phenolics can achieve results very close to optimum, thus making further fortification with other compounds unnecessary.

Addition of urea at the 4% level does not have any effect on the performance of the pitch–based resin. Urea can be added to pure phenolic resins at the 4% (or higher) level on total solids basis as a phenol substitute and a mechanism to cheapen the polymer costs, to shorten hot pressing times, and to enhance resin functionality on hardwood veneers. The improvement of the hot pressing time of the phenosolvan pitch–based resin appeared unlikely since the pressing time used in this study was already quite short; only 4 minutes for a 3–ply panel with 2.5 mm thick surface veneer. The standard pressing time of such panels when pure PF adhesives are used is 4.5 minutes. This relatively short pressing time is due to the high reactivity of the phenosolvan pitch. The functionality of the resin on hardwood veneer was also good; its specific adhesion to okoumé hardwood face veneers was good, resulting in high strength results. Thus, further improvement by the addition of urea seemed to be unlikely. Finally, evaluation of the effect of the urea on the economics of the resin can only be made once the cost of the final resin is determined. The fact that urea can act as a cost decreaser in the case of pure PF resins does not imply the same for the phenosolvan pitch–based resin because this resin is likely to have a lower price than the pure PFs.

The addition of commercial UF, 7% on resin solids basis, also appears to have no noticeable effect on the performance of the resin. When present at such a small level of addition, the UF resin is sufficiently protected by the phenosolvan pitch against water attack (c.f 2.7.4) and therefore, the resin does not lose its water resistance. The cost of UF resins is relatively low compared with exterior grade adhesives. There could be some economic advantage in its addition, especially if after further experimentation, the UF resin could substitute some of the PF fortifier which is currently used at the 20% level.

Extra fortification with both 11% wattle tannin extract or with 20% phenol–resorcinol–formaldehyde (PRF) resin does not improve the strength further. The fact that the addition of a high quality resin such as the PRF does not further improve the performance of the PF/phenosolvan pitch (20/80) mix implies that the mix has reached its optimum performance under the experimental conditions for glue–mix and test sample preparation used in this research program.

2.11 ASSEMBLY TIME TOLERANCE

Assembly time is measured from the time dry veneer is processed through a glue spreader until it is under pressure–curing (glueline strength development) conditions. The importance of assembly time is interrelated with the many factors involving solvent loss of the adhesive film. These factors include time, veneer moisture content, veneer temperature, prepress, ambient temperature, and adhesive spread. Certain factors affecting assembly time can be adjusted if necessary. These adjustments, such as the delay time before hot pressing or adhesive spread, are needed for the development of improved prepress tack and improving hot press curing of the plywood panels. If the delay time before pressing is too short, the adhesive film's solvent loss will not be great enough to thicken the adhesive film and preserve sufficient tack. If the solvent loss is too great, due to long delay times, the adhesive–wood bond after hot pressing will be poor due to poor flow of the resin–adhesive (dryout).

If pine veneer average moisture contents are greater than 5 or 6 percent, a longer delay time before pressing may be required for the phenolic adhesive film solvent loss to reach optimum levels. If pine veneer average moisture contents are zero to two percent, shorter delay times will be needed to prevent too rapid solvent loss from the adhesive spread prior to hot pressing.

