be used to establish what percentage of the resin is able to combine effectively with formaldehyde (in formalin). Thus comparisons between various resins can be made. With the knowledge that the higher the number of polyphenolic groups, the greater the capacity for cross-linking and thereby the greater the strength of the cured resin, Stiasny numbers can be used to predict relative adhesive strengths.

b) <u>The effect of the Stiasny numbers obtained for the Diteco extracts</u>

The Stiasny numbers obtained for both the sulphited tannin extract and the sulphited tannin-urea extract were lower than usually obtained for sulphited tannin. (Table 2.6.1)

The low Stiasny numbers obtained indicate that the cross-linking functionalities were less predominant than usual.

This would result in fewer cross-linking functionalities being present to react with the formaldehyde in the resin formulation, resulting in poor adhesive properties.

The reason for the low proportion of reactive functional phenolic groups could have been due to the extraction of very young bark (*cf* 2.5.3 c).

Young bark contains tannins of a lower average molecular weight. This in turn results in shorter tannin molecules each having a lower capacity for cross-linking than longer molecules, resulting in a decrease in the observed Stiasny number and in a decrease in adhesive strength.

c) The effect of sulphitation on the Stiasny number

The Stiasny number obtained for sulphited (5%) tannin was also much lower than that obtained for "natural" tannin (2-2.5% sulphitation during extraction).[29] These Stiasny numbers (table 2.6.1) indicate that sulphitation must have a deleterious effect on the effectiveness of the tannin in adhesive applications, since the phenolic groups have been markedly decreased.
This had an effect in the adhesive quality of the extract since the percentage glue solids in the adhesive were generally calculated on an average Stiasny number.

For example, a 10% glueline is desired for a particular particle board and 70% of the glue solids are derived from the tannin with 30% fortifier present. These values are calculated for a standard sulphited tannin solution with a Stiasny number of 58%. In the extracts obtained in these experiments, the Stiasny numbers were in the region of 45%.
Thus instead of 70 parts of reactive tannin being used, the extracts would yield an effective 54 parts of reactive tannin for the same quantity. Since the tannin mixture is less effective in its adhesion, it becomes more costly since a greater quantity of the extract must be used to obtain the same adhesive results as an extract with a higher Stiasny number.
In contrast, if a solution of non-sulphited tannin was used (Stiasny number = 75), then the final glue-mix would contain 90 parts of reactive

tannin. This would result in less tannin being required to obtain the same adhesive effects as the sulphited tannin solution. This would be more cost effective if based entirely on the Stiasny number.

However, the difficulty in dissolving non-sulphited pine tannin to the desired concentration plays an important role in the considerations and is a major reason why sulphited tannin is used in adhesives.

2.6.2 Particle-board prepared using the DITECO extracts to examine the effects of the urea

Several particle boards were prepared to establish the effects of the urea on the board strength whilst other parameters were changed.

Three-layer boards were prepared in which the surface paraformaldehyde content was maintained at 10% of the tannin solids in the surface glue. In each case, the boards pressed were 18mm boards of an average density of 0.650g/cm^3 (*cf* 5.6.1, 5.6.2, table 2.6.2).

a) The effect of varying the pressing time

Very short pressing times were employed in all cases. The general pressing time employed was 4.5 minutes. This was compared with a shorter time of 3.5 minutes.

i) Internal bond strength effects (*cf* 5.6.3)

When 10% paraformaldehyde (on tannin solids) was employed in the core of the boards, an average 14% decrease in the internal bond strength was experienced, for both the urea and non-urea containing extracts, as the pressing time was decreased (table 2.6.3). A decrease in internal bond strength was also noted for the shorter pressing time, when the core paraformaldehyde was decreased to 8%. Again, the decrease in the strength was very similar (5%) for both the urea- and non-urea containing tannin solutions.

These results demonstrated that the pressing time had a marked effect on the variation in the strength of the boards and that the decrease in strength was largely dependent on the pressing time rather than any variations in the compositions of the glue-mixes.

ii) Board swelling variations (*cf* 5.6.5)

Comparing the swelling of the boards for the two pressing times, demonstrated that variations in the glue-mixes had important effects.

