The results were compared with the aid of gravimetry.

2.2.1 Phlobaphene Precipitation

Phlobaphenes are known to be precipitated in the presence of a concentrated mineral acid such as hydrochloric acid.[5] In addition, it has been found that large quantities of sodium sulphite can also effect the precipitation of phlobaphenes from a tannin solution.

a) Acid precipitation

To solutions containing a known quantity of pine tannin, various known volumes of concentrated hydrochloric acid were added (cf 5.4.1). The resultant red phlobaphene precipitate could not be filtered but was centrifuged and the phlobaphenes dried and weighed. (Table 2.2.1 and figures 2.2.1 and 2.2.2). As the quantity of acid added was increased, so the precipitated phlobaphenes increased. However, the percentage increase in the precipitate mass decreased. This indicated that a saturation level could be reached above which no further precipitation would occur, probably since complete phlobaphene formation had been reached.

b) Sulphite precipitation

Solid sodium sulphite was suspended in a small volume of water (1-2ml) prior to its addition in varying known quantities to solutions containing known amounts of pine tannin (cf 5.4.2). The phlobaphene precipitates formed were light red brown in colour compared to the brighter red acid precipitated phlobaphenes. This possibly indicated that a different mechanism and slightly different structure had occurred, compared to those induced by acid. These phlobaphenes were also too fine to be filtered and thus were centrifuged prior to drying and weighing. The results for the sulphite precipitated phlobaphenes are found in table 2.2.2 and figures 2.2.1 and 2.2.2. Once again a systematic increase in the sulphite added did not result in equivalent increases in the precipitate observed. Initially, the sulphite may have been involved both in solubilising the tannins due to the opening of the heterocyclic ring and in precipitating phlobaphenes in its acidic capacity. As the sulphite was increased, the precipitating function was more important. When large quantities of sulphite were added, the percentage phlobaphenes precipitated from the tannin solution did not increase markedly. This so, since the high molecular weight fractions were rapidly precipitated and the lower molecular weight fractions, whilst they may have increased in molecular weight, were still small enough to remain in solution.

2.2.2 Effect of Ammonia on Phlobaphene Formation

The ammonia was added to the tannin containing solution prior to the addition of either the acid or the sodium sulphite (cf 5.4.3). Ammonia is a strong base with a single lone pair of electrons. This allowed it to react with a carbocation centre on a tannin molecule. However, the resultant NH_2-tannin complex had not altered the effects on the nitrogen centre markedly. Thus, the reactivity of the molecule was almost as high as that observed for the first reaction. This allowed a second tannin molecule to react with the complex and resulted in an unreactive compound - tannin-NH-tannin. Thus, the molecular weight was increased on the addition of the ammonia, observed in the agglutination.

a) Acid-ammonia precipitation

As the volume of hydrochloric acid added to the tannin-ammonia solutions was increased, so the pH decreased (table 2.2.3).

As the pH decreased, an increase in the quantity of phlobaphenes precipitated was expected due to the increasing presence of acid catalyst.

Using the precipitate masses obtained using acid only in the precipitation, the effect of the added ammonia could be examined (table 2.2.3).

A decrease in the percentage precipitated phlobaphenes was noted. As the quantity of acid was increased so the precipitate mass increased, with one exception. When 0.064 moles HCl (2 ml) was added to the solution containing 0.012 moles ammonia (1 ml), a dramatic decrease in the precipitate mass was noted - only 75% of the expected precipitate was obtained. Since this value does not fit into the trends followed by the other solutions, it can probably be explained in terms of experimental error. The results can be seen in table 2.2.3 and figure 2.2.3.

Sulphite-ammonia precipitation

On addition of the sodium sulphite suspension to the ammonia containing tannin solution, the pH was fairly high (cf 5.4.3). This indicated a decrease in the presence of any acid catalyst. However, the precipitate masses obtained here were higher than expected (table 2.2.4, figure 2.2.4). The high quantities of precipitate decreased as the sulphite concentration increased.