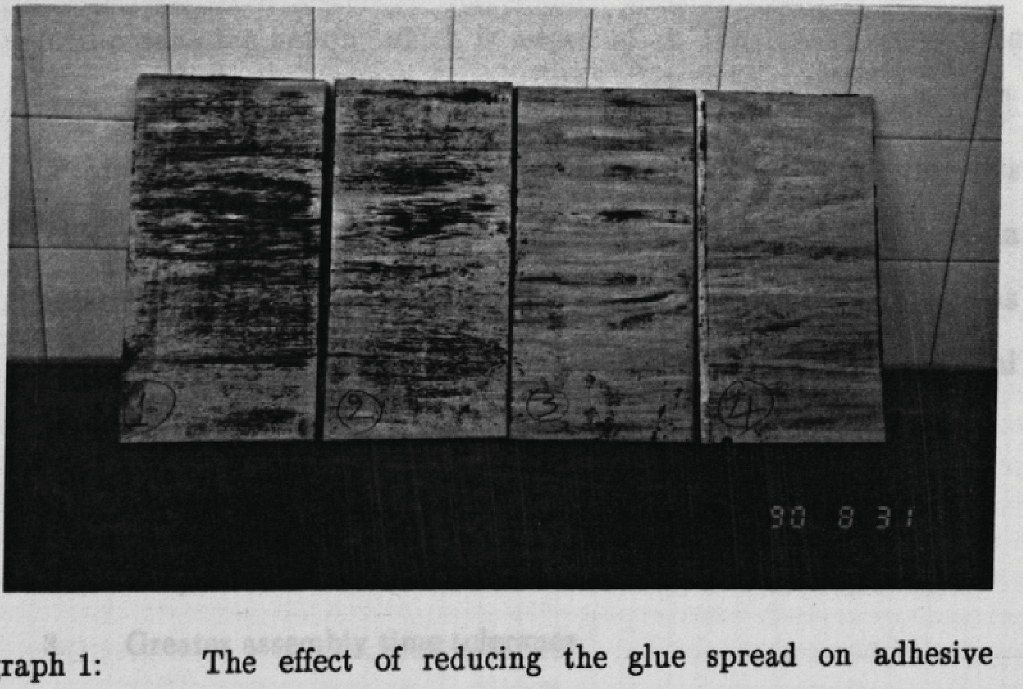
Veneer temperature has a dramatic effect on adhesive film solvent loss. By adjusting stand time, veneer temperature effects can be optimized. If veneer temperatures are too high (over 43°C), delay times may need to be shortened. If veneer temperatures are substantially below 20°C the delay times may need to be lengthtened. By adjusting delay times, prepress tack and adhesive–wood bonds are likely to be improved. Total assembly times used to produce satisfactory pine plywood are typically in the range of 20 to 45 minutes. High veneer and ambient temperatures, as well as very low veneer moisture contents, shorten the total permissible assembly time.

From the results of Table 2.27 it appears that the best results given by the PF/phenosolvan pitch (20/80) adhesive–resin are obtained when the total assembly time is between 1.0 and 1.5 hours. A 350 g/m^2 (double glue line) d.g.l. glue spread was used at a veneer moisture content of 3 to 4 percent. The assembly time tolerance of the pitch–based resin appears to be considerably longer than the assembly time of the usual resins used for pine plywood. The extended assembly time tolerance of the pitch–based resin can be attributed to the high content of cresols and xylenols in the phenosolvan pitch (30.7% of total pitch weight). Such substituted phenols are usually used at the 3 to 4 percent level to improve the assembly time tolerance of phenolic resins that exhibit dryout problems. The long assembly time that can be tolerated by the PF/phenosolvan pitch resins is therefore, of great advantage as far as dryout problems are concerned. However, such long assembly time required for optimum performance of the resin might be too long for a production line. Such a problem could be eliminated, or at least reduced by using some of the approaches mentioned earlier such as lower veneer moisture content and higher veneer temperature.

2.12 THE BLEED–THROUGH PROBLEM

During pressing, the PF/phenosolvan pitch adhesive penetrates through the face veneers and reaches the surface of the panel thus giving it a matty, spotty, black colour (see photographs below). Such plywood might still be used for industrial applications like shutter boards, provided it has the right strength, but its colour would definitely not allow its use for decorative applications. Bleed–through is associated with most industrial adhesives but to a much lesser extent. The bleed–through problem of the pitch–based adhesives is more acute because of its black colour. As explained earlier, the bleed–through of these adhesives can be attributed to the presence of large quantities of substituted phenols in the phenosolvan pitch (5.1% cresols and 25.6% xylenols). Cresols and xylenols are usually added to highly polymerized PF polymers at a 3 to 4 percent level to improve resin flow at the hot press. The bleed–through observed with the pitch–based resins could therefore, be attributed to excessive resin flow due to the strong presence of these flow promoters. Hence, the most obvious approach towards the reduction and possibly the elimination of this problem would be the removal of the cresols and xylenols from the phenosolvan pitch through distillation or other means. However, this approach would increase the production cost of the resin unless the marketing of the recovered chemicals could cover the extra costs. However, several other approaches were adopted in an effort to solve the problem without altering the composition of the phenosolvan pitch:

(i) Decrease of the amount of glue spread: it is quite logical and clearly demonstrated by the photograph below that the bleed–through decreases as the amount of the resin applied on the glue line is reduced.