After two hours soak, the non-urea containing board had a decreased swelling for the shorter pressing time of approximately 8% (table 2.6.3). In contrast, the urea containing board had experienced a swelling increase of 8.5% with the decrease in pressing time. Both of the above were for the boards containing 10% paraformaldehyde. In the case of a board pressed for a shorter length of time, it was expected that the cross-linking would be less complete than in the case of a board pressed for a longer time.

This so, since cross-linking was dependent both on the pressure applied and the temperature during this time. In this case, the board containing urea behaved as expected with an increased swelling in the case of the shorter pressing time, owing to the presence of unreacted -OH groups which could hydrogen-bond with water and thereby induce swelling. In addition, the urea groups and the sulphite groups would hydrogen-bond with the water. These latter effects would however be present in both the boards although could be more marked in less reacted board (ie shorter pressing time).

The decrease in the swelling in the board containing no urea could indicate that the hydrogen-bonding effects due to the sulphite groups and the available -OH groups was negligible and that the urea's effect on the swelling is very marked for the shorter pressing time.

When the paraformaldehyde was decreased to 8% in the core, the complete opposite was observed. The non-urea containing board swelled by an extra 3% for the shorter pressing time whilst in the urea containing boards, a 14% decrease in the swelling was noted for the shorter- compared with the longer pressing time.

iii) <u>Water absorption variations</u> (*cf* 5.6.6)

In all cases, the absorption of water by the particle boards increased as the pressing time decreased (table 2.6.3). This could be explained by the fact that the shorter pressing time resulted in a weaker board. This in turn, implied that there was greater availability of unreacted hydrogen-bonding groups in the boards pressed for a shorter time. After two hours soak, the urea containing board from the shorter pressing time (10% paraformaldehyde) had absorbed 13% more water than the board which had been pressed for longer. In comparison, the board containing no urea had only absorbed 2% more water in the case of the shorter pressing time. The effect of urea in increasing the percentage of water absorption was seen when the pressing time was shortened. This could be explained by the incomplete reaction of the urea groups in the cross-linking and therefore the increase in the relative absorption.

On increasing the soaking time to 24 hours, the trend of increased absorption with decreased pressing time was again noted. The difference between the pressing times had a lesser effect on the change in absorption in the case of the urea containing boards. This implied that the urea increased the absorption of water in a pressing time related way, but this effect was minimised as the time of exposure to the water increases.

In contrast, the boards which did not contain urea experienced an increase in the percentage water absorption as the pressing time decreased and the soaking time was increased.

b) A comparison of the effects of the presence and absence of urea in the boards

The effect of the urea on the three areas of internal bond strength, board swelling and water absorption was examined.

i) Internal bond strength effects (cf 5.6.3)

Comparing the boards containing 10% paraformaldehyde, the urea was found not to have any deleterious effects on the internal bond strength after 4.5 minutes pressing time. When the pressing time was decreased, the presence of the urea in the board seemed to be advantageous since the board was 6% stronger than that board containing no urea. A general problem experienced with the use of pine tannins in adhesives is that before the molecules are effectively cross-linked to give high strength to the system, their molecular weight increases to the point where the molecules are so large and bulky that they precipitate from the solution preventing further formaldehyde induced cross-linking from occurring. This would explain why the non-urea containing board was weakened. The increase in comparative strength of the urea containing board could be attributed to the effect of the urea in maintaining a decreased molecular weight by blocking some of the reactive ends of the tannin molecules in the extraction process. This would allow shorter tannin molecules to exist in close contact with each other during the gluing process. The formaldehyde in the system would be able to form numerous cross-links before the molecular weight increased to the point of precipitation, resulting in an increase in the strength of the board.