Thus, the precipitation occurred due to the effect of the ammonia in increasing the molecular weight (cf 2.2.2). The effect of the pH on the ability of the ammonia to form a bridge between tannin molecules, thereby increasing their molecular weight was noted. At high pH values, the reactivity of the RNH_2 fraction was almost equivalent to that of the NH_3. However, as the pH decreased, the reactivity of the RNH_2 group decreased, thus the molecular weight increase was smaller. The influence of the sulphite was twofold. On increasing the sulphite, the pH decreased slightly and this caused a noticeable decrease in the precipitate mass because of the effect on the ammonia (see above). In addition, the sulphite was employed in the dual function of redissolving and precipitating the phlobaphenes. Thus to prevent the precipitation of phlobaphenes, using sodium sulphite and ammonia, lower pH conditions must be induced.

From these results it can be seen that ammonia is not successful in preventing the precipitation of phlobaphenes when sodium sulphite is present.

Since sulphite and not acid is used in aiding the industrial extraction of pine tannins, ammonia will not effectively increase the yield of the extracted tannins by preventing the formation of phlobaphenes.

2.2.3 Effect of Urea on Phlobaphene Precipitation

Urea was added in solid form to the tannin solution and with stirring, dissolved with ease (cf 5.4.4). None of the physical characteristics of the solution appeared to have altered, neither was there a great change in the pH which remained in the tannin region of 4.4.

a) Acid-urea precipitation

As the volume of acid added to the tannin-urea solution was increased, the effects of the urea in inhibiting the phlobaphene formation became more noticeable (table 2.2.5, figure 2.2.5).

The inhibition of tannin condensation and phlobaphene formation could be explained as a combination of two effects. The urea was able to react rapidly with carbocationic centres presented to it by the tannin molecules. In so doing, the number of sites available to the tannin molecules for self-condensation were reduced. After the first reaction, the reactivity of the second reactive site of the urea was greatly reduced due to an alteration in the electronic effects. Thus, urea was not involved in increasing the molecular weight of the tannins to the same degree as the ammonia had been. This allowed less phlobaphene formation to be experienced. To a lesser degree, this effect could also be explained with reference to the pH changes. On the addition of the smallest volume of HCl (0.5 ml), there was a very slight change in the acidity of the solution but this was too small to be noticed in any great decrease in the quantity of precipitate obtained. As the volumes of acid added to the solution increased, it was noticed that the drop in pH expected, did not occur. This implied that a buffering effect by the urea was encountered. Whilst the urea was less effective than the ammonia in preventing a dramatic pH drop, the effects on the phlobaphene prevention were very similar. (Table 2.2.5, figure 2.2.5)

Both the urea and ammonia results demonstrated that the phlobaphene formation reaction was acid catalysed and by decreasing the acidity of the solution, the reaction could be inhibited.

b) Sulphite-urea precipitation

On the addition of sulphite to the tannin-urea solution, different pH effects were noticed. In the presence of small quantities of sulphite, the pH was increased quite markedly. As the quantity of sulphite increased, the urea was less effective in altering the pH from the sulphite induced value, which increased as the sulphite increased. Despite the increase in pH, the urea was effective in partially inhibiting the high pH induced phlobaphene formation (table 2.2.6, figure 2.2.6). This could be explained by the reaction between the urea and the tannin molecules (cf

2.2.3, a) A decrease of up to 40% in the phlobaphene mass compared with the value obtained with sodium sulphite only, was achieved. Thus the urea was able to inhibit the phlobaphene formation, not only by altering the pH but also due to its chemical reaction with the tannin, as seen in the results obtained in the sulphite precipitation reactions. the reaction between the urea and the tannin could have been a reaction similar to that occurring between formaldehyde and tannin. The alcoholic groups could leave the phenolic ring under the acidic conditions and the urea could react via its nucleophilic centre, attaching to the ring as a $-C(NH_2)_2OH$ functionality.

c) Effect of varying the urea concentration

Having established that urea was very effective in decreasing the phlobaphene precipitation, variations in the amount of urea used, were examined to establish if there were any urea concentration effects.

As the quantity of sulphite added was increased, the percentage of the tannin precipitated from the solution increased exponentially. (figure 2.2.7)

With a few exceptions, as the amount of urea added to the solutions was increased, so its effectiveness in depressing the phlobaphene formation became more noticeable. When the sulphite was present in its lowest quantities, the urea seemed to be most effective in reducing the precipitation of the phlobaphenes. A decrease in the phlobaphene yield of 75% was noted (table

2.5.7). The initial quantity of sulphite was approximately 3% by mass of the tannin solids in the solution, and resulted in 6% (by mass) of the tannin solids precipitating as phlobaphenes. On the addition of comparatively large quantities of urea, (2 g or 26% on tannin solids), the precipitation was decreased to only 1.6% on the tannin solids. While the loss of some precipitate may have occurred during centrifugation and the removal of the precipitate from the tubes for drying and weighing, the variations between the sample losses was probably quite low since the same procedure was used in each case.