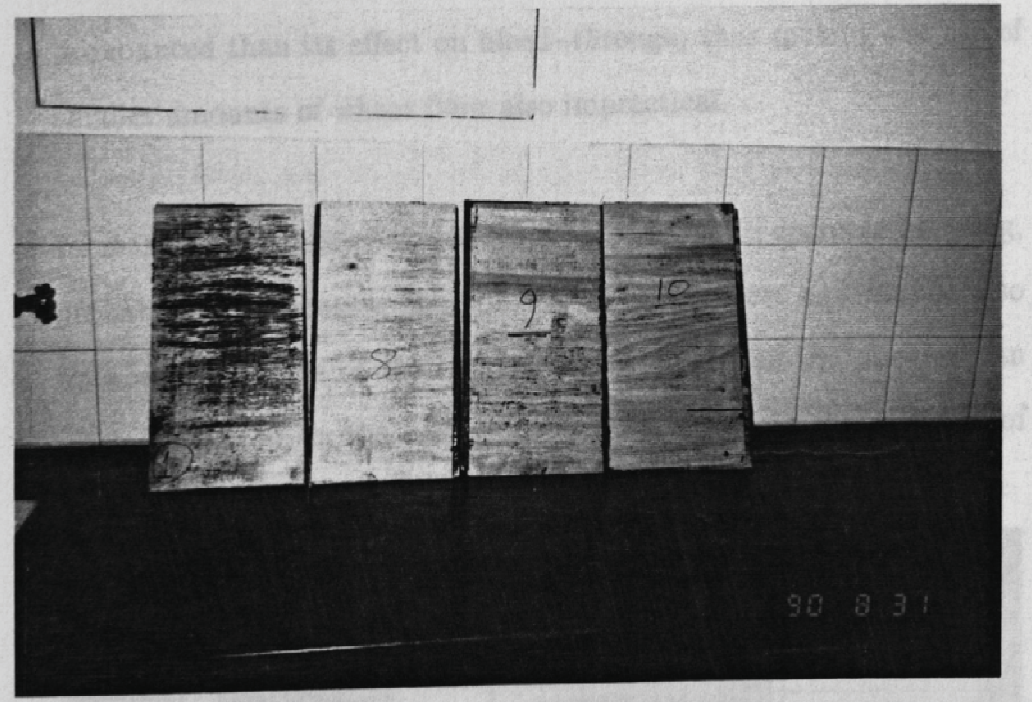
Photograph 1: The effect of reducing the glue spread on adhesive bleed–through. The glue spread was reduced by 50 g/m^2 d.g.l. per sample, from 400 g/m^2 d.g.l. in sample 1 to 250 g/m^2 d.g.l. in sample 4.

However, there is a limitation on how much one can decrease the glue spread without markedly reducing the strength of the panels. The shear strength results, Table 2.2.1 , indicate that the glue spread can be reduced from 400 g/m^2 d.g.l. used initially, to 350 g/m^2 d.g.l. without any greatly noticeable effect on the strength whereas further reduction of the amount of resin lowers the strength below the values required by the South African plywood standard specification (Table 2.15). However, there are strong indications that if optimized conditions of resin and sample preparation are used the glue spread could be reduced to 300 g/m^2 d.g.l. (Note: this series of experiments was done before optimization of pH, PF fortifier, veneer moisture content, assembly time etc.).