When the formaldehyde in the core of the boards was decreased to 8%, the urea containing boards were stronger than those containing no urea, for both pressing times (table 2.6.3). The comparative increase in strength for the tannin-urea boards was approximately 9% for both pressing times. This indicated that the smaller molecular weight molecules, present due to the effect of the urea, were more efficiently cross-linked by the formaldehyde than the longer molecules which did not encounter urea. Thus, in the presence of a lower proportion of formaldehyde, the urea enhanced the strength of the board.

ii) <u>Board swelling variations</u>

When 10% paraformaldehyde was used in the core (table 2.6.2), the boards with and without urea swelled to the same degree in the case of the longer pressing time (table 2.6.3). This implied that the pressing time was effective in both instances and successfully shielded any compositional effects from being displayed. In the case of the shorter pressing time, the urea caused a greater degree of swelling than when it was not present in the board. The extra swelling could be attributed to the presence of amine groups in the board which were capable of bonding strongly to water molecules. If these hydrogen bonds formed within the board, the presence of the water would cause an increase in the thickness of the board which would experience a swelling.

When the formaldehyde was decreased to 8%, the swelling of the boards was generally smaller than for the higher percentage of formaldehyde. This implied that the formaldehyde which remained unreacted in the 10% boards may also have contributed to the swelling, since the decrease in formaldehyde resulted in a general decrease in swelling. The same swelling trend was noted for the two types of board in the presence of lower quantities of formaldehyde, with the urea containing boards experiencing a slightly higher degree of swelling than those boards in which there was no urea.

iii) Water absorption variations

Those boards containing urea were found to absorb less water (by mass), regardless of pressing time and formaldehyde content, than those boards which did not have any urea in them (table 2.6.3). Thus it appeared that the presence of water caused a variation in the alignment of the urea molecules in the board allowing the absorption of a smaller quantity of water than the board containing no urea.

c) The effect of decreasing the quantity of formaldehyde in the core of the three-layer particle board

Altering the quantity of formaldehyde in the core of the three-layer particle board altered its strength.

i) Internal bond strength

Without exception, the internal bond strength decreased as the formaldehyde was decreased. This decrease in strength averaged at 7% for all the boards tested (table 2.6.3). The resultant strength of the board was in the region of $0.65N/mm^2$, an acceptable strength considering the short pressing times used and the fact that 18mm boards were prepared instead of the usual 12mm boards.

ii) Variation in swelling

Generally, the percentage swelling of the boards containing less formaldehyde was smaller than in those containing a higher proportion of formaldehyde (table 2.6.3). This occurred for both the two hour and the twenty-four hour soak. The decrease in swelling on decreasing the formaldehyde content seemed to indicate that the excess, unreacted formaldehyde was involved in the swelling experienced by the board. Those boards containing a high percentage of formaldehyde also contained a higher proportion of unreacted formaldehyde and would experience greater swelling. The swelling could be due to the aldehyde oxygen in the formaldehyde, which was capable of hydrogen-bonding with water during the cold soak.

iii) Water absorption variations

The boards containing lower proportions of formaldehyde were found to absorb less water. A decrease of 10% in the water absorbed by the boards containing 8% formaldehyde was noted for the two hour soak. The decrease in the absorption after 24 hours of soaking was found to be 8% on average (table 2.6.3).

iv) Formaldehyde released

As expected, on decreasing the formaldehyde added to the glue-mix, the formaldehyde released from the board decreased correspondingly. Despite the decrease in the formaldehyde released, the values obtained were unacceptably high in both cases. This excessive formaldehyde release was not entirely attributable to a higher-than-usual quantity added to the glue-mix. The explanation for the apparent excess of formaldehyde could be explained with reference to the Stiasny number. The Stiasny numbers obtained for the two extracts used were lower than expected (see 2.6.1). This in turn implied that the percentage of polyphenols in the extracts was lower than expected and that the adhesion would be worse than expected.

The quantity of paraformaldehyde to be added to the glue-mix to achieve 10% formaldehyde on tannin solids was calculated assuming that a normal Stiasny number was obtained.

Calculations based on the non-urea containing board (10% paraformaldehyde) are used to explain the origin of the high percentage of formaldehyde released.