As the amount of sulphite added to the system was increased, the urea's prevention effects became less linear. This may have been attributed to errors in the experimental procedure, or to a masking effect where the high percentage of sulphite added may have adversely affected the ability of the urea to prevent phlobaphene formation, since there seemed to be little comparison between the amount of urea added and its effects. In addition, the tannin solution consisted of so-called "sulphited tannin", extracted from the bark using 2.5% sulphite on the dry bark mass and then reacted with a further 2.5% sulphite (on the tannin mass) to improve the solubility of the tannin. The presence of this extra sulphite in the solution, prior to the addition of the urea and the sulphite in the precipitation reactions may well have had some influence on the lack of linearity of the urea effects on the phlobaphene precipitation.

Despite these complications, it can be seen (table 2.2 7) that the addition of urea does effectively reduce the phlobaphene precipitate and that its concentration does have an added effect which can be optimised for specific conditions.

2.3 Extrapolation of the Model Compound Results to the Extraction of Tannin from "pinus radiata" Bark

The bark used in these tannin extraction experiments was obtained from the Knysna-George region in South Africa, from trees 20-25 years of age.

2.3.1 Standard conditions

a) Sulphitation values

In setting up these extraction experiments, it was debated whether the reported 2.5% sulphite used in the extractions was based upon the mass of the water used in the extraction, the bark mass or the mass of the tannin expected to be recovered.
Each of these variations was tested in the soxhlet-type extraction (*cf* 5.5.1). The resultant extract masses seemed to indicate that the sulphite used should be based on the mass of water used in the extraction. Subsequently, it was discovered that the calculations should have been based on the mass of bark employed in the extraction. For this reason, experiments were performed in Chile to obtain correct data (*cf* 5.5.3, 2.4). In addition, the masses of the additives (phloroglucinol, urea and

m-phenylenediamine) were also calculated according to the mass of water used. (Tables 2.3.1 and 2.3.2). The mass of water used was approximately thirteen times greater than the mass of the bark and the tannin yield obtained was established using UV-visble spectroscopy. (cf 5.2.2, figure 2.3.2)

b) Establishing the optimal temperature conditions for the bark extraction

It was known that the conditions for the extraction of pine tannin from the bark included the operation at 70°C although the extraction time was unknown. In these experiments it was decided to operate at 70°C for three hours as the standard conditions.

A comparison to see the effect of temperature on the extraction showed that operating at both 50°C and 100°C gave results for the extraction which were an improvement on those obtained for the 70°C extraction (tables 2.3.1, 2.3.2).

This result was in direct contrast with results obtained at the University of Concepcion, Chile,[23] and could be due to one of several factors.

i) The variation in the bark of the pinus radiata species owing to different climatic conditions.

ii) The different methods used to extract the bark.

c) Extract properties

In all instances, the resultant extract liquor was pale yellow-brown in colour, not the expected dark tannin brown. After drying the solutions, the crystals were also shades of yellow and pale brown. In addition, if an additive such as urea or phloroglucinol had been used, these crystals were visible in the precipitate and had to be taken into consideration when calculating the yield of the extraction process. Generally, the precipitate was not completely dry after evaporation of the extraction liquor. Thus it was necessary to establish the mass of the precipitate using gravimetric analysis.

In some instances, the precipitate was not homogeneous and sampling errors were encountered during the gravimetric analysis.

d) UV-visible spectrophotometry

In order to establish the concentration of pine tannin in the extracts, UV-visible spectrophotometry was used (cf 5.2.2). Dissolution of the solid extract samples proved problematic, since they appeared to have undergone some physical changes during the removal of water, resulting in incomplete solubility. However, the undissolved fractions were filtered and weighed and were found to contain less than 1% of the sample being analysed.

A standard curve was obtained by measuring the absorbance of a series of pine tannin solutions of known concentration. The resultant curve obtained obeyed Beer's law (figure 2.3.2) and allowed the determination of the tannin content of the extracts.