(ii) Extenders and fillers: according to the American Society for Testing and Materials (ASTM), an extender is a substance, generally having some adhesive action, which is added to an adhesive to reduce the amount of the primary binder required per unit area [37]. Proteinaceous and amylaceous materials are included in this category, and some of their more important rheological properties in adhesive mixes cannot be duplicated by lignocellulosic fillers such as the wood flour used throughout this research. These rheological properties applicable to plywood include [38]:

1. Tackier consistency (more wipe resistance)
2. Deeper adhesion on dense woods
3. Greater assembly time tolerance
4. Better resistance to overpenetration
5. Faster and stronger prepress bonds

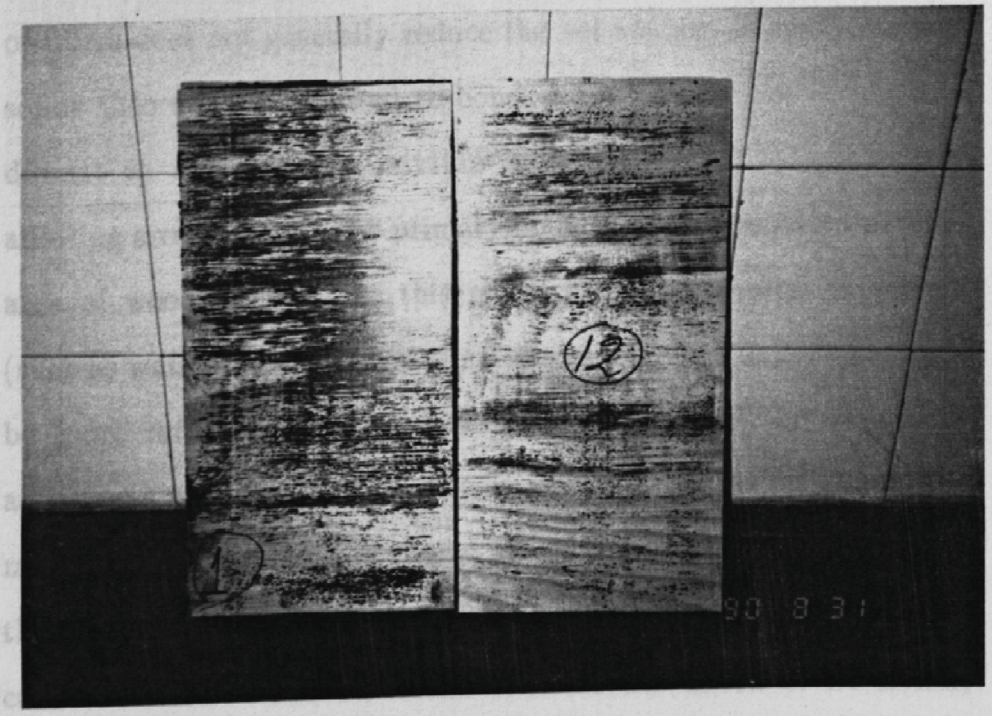
The reduction of bleed–through in panels 8, 9 and 10 (Table 2.20, photograph 2), demonstrates the improvement of resistance to overpenetration when cake grade wheat flour is used (2.4% by mass in panels 8 and 9, and 6.8% in panel 10).



Photograph 2: The reduction of bleed–through with the addition of amylaceous extender–cake flour (2.4% in samples 8 and 9; 6.8% in sample 10).

The strength also improves with the addition of cake grade wheat flour (Table 2.21), probably due to improved tack of the glue mix rendered by the starch and initial pregelling which reduces hot–press mobility of the phenosolvan pitch resin. The addition of wheat flour however, has a catastrophic effect on the water resistance of the resin, thus eliminating the possibility of using such products for exterior applications. Thus, the use of amylaceous materials for the reduction of bleed–through is not feasible for exterior grade products as it makes the resin susceptible to water attack. The effect of such an addition on the water resistance of the resin is much more pronounced than its effect on bleed–through, thus making the use of smaller amounts of wheat flour also impractical.