125.4 mg HCHO/100g dry wood

sample mass	131.3g
moisture content	6.4%
dry sample mass	122.9g
HCHO emitted from dry sample	151.1mg

The board comprised 40% surface and 60% core (m/m)

mass of surface	49.2g
% HCHO in dry glue-mix	0.99%
mass of HCHO in surface	0.49g
mass of core	73.7g
% HCHO in dry core glue	0.60%
mass of HCHO in core	0.44g
Total HCHO present in dry sample	0.93g

Since the Stiasny number was 45.2% compared with the normal average of 58%, the formaldehyde added to the example should have been 0.72g.

Thus, the HCHO excess was 205mg.

The HCHO analysed was 151mg

From this example it could be seen that the lower Stiasny number obtained could be used to explain the high percentage of formaldehyde analysed as being released from the boards. This formaldehyde did not arise, in the main, from that actually released during the degradation of the adhesive and which occurs continuously with time. Rather, this formaldehyde was released on a "once-off" basis as a result of the excess present during adhesion and which was not reacted during the pressing. Thus, it was expected that once this excess formaldehyde had been released, probably over a period of three to four months, the formaldehyde release values obtained would revert to the expected and more acceptable values in the region of 30-40mg HCHO/100g dry sample.

2.7 Fast Setting Honeymoon Adhesives Using Urea and Non-urea Tannin Extracts

The Chilean system of honeymoon adhesive preparation was employed during a factory trial for fingerjoint formation at Villacura, Ltda., Concepcion in Chile. The fingerjoint profiles were prepared from pinus radiata wood.

2.7.1 Sulphited pine tannin

Components A and B were prepared and the fingerjoints glued as described (cf 5.7.1). A time trial was conducted to establish at what time, 100% wood failure occurred (cf 5.7.3). At 90 minutes after gluing, the wood failure was found to be 100%. (Table 2.7.1). Theoretically, the time after which 100% wood failure would be found was 79.6 minutes, with 97% significance. The equation of the power fit curve was established to be $y = 3.04x^{0.8}$.

2.7.2 Urea-sulphited pine tannin extract

Components A and B were prepared and the fingerjoints glued as described (cf 5.7.2). A time trial was conducted to establish at what time, 100% wood failure occurred (cf 5.7.3). The increase in strength of the honeymoon adhesive was similar to that containing no urea. The maximum wood failure (100%) was noted after 90 minutes. (Table 2.7.2). This was recalculated theoretically and found to be at 87.5 minutes, with a reliability of 99%. The equation of the power fit curve was found to be $y = 0.05x^{1.71}$.

CHAPTER 3 DISCUSSION - PART 2

REDISSOLVING PINE TANNIN PHLOBAPHENES

During the extraction of the bark of pinus radiata, high molecular weight fractions, called phlobaphenes, are formed. These phlobaphenes are insoluble in the aqueous extraction liquor and cause a decrease in the total extraction yield from the pine bark.

3.1 Artificial Phlobaphene Formation

A source of phlobaphenes was required which could be used to conduct investigations into their successful redissolution.

The pine tannins supplied were "sulphited" pine tannins. This title arose because the tannins, having been extracted in the presence of 2.5% sulphite, had been further sulphited to yield a final sulphite concentration of between four and five percent. During the sulphitation of the tannins, many of the high molecular weight molecules had been cleaved to smaller molecules by the sulphite, by a ring opening mechanism[3] (figure 1.2), or had been precipitated in the factory and removed during the spray-drying process. The resultant "sulphited" pine tannin extract contained a low proportion of high molecular weight fractions and no natural phlobaphenes. The phlobaphenes used experimentally had therefore, to be prepared under forceful conditions. This preparation proved quite formidable.