Adhesive properties

In order to confirm the adhesive properties of the extracts, samples of each extract were dissolved and mixed with formalin and acid (*cf* 5.5.2). The combination of the formaldehyde in the formalin solution and the acid would allow those samples containing urea to gel due to both the reaction of the urea and less importantly, the tannin, with the formaldehyde in acid conditions. However, the conditions did not totally preclude the tannin from gelling without the presence of urea. Interestingly, the extracts obtained at temperatures other than 70°C did not gel possibly due to some temperature induced effects. Those extracts containing phloroglucinol and some of those containing urea did gel in the acidic conditions. However, certain urea-containing extracts did not gel. The reason for this lack of gelation could be attributed to a low concentration of urea which may have encountered some steric hinderance. In addition, if the urea concentration had been very high, the possibility of a second cross-linking with the tannin, such as experienced with ammonia might have occurred, lowering the reactivity of the urea with the formaldehyde. The possibility of non-homogeneous samples could not be excluded and these may have contained large quantities of unreactive components from the bark extracts.

2.3.2 Comparing the effects of phloroglucinol and m-phenylenediamine on the extraction efficiency.

a) m-Phenylenediamine

When m-phenylenediamine was used in addition to 2.5% sulphite (on the mass of water), the extraction yield of tannin appeared to increase ten times (*cf* 5.5.1, table 2.3.1, 2.3.2).
However, the extract was darker in colour than the others obtained. This colour was probably due to the colour of the m-phenylenediamine itself. The colour effect of the m-phenylenediamine may explain the relatively high tannin concentration (26.66E-2g/l) since it may affected the light absorbance of the sample (*cf* 5.2.2). However, the reactivity of m-phenylenediamine is known to be high and this too could explain the large proportion of tannin extracted. mPhenylenediamine was only used in one extraction since it did not dissolve completely and was problematic during the extraction, causing blockages in the pump. In addition, it is fairly costly and toxic, minimising its desirability for industrial use.

b) Phloroglucinol

Phloroglucinol was used in three extractions. An interesting observation made, was that there was very little change in the yield of tannin extract obtained despite the variation in the quantities of phloroglucinol used and the extraction time employed. In each of the extractions, the yield of tannin increased between six and seven times, compared with the sulphite-only extraction (tables

2.3.1, 2.3.2). Again, the similarities between the phloroglucinol and the tannin structure may have caused interference in the absorbance spectroscopy, especially since the mass ratio of the bark to the phloroglucinol was relatively high, in the region of 2:1. However, since the tannin concentrations obtained were three times less than that obtained with m-phenylenediamine, the absorbance interference was probably less important in the case of phloroglucinol.

2.3.3 The effect of urea on tannin extraction

The extractions with urea were repeated using varying quantities, times and temperatures. (cf 5.5.1, tables 2.3.1, 2.3.2)

a) Effect of varying the extraction time

At 70°C, using 1.5% urea on the mass of water used or 20% on the bark mass, a variation in the extraction time from one hour to three hours had a marked effect on the amount extracted (tables 2.3.1, 2.3.2). The one hour extraction yielded very low amounts of tannin. Only half of the tannin obtained in the sulphite only (three hour extraction), was obtained in the presence of both sulphite and urea for one hour. The lower yield was probably due to the decreased time of extraction, since in the three hour extraction using both the urea and the sulphite, the tannin yielded had doubled.

After two hours, the presence of the urea appeared to have no increased effect on the extraction process compared to the extraction using sulphite only. Again, this apparent lack of increased yield was probably due to the shorter reaction time rather than due to an inefficiency in the self-condensation blocking effect of the urea.

b) <u>Effect of varying the urea concentration</u>

Variations in the quantity of urea used in the extraction yielded interesting results (tables 2.3.1, 2.3.2). On halving the urea in the three hour extraction, the total tannin yield was seen to quadruple when compared to the extraction containing no urea. This increase in the extraction yield whilst decreasing the amount of urea seemed puzzling and was explained by the reasoning that urea too has its optimal value in the extraction process.

The function of the urea in improving the extraction was probably in preventing the tannin molecules from self-condensing with each other due to the elevated operating temperatures, and precipitating within the bark, prior to being extracted. Once the urea was increased beyond its optimal value, the extraction yield decreased owing, perhaps, to interference effects by the urea on itself, causing the formation of larger molecular weight tannin compounds which were unable to be extracted from the bark.