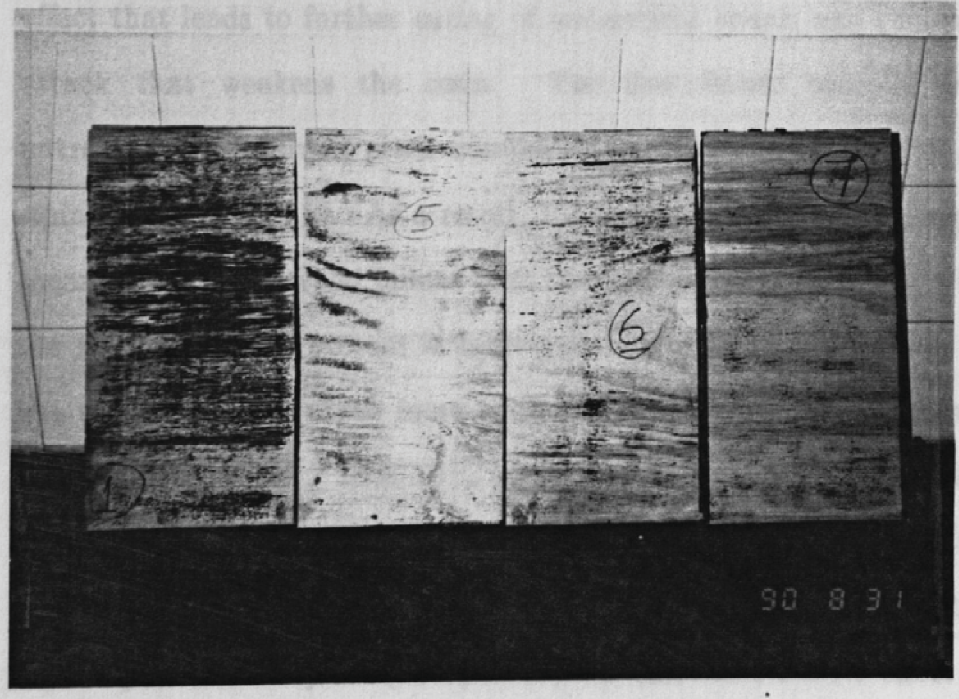
Increasing the amount of wood flour also helps to decrease bleeding, probably by decreasing the porosity of the veneers and maybe also by absorbing some of the high flow components of the phenosolvan pitch. This too, in the end, is a system to decrease the mobility of the resin during hot–pressing.



Photograph 3: Effect of increased amount of wood flour filler on bleed–through (4.8% in sample 1 ; 9.6% in sample 12).

A filler is a substance lacking adhesive capabilities which is added to an adhesive to improve its working properties, performance, strength, or other qualities [37]. Other qualities could include filling irregularities in the wood surfaces as well as decreasing porosity of the surface. Lignocellulosic and inorganic materials are included in this category. Fillers have the physical function, in the adhesive, to improve properties such as helping to control adhesive penetration into the veneer and to help to build up the level of solids into the mix. Fillers are particularly useful where rough and very dry veneer is used. Fillers help improve glueline wood failure with very low moisture veneer, and fillers help in the combination of smooth and rough veneer. The fillers are needed to give greater latitude to the adhesive in plywood processes, for structural plywood. The addition of fillers does not generally reduce the net amount of synthetic resin solids theoretically required to bond wood veneers, but it acts as a diluent to the adhesive mixture in a mechanical (physical) way allowing a reduction in the primary binder which is required per unit area of wood surface. In this sense, fillers are similar to solvent (such as water), in allowing a working property that otherwise would be more difficult. Fillers, like water, do extend the volume of adhesive mixture and often reduce the cost of the resin–adhesive mixtures. The addition of fillers, however, increases the viscosity of the glue mix, thus putting limitations on the maximum amount that can be added. However, if the adhesive can afford to be diluted further more fillers can be added after the addition of an excess of water.

(iii) Use of high Ring and Ball (RxB) phenosolvan pitch: Since high Ring and Ball phenosolvan pitch consists mainly of large molecular size species, its ability to penetrate through the surface veneers is lowered, thus reducing the bleed–through effect.