Foo et al[27] note that two types of phlobaphenes exist, namely those formed naturally by oxidation and polymerisation of condensed tannins and those phlobaphenes resulting from the action of mineral acids on tannin extracts. Because of the different reactions resulting in the formation of the two types of phobaphenes, some physical differences between them are expected, however, few of these differences have been fully investigated.[27]

3.1.1 Comparison of the effects of hydrochloric acid and sulphite on the phlobaphenes precipitated

The effects of the addition of varying quantities of sulphite and hydrochloric acid on the phlobaphene precipitate were examined (cf 5.8.1). (Table 3.1.1) From this table it can be seen that in terms of the numbers of moles of precipitating agent added to the tannin solution, the sulphite is far more effective in precipitating the phlobaphenes than the hydrochloric acid. However, the addition of the sulphite was problematic as it had to be dissolved prior to its addition to ensure that it was effectively distributed in the tannin solution. The volume of water required for the solubilisation was large since sodium sulphite only has a solubility of 12.5g per 100g water.[30] The addition of concentrated hydrochloric acid to the pine tannin solutions was easier and had the added advantage that a smaller volume contained a larger number of moles of precipitating agent allowing smaller volume changes to be effected for a larger percentage of additive.

3.1.2 Phlobaphenes prepared from natural and sulphited pine tannins - "pinus radiata" D.Don

Since large quantities of phlobaphenes were required for the investigations, the tannin type yielding the highest percentage of phlobaphenes (m/m) would be the most viable. Similar solutions of the two types of tannin, natural and sulphited, were prepared and phlobaphenes were precipitated using equivolumes of concentrated hydrochloric acid (cf 5.8.2).
The "natural" tannin solution contained tannin extracted using 2.5% sulphite on the bark mass but to which no further sulphite had been added.
63% of the tannins were precipitated as phlobaphenes from this natural tannin solution.
In contrast, the sulphited tannin solution yielded 88% of the initial tannin mass as phlobaphenes. (Table 3.1.2)

a) Effect of the extra sulphite on phlobaphene precipitation

The additional sulphite reacted with the tannin solution prior to spray-drying, in the "sulphited" tannins, afforded easier dissolution of the tannins in water. This was due to the reaction of the sulphite with the tannin ring, in which the heterocyclic ring was opened[5]. This resulted in pine tannin solutions was easier and had the added advantage that a smaller volume contained a larger number of moles of precipitating agent allowing smaller volume changes to be effected for a larger percentage of additive.

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Whilst in storage, the tannins possibly underwent many other alterations. These were incurred due to effects such as oxidation of the tannin molecules causing an increased molecular weight. Additional polymerisation reactions may occur if the tannins are exposed to ultra-violet light and this has been shown to result in the formation of phlobaphenes and their pre-cursors.[24,31]

These reactions worked together in the sulphited pine tannin which finally contained molecules of a reasonably high molecular weight. On the addition of the concentrated hydrochloric acid, the high molecular weight fractions were quickly linked by the action of the acid (figure 1.2). This resulted in a large proportion of the dissolved tannins precipitating as phlobaphenes.

b) Effect of hydrochloric acid in increasing the molecular weight

The addition of hydrochloric acid to the tannin solution resulted in the formation of phlobaphenes formed in one of two possible methods.

The first method is the classical condensation reaction as a result of the hydrolysis of the

heterocyclic rings (p-hydroxybenzylether links).[8] (Figure 1.2)
A second method was postulated when sulphurous acid released by the solution was detected. This indicated that a replacement reaction was occurring whereby the solubilising sulphite groups were released from the tannin molecules which could then cross-link forming phlobaphenes. (figure 3.1).

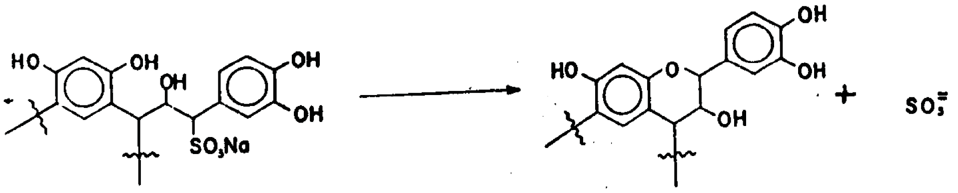

fig 3.1

3.1.3 Maximising the phlobaphenes precipitated with the minimum amount of acid

In an effort to establish the amount of acid required to precipitate the maximum quantity of phlobaphenes, a small gravimetric study was employed (cf 5.8.3). From the study, it was found that on increasing the volume of acid added to the tannin solution, the phlobaphenes precipitated increased until a plateau stage was reached where the volume of acid added was 2.5 times the original tannin mass. (Table 3.1.3, figure 3.1.1) In this study, it was noted that the maximum precipitate formed was 62% of the original tannin mass and required twice the volume of acid as the original tannin mass. This was compared to the 88% phlobaphene precipitate obtained using a 1:1 ratio (v/m) of hydrochloric acid and tannin solids. (Table 3.1.1). The variation in the values obtained are attributed to the interactions that can occur in the tannin solutions.