A further reduction in the quantity of urea used, (25% of that used originally), resulted in the same quantity of tannin being extracted as with the original amount - i.e. twice that obtained with only sulphite present in the extraction.

c) Temperature effects

At both 50°C and 100°C, the extraction yields were higher than at 70°C, for the extractions containing only sulphite in the extraction liquor. When urea was included in the extraction liquors for the extractions at these temperatures, interesting observations were made.

In both cases, the urea caused a decrease in the tannin extracted although the resultant extract was still higher than that obtained at 70°C.

i) 50°C

At 50°C, the extraction yield was three times that obtained at 70°C although only 77% was extracted compared with the sulphite only extraction at 50°C. The lower temperature appeared to afford a higher extraction yield in the extraction system used, although the reason for the lowering of the yield on the addition of urea seemed unclear.

ii) 100°C

The extraction yield using both urea and sulphite, at 100°C, was twice as high as the "standard" extraction conducted at 70°C in the presence of sulphite only. In comparison with the extraction conducted at 100°C in the presence of sulphite only, only 85% of the tannin was extracted, when urea was added. The increased yield at the higher temperature could be attributed to an increased solubility of the tannin due to the increased temperature. This increased solubility would have been in tension with the increased phlobaphene formation due to an increased reaction rate due to the higher temperature. The presence of sulphite in the extraction liquor would have aided the solubility since the extraction yield increased. The influences of the increased temperature on increasing the precipitation of phlobaphenes and causing an increased solubility effect of the sulphite is postulated in figure 2.3.3.

2.3.4 Second series of 'pinus radiata' bark extractions

In the first series of extraction experiments, a cellulose thimble was used to contain the bark within the glass soxhlet apparatus. The low extraction yield obtained in these extractions may have been attributed to absorption of the tannin by the cellulose thimble. A second series of experiments were conducted without using a cellulose thimble, to establish whether or not the cellulose extraction thimble had affected the results in the previous series of experiments (cf 5.5.1).

a) Changes in the extraction liquor

The first interesting observation made was that the extraction liquors were no longer pale straw coloured but were shades of red. This change in colour seemed to indicate that more tannin was contained in the solution than had been noted previously. In addition, the solutions contained slight suspensions. These could have had two sources. The formation of phlobaphenes during an extraction is neither unexpected nor surprising, since the presence of sulphite can cause phlobaphene precipitation. However in the small quantities being extracted, they would not precipitate as such but rather remain in suspension. The second potential source of the suspension could have been fine particles of bark which had escaped from the glass soxhlet apparatus into the main solution where their presence was noted.

b) Changes in the tannin content of the extracts

The second series of extractions yielded results which were more acceptable. As seen in table 2.3.4, the addition of urea to the extraction liquor resulted in almost twice as much tannin being extracted from the bark as achieved with only sodium sulphite in the extraction liquor. As the amount of urea added to the extraction system was decreased, so the amount of tannin extracted decreased. Thus while 3g urea added to the system caused a 90% increase in the tannin extracted when compared with the sulphite only extraction. Halving the quantity of urea resulted in only a 50% increase in the tannin extracted being achieved whilst quartering the urea achieved a 45% increase in the tannin extracted when compared with that extraction achieved in the presence of sulphite only.

These results demonstrated the effect of the urea in improving the extraction of pine tannin from the bark in the presence of sulphite.

2.4 Examination of the Effect of Urea on the Extraction of Tannin from "pinus radiata" D.Don - Laboratory Extractions conducted in Chile

Fresh bark obtained from pinus radiata D.Don, in Chile was used in these extractions.

Instead of pumping the extraction liquor through the bark using a modified soxhlet apparatus, the bark was stirred in the extraction liquor in a glass beaker for a period of one hour (cf 5.5.3). This allowed the tannin to be extracted without it being trapped in pipes and tubes in the apparatus.