Photograph 4: The reduction of bleed–through by the use of high Ring and Ball phenosolvan pitch

Samples 5,6 and 7 (Table 2.20) demonstrate the reduction of bleed–through with increasing amount of high RxB pitch in the glue–mix. However, the samples strength weakens and the wood failure drops as the amount of the RxB fraction increases. This might be due to inefficient cross–linking between the large molecular size components of the high RxB fraction. The cold water resistance of the resin is assisted by these large molecules whereas under boiling conditions this trend is reversed; the larger the RxB fraction in the resin, the greater the vulnerability to hot water attack. This infers that the weather durability of the resin is badly affected by the addition of high RxB phenosolvan pitch. There are two opposing effects that occur during the boiling of the samples; (i) the heating effect that leads to further curing of undercured resins, and (ii) water attack that weakens the resin. The first factor prevails when untreated phenosolvan pitch comprises the main component of the resin (samples 1 to 5). As a result, the boiled samples exhibit higher shear strength and wood failure than the soaked ones. However, when the RxB fraction is present in large quantities (samples 6 and 7), the hot water attack is much more severe, thus lowering the strength of the samples. Sasol 2 RxB 76°C phenosolvan pitch was employed in this series of experiments as high RxB Sasol 1 phenosolvan pitch fails to produce samples of acceptable strength (Table 2.19). Lower RxB Sasol 1 phenosolvan pitch (RxB, 24°C) was also tried but its effect on bleeding was minimal, whereas the drop in strength observed was considerable.

In conclusion, the employment of Phenosolvan pitch with high R×B softening point can contribute significantly in the reduction of the bleed–through problem. The best combination of high internal bond strength of the final product and reduced bleed–through is obtained when 25 to 30 percent of the Sasol 1 Phenosolvan pitch is replaced with high RxB Sasol 2 Phenosolvan pitch.

(iv) Use of hardwood surface veneers: High density veneers differ morphologically and are much less porous than low density ones and therefore is more difficult for the adhesive to penetrate through and reach the surface of the panel. This is demonstrated by samples 11 and 13 (Table 2.20) where Tepa hardwood veneers, 1.5 mm thick, were used for the surfaces of the plywood panels.

Photograph 5 The reduction of bleeding by using hardwood surface veneers.

Sample 11 indicates that a great improvement in reducing bleed–through can be obtained by using hardwood face veneers. Sample 13 suggests that bleed–through can be completely eliminated by combining hardwood surface veneers with other factors which prevent bleeding such as inclusion of high RxB phenosolvan pitch and amylaceous extenders. The low strength results of the above two samples are due to the fact that Tepa veneers are very difficult to glue. The same tests were repeated with okoumé hardwood veneers (2 mm thick). Bleed–through was completely eliminated without the use of amylaceous fillers or high RxB phenosolvan pitch. Plywood panels with clean surfaces and high water resistance can, therefore, be produced from phenosolvan pitch–based adhesives. The fact that the use of a high RxB material is not necessary makes the process simpler and most probably economically more viable. The interaction between the resin and the okoumé veneers appears to be better than for pine veneers resulting in higher shear strength values and percentage wood failures. This could be due to better specific adhesion of the adhesive to okoumé, but also to the fact that the low porosity and very different cellular morphology of this hardwood helps to retain the adhesive on the glueline thus enhancing the bond between the veneers. When lower density veneers such as pine are used resin flow during hot–pressing causes a considerable proportion of the resin to "sink" into the veneer, thus starving the glueline and weakening the final bond.

Another important advantage of using okoumé as surface veneers is the reduction of the smell of the final product. All plywood samples prepared with phenosolvan pitch–based resin bear its characteristic strong smell of coal tar. The use of okoumé surface veneers minimizes this problem as it does not allow the resin to reach the surfaces of the panel, i.e. by eliminating bleed–through. Also, the escape of the volatile components from the glueline to the surface of the panel through the pores of the face veneers is limited by the high density of the okoumé veneers. The main route of escape of the volatile odour is then through thin glueline edges on the sides of the panel which, however, having a very small surface area, do not allow any strong odour.