In larger volumes of tannin solution, the phlobaphenes formed appeared to exert some attractive force on those tannins remaining in solution which then also appeared to condense and precipitate. Smaller volumes of equal concentration appeared to have fewer noticeable effects in terms of attraction by the phlobaphenes formed on those tannins of a high molecular weight remaining in the solution.

Large quantities of phlobaphenes were required for the purposes of research into the redissolution of pine tannin phlobaphenes. For this reason, a 1:1 ratio (v/m) of hydrochloric acid to tannin solids was used in all the preparations of phlobaphenes.

3.2 Studies into the Redissolution of Phlobaphenes

Phlobaphenes can be redissolved in pure ethanol with relative ease, although maintaining their solubility for any great length of time is less easily achieved. Industrially, however, the use of pure ethanol to redissolve a fairly low-cost product, such as phlobaphenes, is not economically viable, especially if the dissolved phlobaphenes do not have a reasonably long shelf life. According to Baeza,[7] small quantities of phlobaphenes could be redissolved in ethanol and maintained in soluble form with the addition of sodium sulphite.

3.2.1 Using reflux conditions

Small quantities of phlobaphenes were found to dissolve readily in ethanol at slightly elevated temperatures (35-40°C). After refluxing the alcoholic phlobaphene solution in an aqueous solution of sodium sulphite, no suspension of phlobaphenes was noted. A suspension often formed on the addition of the pure water, as the phlobaphenes contacted the water and the solubility balance was upset causing them to precipitate.

a) "Wet" phlobaphene redissolution

Initially, the redissolution of phlobaphenes was conducted using so-called "wet" phlobaphenes (cf 5.9.1). Redissolution of small quantities of wet phlobaphenes, under reflux conditions, generally occurred with ease and they remained in solution for several weeks (cf 5.10.1). Larger quantities of phlobaphenes were less disposed to redissolve during the refluxing conditions resulting in further investigations into the redissolution (cf 5.10.6)

b) Air-dried phlobaphene redissolution

Phlobaphenes which had been allowed to dry without the application of heat (cf 5.9.2) were found to dissolve to a large extent using ethanol and reflux conditions, (cf 5.10.1, 5.10.2) Approximately 90% of the phlobaphenes remained in solution after the cessation of the reflux conditions (table 3.2.1). The undissolved fraction consisted of a fine suspension of phlobaphenes which was removed by filtration. After twenty-four hours of standing, a further fraction of phlobaphenes had precipitated. This fraction probably constituted those phlobaphenes that were able to remain in solution if it was warm. On cooling, the solution was no longer able to sustain the solubility of the high molecular weight fraction which then precipitated. This precipitate reduced the total dissolved phlobaphenes to approximately sixty percent of the original phlobaphene mass.

c) Heat-dried phlobaphene redissolution

The effect of heat on the phlobaphenes to be redissolved, was studied.

i) 45°C

A small sample of phlobaphenes was dried using a rotary evaporator (*cf* 5.9.3). The temperature of the sample was raised to 45°C to aid the evaporation of the water. Once dry, the sample was suspended in ethanol, in which it did not completely dissolve (*cf* 5.10.1). This lack of complete dissolution was the first area in which a deviation from expected effects was noted. It was expected that the effect of heat on the phlobaphenes would be such that they polymerised to a point where they could not be redissolved at all. However, after the refluxing process, no precipitate was noted after filtration. After twenty-four hours, almost complete precipitation was noted. This indicated that whilst the solution was warm, the solubility of the phlobaphenes was complete. On cooling, however, the high molecular weight compounds could remain in solution no longer and almost complete precipitation was noted. (Table 3.2.1).

ii) 100°C

Phlobaphenes dried in an oven set to 100°C (*cf* 5.9.3) did not redissolve at all. This was probably due to charring of the phlobaphenes occurring at the elevated heating temperatures.