2.4.1 Single extractions of the bark

The single extractions allowed a comparison between the quantity of tannin extracted with warm water only, that obtained in the presence of sulphite only and that obtained in the presence of sulphite and urea.

a) Tannin extracted (table 2.4.1)

With no additives present in the extraction liquor of the single extraction, 5.1% tannin on the basis of dry bark, was obtained. This increased to 7.9% (on dry bark) when sulphite was added to the liquor. A further increase of 0.8% extracted tannin was achieved when 2% urea was added to the system. However, when the urea was doubled with respect to the sulphite, there was no increase in the amount extracted. In fact, the effect of the urea seemed to be negligible and the extract obtained was equivalent to that where no urea and only sulphite was used. On doubling the amount of sulphite used (5%) and keeping the urea constant at the lower concentration (2%), the extract obtained was very high, in comparison with the other results obtained, at 10.5% tannin (on the mass of dry bark). The reason for this higher extraction result could be due to the solubilising effects of the sulphite, aided by the presence of the urea.

b) Phlobaphenes extracted (table 2.4.1)

The quantity of phlobaphenes precipitated in the presence of water only, was fairly low. (1.9%)
This can be attributed to the inefficiency of the water to extract large proportions of either the tannins or the phlobaphenes, without some "additive".
On adding sulphite to the extraction, the phlobaphenes precipitated doubled and 4% of the dry bark was obtained in phlobaphenes. This was expected, since the sulphite caused an decrease in the pH resulting in phlobaphene formation. In addition, the sulphite facilitated solubilisation by cleaving some of the heterocyclic rings and inserting $-SO_3H$ groups which increased the water solubility of the molecules.
As the urea was added, it caused a decrease in the phlobaphenes obtained. Although this decrease was small, it demonstrated that the urea did perform a valuable function in minimising the phlobaphene formation. This effect was even more noticeable when the quantity of urea used in the extraction was doubled (5%). In this instance, although the tannin extracted was the same as if no urea was present, the quantity of phlobaphenes was reduced

from 4% to 2.8%. This extraction demonstrated the usefulness of the urea in decreasing the phlobaphenes in the presence of sulphite.
When the sulphite was doubled (5%), the phlobaphenes precipitated also increased. This increased precipitate was not double that obtained when half the quantity of sulphite was used without the presence of urea. (5.2% phlobaphenes were obtained with respect to dry bark)
Rather, the presence of the urea had again inhibited the formation of phlobaphenes during the extraction in the presence of sulphite.

Thus the single stage extractions of the bark demonstrated that the urea was effective in increasing the tannin extracted and effective in minimising the phlobaphenes obtained during the extraction process.

2.4.2 Multi-extraction of the bark

In the "multi-extractions" (cf 5.5.3), the bark was extracted at 75°C by three consecutive solutions, each of which contained five times the initial dry mass of bark in water and 2.5% (on the mass of dry bark) each of urea and sodium metabisulphite After completion of the three stage extraction, the mass of phlobaphenes and of tannin in the extract was established and was found to total 33.5% on the dry bark mass. Of this, 25.4% was tannin extract and 8.1% was phlobaphenes. This is in comparison with a generally accepted sulphite only extraction of approximately 18%. The higher extraction of tannin indicated that the urea was very successful in improving the extraction of pine tannin by preventing the formation of large molecular weight fractions within the bark that could not be extracted. In addition, more effective stirring than is possible on larger scale and maintaining the temperature at 75°C within 0.2°C, also assisted in maximising the tannin extracted from the bark.

2.5 Industrial Implementation of Urea Assisted Tannin Extraction from the Bark of "pinus radiata" D.Don - Chile

2.5.1 Normal extraction conditions used at DITECO, Ltda

Generally, the pinus radiata bark employed in the extractions contains 20-25% moisture in summer and 30% moisture in the spring. Two to three tonnes of the bark (ie. 1000kg of dry bark) is mixed with water (five times the mass of the dry bark) to which 2% sodium metabisulphite (on dry bark mass) has been added. The extraction is a semi-batch process requiring up to ten hours. The freshness of the bark has been found to influence the extraction yield quite markedly[23]. Fresh bark, recently removed from the trees, can yield up to 18% tannin (calculated according to the dry bark mass) in the extraction. In contrast, old bark yields far less tannin due to the self-condensation of the tannin to higher molecular weight fractions in the living tree and oxidation of the tannin when exposed to the atmosphere for long periods of time[27]. In addition, light induced polymerisation of the tannins can occur resulting in the formation of phlobaphenes within the bark[28]. These are not extracted from the bark, even in the presence of sulphite, since their molecular weight is generally too great.