Okoumé veneers are the standard hardwood veneers used in South Africa for top of the market marine–grade plywood and their availability is not problematic.

2.13 BAD ODOUR OF PANELS

All phenosolvan pitch–based resins carry a strong tar–like odour characteristic of the phenosolvan pitch. This odour constitutes a problem at two stages; (i) during sample preparation and hot pressing, and (ii) in the finished product. The odour developed during spreading of the glue–mix and hot pressing was initially a problem but after resin optimization and especially pot life extension, this problem was minimized. However, the final plywood panels made with pitch–based adhesive–resin still bear the characteristic tar smell of pitch. This smell is not too great a problem for plywood exclusively used in industrial applications but it had to be reduced in order for the products to suit other applications as well. This was achieved by resin optimization and mainly by minimization of the bleed–through. As discussed earlier (c.f. 2.12 – (iii)), the reduction of adhesive bleeding also minimizes the characteristic tar odour of the final product as less resin is exposed to the surface. This is best achieved when okoumé hardwood surface veneers are used, in which case the bleeding is eliminated. The bleed–through and the smell have also been gradually decreased as a result of optimization of conditions of resin preparation and its application onto pine veneers. However, if the remaining bad odour still poses a problem in certain applications, the approach of masking the smell of the pitch with a more pleasant smell could be adopted.

2.14 MOISTURE FLOW IN THE HOT PRESS

There are many process variables in plywood manufacture that prevent optimum adhesive–wood bonds.

The great majority of deficient bonds in pine plywood involve a form of adhesive dryout. Dry veneer below 3% moisture content can result in severely dried–out gluelines. When wood is glued at low moisture content, excessive moisture is lost from the adhesive film by excessive wetting of the veneer at ambient temperature due to such a low wood moisture content. The result, especially at long assembly times, will be dried–out gluelines that do not flow or transfer adequately when hot pressed. Another moisture–generated problem which can occur during hot pressing, but which is less frequent in pine plywood, is the occurrence of undercured and overpenetrated gluelines resulting from moist veneers and/or short assembly times. Undercuring and overpenetrating comprise some of the most common problems of the pitch–based resins. As discussed earlier (c.f. 2.11), this is probably due to the presence of a high percentage of cresols and xylenols in the phenosolvan pitch. Undercuring leads to low percentage wood failure in the shear strength testing of the samples whereas overpenetration is responsible for the bleeding problem.

When wood is glued at high moisture content, the adhesive film loses little moisture during assembly and usually overpenetrates the wood during hot–pressing due to its excessive mobility and flow at high temperatures. The gluelines may appear washed out or starved of adhesive, filtered, or graying from residue filler and possibly undercured [39]. This problem is very acute in the case of phenosolvan pitch–based adhesives since overpenetration is an intrinsic problem of the resin possibly due to its chemical composition. Hence, dry veneers (moisture content $\leq$ 2%) and long assembly times are required.

Even when veneers subjected to severe drying conditions which result in changes in surface wettability are glued, the sodium hydroxide in the resin and adhesive formulation improves the hygroscopicity of the surface of inactivated core–hardened veneers restoring to a degree the ability of the wood to absorb water from the adhesive [39]. Water is usually needed as a vehicle to transfer the adhesive film to the plywood veneers, but it also has to be eliminated or dissipated before proper adhesive–wood bonds can form and consolidate during the hot pressing. An understanding of the movements of water and water vapour in the panel during hot press curing of the adhesives is critical in successful plywood production.

2.15 THE EFFECT OF VENEERS PHYSICAL VARIABLES ON PLYWOOD STRENGTH

Several of the many variables in plywood manufacture that affect the adhesive–wood bond are associated with the wood veneers. Some of these variables such as moisture content and wood type have been discussed earlier. Several other variables, however, also play an important role in the quality of the final product. When, for example, the 4mm thick core veneer was replaced by a 3mm thick veneer the strength improved considerably. This can be attributed to several factors:

(i) the thicker veneer acts as a heat sink thus increasing the probability for undercuring of the resin.

