaldehyde content and 13% MDI for the board containing 5% paraformaldehyde (table 3.5.1, 3).

b) <u>Variation in the surface formaldehyde used</u>

The surfaces of the boards generally contained the same percentage of formaldehyde as the core. However, the 5% paraformaldehyde core board contained 10% paraformaldehyde in the surface. This so, since this allowed the examination of the effect of varying only one paraformaldehyde concentration of the three layer board, compared with the varying of both quantities of paraformaldehyde. In each board, a paraffin wax emulsion was added to the surface as approximately 2% of the overall glue-mix. This prevented the pressed board from remaining adhered to the cold sheets, on removal from the press.

c) <u>Variation in board density</u>

The density of the three boards was comparable, ranging from 0.624g/cm$^3$ for the 15% paraformaldehyde board to 0.632g/cm$^3$ for the 10% paraformaldehyde board to 0.630g/cm$^3$ for the 5% paraformaldehyde board.

d) <u>Variation in physical attributes</u>

Despite the similarities in the densities of the three boards, they varied in their physical strengths (*cf* table 3.5.2). Variations in the physical strength of the board were demonstrated during the internal bond strength determinations (*cf* 5.6.3). All three boards passed the SABS exterior grade standard of a dry internal bond strength greater than 0.55N/mm$^2$.

The strongest board (dry) was the 10%