2.5.2 Industrial extractions conducted to establish the effectiveness of urea in the extraction liquor

The extraction procedure at DITECO, Ltda was slightly modified. The main reason for the modifications was the time limitation that existed for the extractions to be completed. In addition to this, relatively small quantities of the final product were required. Since the bark obtained contained a moisture content of approximately 50%, one tonne of bark was used in each extraction tank, effectively resulting in 500kg of dry bark being used (cf 5.5.4, 5.5.5, figure 2.5.1).

a) Sulphite only extraction - a standard

The first extraction was a conventional sulphite extraction where only sodium metabisulphite was used. The extraction was cycled through the extraction tanks as shown in figure 2.5.1. After the initial set-up, each mass of bark contacted five different extraction liquors, whilst each volume of extraction liquor contacted five different bark masses. This extraction procedure has been demonstrated industrially to yield the highest quantity of tannin for the smallest contact time without effecting excessive tannin wastage[20].

i) Tannin concentration

Before concentration, the extraction liquor contained approximately to 4.3% tannin solids. The solution had an exceptionally low viscosity (less than ten centipoises).

After concentration in an evaporator, the viscosity had risen to 4800cps and contained 48.4% tannin solids. This concentration was higher than that usually obtained in the factory after evaporating, but the reason for its occurrence was not elucidated.

Further sulphitation of the tannin was effected before spray-drying, since it improves the solubility of the dry tannin.

ii) Tannin sulphitation

In order to effectively compare the adhesive properties of the tannin, the tannin was further sulphited with an additional 2% sulphite on the mass of dry tannin, to a total of 4-5% sulphite. After sulphitation, the solution contained 49.2% tannin solids and the viscosity had been reduced to 1300cps.

iii) Viscosity related concentration effects

In both the initial concentration stage and in the sulphitation stage, the percentage of tannin solids obtained was considerably higher than those usually obtained in the factory.

This occurred since the viscosity achieved was lower than expected for the concentration of the tannin. One explanation for this could be that the bark was extremely fresh, approximately two days old prior to use. That the bark had not been exposed to either light or air very long before being extracted may have influenced the extraction and allowed the high concentrations of tannin in solution to be achieved. In addition, the exact age of the bark was unknown. If the bark had been from young trees (15-20 years of age), the distribution of the degree of polymerisation of the tannin would have peaked at a lower molecular weight than expected. The lower average molecular weight would explain the lower viscosity obtained for higher tannin concentrations.

b) Urea - sulphite tannin extraction

After the "sulphite-only" extraction had been completed, a second extraction, using both sulphite and an equivalent quantity of urea, was made (*cf* 5.5.4). The effects of the urea on the extraction were noticeable during the first stages when the concentration of the extraction liquor was found to contain 5.0% tannin extract, compared with 4.3% obtained in the sulphite only extraction.

i) Tannin concentration

The viscosity of the dilute extraction liquor was too low to be measured accurately but was found to be less than ten centipoises. This corresponded to an extraction of 4.8% tannin solids. During the evaporation, this increased to 47.7% solids and the solution had a viscosity of 3600cps.

This viscosity was considerably lower than that of the concentrated liquor from the extraction using sulphite only. The urea, in conjunction with the sulphite, lowered the viscosity of the solution more effectively than the sulphite alone. The lowering of the viscosity could have been due to the presence of the urea on the tannin molecules. Because the tannins had been blocked by the urea, they had been unable to condense greatly and increase their molecular weight and viscosity, as observed in the lowered viscosity.

ii) Further sulphitation

After further sulphitation (to 5%) of the urea-sulphite tannin extract, an interesting observation was made. The tannin concentration decreased slightly to 47.1% and the viscosity decreased to 1740cps. This slight decrease in the percentage of tannin solids in the concentrated solution is only a 1.2% decrease, and very likely due to experimental error rather than an extraction related alteration. However, the decrease in the viscosity is interesting since it is not as great a decrease as observed when the tannin extracted with sulphite and no urea was further sulphited. This lower decrease in viscosity again appeared to imply that the urea, while preventing polymerisation of the tannins, causing a decrease in the molecular weight, had increased the molecular weight slightly due to its own addition to the tannin molecules resulting in a slight increase in viscosity. The net result of these two effects was a decrease in the viscosity.