The investigations using dried phlobaphenes, either air or heat dried, indicated that drying does cause changes in the structure of the phlobaphenes. During drying, the water molecules found in association with the numerous hydroxyl groups on the phlobaphene structure, were removed to a greater or lesser extent. As the drying temperature increased, the number of hydrogen-bonded water molecules associated with the phlobaphenes decreased. The removal of the water would have decreased the solubility of the compound. In addition, it may have altered the structure of the phlobaphene preventing the entrance of other hydrogen-bonding groups into the macromolecular structure, thereby preventing redissolution from being effected.

These changes prevented the complete redissolution of the phlobaphenes in ethanol-water-sulphite solution under reflux conditions.

d) Neutralisation effects on phlobaphene redissolution

To establish whether the difficulties encountered during the redissolution of the phlobaphenes were an effect of the acidic conditions, a sample of phlobaphenes was neutralised prior to filtering (cf 5.9.4). These phlobaphenes did not completely dissolve in the ethanol and the refluxing of the suspension did not result in full dissolution (cf 5.10.2). The incomplete dissolution of the phlobaphenes could be attributed to the neutral pH since without the increase in pH, the sample would have dissolved. By increasing the pH, an alkaline induced autocondensation was probably initiated. Alkaline auto-condensation is not unknown in tannin solutions[32]. This condensation probably occurred both between tannin molecules yet uncondensed in the solution and in further condensing those high molecular weight phlobaphenes previously formed in the presence of the acid.

3.2.2 Using methanol in the redissolution process

Industrially, methanol is a cheaper reagent than ethanol. For this reason, the ethanol redissolutions were attempted using methanol (cf 5.10.3), with a view to replacing a more expensive industrial reagent with a cheaper one.

a) Viscosity effects

In the first experiment, the volume of ethanol was directly replaced with an identical volume of methanol. The resultant solution contained redissolved phlobaphenes although the viscosity had increased markedly and the solution could not be filtered. This increase in the viscosity could have been due to a 45% increase in the number of moles of methanol added to the system compared with the equivolume ethanol.

b) Decreasing the methanol

In an attempt to decrease the viscosity of the solution, the volume of methanol was decreased whilst the water volume was increased. The phlobaphenes used in this experiment failed to dissolve completely. This was probably due to the increased proportion of water.

The phlobaphenes dissolved with ease in an organic solvent due to the hydrophobic groups present in the solvent. These groups were attracted to the hydrophobic areas of the phlobaphene molecules which then became masked by the solvent. If the solvent also contained alcoholic groups, they would have been the only areas "visible" or exposed to any added water and apparent dissolution in the water could be effected.

In the case of methanol, the hydrophilic group is attached to a relatively small organic group in comparison with the phlobaphene molecule. Thus, the methanol was less effective in masking the phlobaphene molecules especially when the concentration of methanol was decreased in the solution.

c) Increasing the methanol relative to the water used

When the methanol used caused a viscosity increase (cf 3.2.2 a), the total solvent volume was far greater than the mass of phlobaphenes used and the final solution contained only 9% solids. Although decreasing the volume of methanol did not appear to be successful in redissolving the phlobaphenes (cf 3.2.2 b), the proportion of water used had maintained the maximum possible percentage of solids at 9%.

For effective use in adhesives, the percentage solids required is between 40% and 50%.

In an attempt to obtain this solution, the volumes of methanol and water were reduced and the volume of methanol was maintained at double that of the water. After refluxing the solution, full dissolution was noted. After cooling for twenty-four hours, the precipitate was removed and the solution was found to contain only 40% of the original phlobaphene mass. This resulted in a final solids concentration of only 13%

This reaction was repeated several times with similar effects occurring each time. An initial dissolution was obtained which with time resulted in a very low percentage solids being obtained.

The precipitation of the redissolved phlobaphenes after cooling indicate that the use of methanol as the solvent prevented very high percentages of the solid phlobaphenes from remaining in solution.

3.2.3 Comparing the effects of methanol and ethanol in the redissolution of phlobaphenes

Wet phlobaphenes were prepared (cf 5.9.1) and their redissolution in ethanol and methanol were carried out simultaneously (cf 5.10.4). The redissolution in each case was calculated for 15% phlobaphene solids to be obtained in the solution. After refluxing both solutions, the phlobaphenes in both solutions appeared to have redissolved. After twenty-four hours, the differences between the effectiveness of the two solvents became more noticeable (table 3.2.2). The solution prepared in ethanol had remained fully in solution and no precipitate was observed. The final percent solids, determined gravimetrically, was established to be 13.0%. In contrast, the methanolic solution contained a precipitate which was established to be 43% of the original phlobaphene mass. The percent solids of the remaining solution was established to be 7.2%. From this experiment, the differences in the effectiveness of the two solvents was clearly noticed. The methanol was far less effective in maintaining the phlobaphenes dissolved at the desired percentage solids, than the ethanol. For this reason, methanol was not used in further investigations into the solubilisation of phlobaphenes.

3.2.4 Sulphite concentration effects on phlobaphene solubilisation

The effects of variations in the concentration of sodium sulphite added to the solution were investigated (*cf* 5.10.5).
The quantity of sulphite used was calculated according to the mass of dry phlobaphenes added to the system. Since the phlobaphenes were added in "wet" form, this mass was established using gravimetric analysis.

a) 120% sodium sulphite

After the addition of the sulphite to the solution, the solution became very viscous. The increase in viscosity could have been due to the action of the sulphite in decreasing the molecular weight by breaking the phlobaphene molecules. The increase in number of irregularly shaped molecules in the solution would probably give rise to a higher viscosity.

After twenty-four hours, the solution was decanted and the remaining precipitate constituted approximately five percent of the total phlobaphenes redissolved. Since the quantity of sulphite was more than sufficient to aid in the redissolution process, this precipitate probably arose as a result of the acidic action of the sulphite which caused self-condensation to occur.

b) 60% sodium sulphite

Sixty percent sodium sulphite added to the solution again resulted in an increase in viscosity (cf 3.2.4 a). After standing for twenty-four hours, a small precipitate was noted which contained almost eight percent of the phlobaphenes (cf table 3.2.3). This solution of phlobaphenes was tested for its gelation properties by adding paraformaldehyde (cf 5.11). Whilst the time taken to gel was only 82 seconds, the resultant gelled product was both brittle and soft. The gelled phlobaphenes were very hygroscopic and on the addition of water, demonstrated a high degree of disintegration. This disintegration could be attributed to the large amount of sulphite present, causing increased hydrophilicity.

c) 40% sodium sulphite

Immediately after the thirty minute reflux, in the presence of 40% sulphite, the phlobaphenes dissolved. In addition, the relative viscosity of the solution had decreased. The solution of phlobaphenes contained 35% solids and no precipitation or settling of phlobaphenes was noted.

d) 20% sodium sulphite

After refluxing the solution, a lack of precipitate and a lowered viscosity were noted. In addition, the phlobaphene solids were present at 37%. After twenty-four hours, no precipitation had occurred and the solution was retained for a further two weeks during which no transformations occurred.

e) 15% and 10% sodium sulphite

On the addition of fifteen percent sodium sulphite to the solution, no dissolution of the phlobaphenes was achieved. Similarly, in the presence of ten percent sulphite, almost no phlobaphenes dissolved. The lack of solubilisation of the phlobaphenes in the presence of the smaller quantities of sulphite indicate that there is a minimum sulphite level required for redissolution to be effected. (Figure 3.2.1)

From the results obtained for the solubilisation of phlobaphenes, the sulphite effect could be recognised. If the sulphite was present in very large quantities, redissolution was achieved. On cooling,