2.5.3 Effect of Urea on the tannin extracted

a) Yield obtained in sulphite only extraction

In the extraction using sodium metabisulphite without added urea, 12.4% tannin was obtained from the bark, according to the dry bark mass, when calculated on the dilute extraction liquor. 6.9% tannin was obtained from the bark when calculated according to the concentrated extraction liquor and after the losses sustained during spray-drying of the tannin solution, the calculated yield was 5.5%. (*cf* 5.5.5)

b) Yield obtained in urea-sulphite extraction

A yield of 13.8% tannin was obtained from the bark (on dry bark mass) when calculated according to the dilute extraction liquor. 7.9% of tannin was obtained in the extraction where urea was utilised, when calculated according to the concentrated extraction liquor. In comparison, the yield of tannin calculated according to the final mass of spray-dried tannin was 6.4%.

c) Comparison of the two yields

These values were lower than those usually obtained in the factory and could be due to one of several reasons.

i) Bark age and freshness

Not only is the extraction yield of tannin from the bark dependent on the time elapsed between the removal of the bark from the tree and its use in the extraction process (i.e. its freshness), but there is also evidence which suggests that the age of the tree from which the bark was obtained is important.[23] It has been demonstrated [23] that the optimal extractions are achieved when the bark is between 20 and 25 years of age. If the bark is too young the tannin yield is low due to the immaturity of the tree and of its defence system. If the tree from which the bark was removed is too old, the tannins have been exposed to a greater degree of light and air causing an increase in the phlobaphenes within the bark and therefore a decrease in the extractable tannin. Unfortunately, the age of the bark used in the extractions at DITECO, Ltda factory could not be established from the suppliers of the bark.

ii) <u>Bark "purity"</u>

The highest concentration of extractable tannin is found in the periderm and the secondary phloem of the tree, the so-called bark. The primary phloem and the inner hardwood or xylem contain relatively little tannin. During the automated bark stripping of the pine trees, a certain percentage of the resultant "bark" is actually hardwood and primary phloem. These fractions both contain cellulose which can absorb some of the tannin during the extraction process. Thus, the yield of tannin was decreased because of two main, bark-related reasons. The mass of bark added to the extraction tanks was assumed to contain only true bark. If the bark stripping yielded a relatively high proportion of hardwood, the actual tannin releasing bark was lower than was calculated and therefore, the yield of tannin would be lower than expected. The second reason also applies. If there was a high proportion of hardwood and primary phloem in the extraction tank, there would be a corresponding high proportion of cellulose present which could absorb some of the extracted tannin thus decreasing the yield even further.

iii) Production length

The length of the two extractions conducted were very short in comparison to those normally conducted in the factory and the plant had not stabilised. The shorter the extraction period, the lower the tannin yield since a fairly large proportion of the extraction liquor is "lost" in the pipes and vessels of the plant. As the time period for the extraction increases, so the losses become less important as a percentage of the overall extraction conducted. The short time for each of the extractions conducted (two days per extraction) only permitted approximately 25000 litres of extraction liquor to be obtained in each case, in comparison with the average 100000 - 200000 litre extractions conducted.

2.6 Examination of the Effect of Urea on Adhesive Performance of the Extracts

An important potential use for the pine tannin extract is in the field of wood adhesives. In order to establish the effects of the urea on the adhesive qualities of the extract, the extracts were utilised in adhesive formulations.

2.6.1 Percentage polyphenols in the extracts

The adhesive properties of any phenolic type resin which is to be cross-linked or hardened using formaldehyde, depend on the percentage of phenolic or polyphenolic groups. These -OH functionalities allow reaction of the phenol with the formaldehyde as depicted below:

$$2Ph\text{-}OH + HCHO \dashrightarrow Ph(OH)\text{-}CH_2\text{-}Ph(OH)$$

There is, however a second source of phenolic functional groups in addition to the phenol-like compounds important in the adhesive. This second group of alcohol-containing compounds consists of carbohydrates. Despite the presence of -OH functionalities in the carbohydrate fraction, these have been shown not to contribute significantly to the cross-linking of the resin.
In contrast, however, carbohydrates have been shown to decrease the strength of an adhesive if present in large quantities.[5]

a) Stiasny number determination to establish the percentage of polyphenols

A method of establishing the polyphenolic groups capable of being used in cross-linking the resin, is the Stiasny number determination (cf 5.2.3). The Stiasny number affords a percentage which can