(ii) the thicker veneers usually have rougher surfaces, thus facilitating excessive absorption of the resin by the veneer i.e. overpenetration. This results in loss of adhesive from the glueline and subsequent weakening of the sample. Higher glue spreads are needed in this case which in the case of phenosolvan pitch will exacerbate the bleed–through problem.

(iii) the freshness of preparation of the veneers is also quite important. The adhesive– wood bond is inhibited by oxidation of the surfaces of the veneers which comes with ageing. Using freshly cut veneers is, therefore, quite important in the establishment of strong adhesive–wood bonds.

In conclusion, the identification and monitoring of the veneer variables affecting adhesion is significant in successful plywood production.

2.16 POT LIFE

The PF/S1 phenosolvan pitch combination appears to give very good strength results that meet the requirements for exterior grade plywood. These results are obtained at pH $\simeq$ 12.5. However, the rate of curing of the mix under such highly alkaline conditions is very fast thus resulting in very short pot life (5 to 10 minutes). The short pot life did not pose any serious problems in the preparation of plywood test samples in the laboratory since each glue–mix was applied within a couple of minutes after its preparation. Such a short pot life, however, would impose serious problems in the event of industrial application where much longer time periods (~ 30 minutes) are required for the application of the glue–mix. Several approaches were used in an effort to lengthen the pot life and thus make the industrial use of this material more feasible.

(i) Lower pH: according to the very first findings of this work, the rate of reaction of the phenosolvan pitch with paraformaldehyde is strongly influenced by the pH of the reaction; the higher the pH the faster the reaction is. Therefore, the first approach in an effort to solve the pot life problem was to lower the pH. The pot life does improve at lower pH values but the resin also loses its strength. As indicated by the results of Table 2.25, in order to ensure strong bonding the pH of the glue–mix must be above 12.0. The pot life at pH 12.0, although slightly improved, is still too short for industrial conditions.

(ii) Use of solvents: as discussed earlier (c.f.2.5), water has an inhibitory effect on the reaction of phenosolvan pitch with formaldehyde.

Because of its availability and its low cost water was the first solvent that was employed in the effort to lengthen the pot life of the phenosolvan pitch glue–mix. A successful inhibition of the reaction and consequent lengthening of the pot life was achieved especially when large quantities of water were used. However, when water was employed at the 50% level or higher, the cured final resin lost its water resistance. Although the high strength values of the adhesive were maintained in the dry tests, boiling or soaking of the samples caused a marked decrease of their strength. Therefore, water can not be used as the sole means to improve pot life. Methanol was then combined with water as it has a stronger inhibitory effect on the reaction; it does so by slowing–down the release of formaldehyde from paraformaldehyde. Certain combinations of water/methanol gave considerably improved pot life results. The problem, however, can not be completely eliminated with the use of solvents; the excessive amounts that are required cause blistering and loss of strength of the final product.

(iii) Prereacted PF/phenosolvan pitch (20/80) mixture: the difficulty in controlling the rate of the reaction of phenosolvan pitch with paraformaldehyde is, at least partially, due to highly exothermic reactions between certain chemical groups in the phenosolvan pitch and paraformaldehyde. These reactions increase the temperature of the mix thus facilitating further reaction and rapid final curing of the resin. Thus, in a different approach to address the pot life problem these groups were prereacted with the PF fortifier before the addition of paraformaldehyde. Instead of simple mixing of the

PF with the phenosolvan pitch during glue–mix preparation the pitch and PF resin were refluxed together (c.f. 3.4.2.4) thus using up at least some of the highly reactive groups of the phenosolvan pitch. This resulted in much less exothermic reaction of the above resin with paraformaldehyde. As a result, the pot life was markedly improved and high strength results were obtained.

In conclusion, the short pot life problem of the phenosolvan pitch–based adhesive can be addressed by combining prereaction of the pitch with the PF fortifier and addition of solvents (~ 30% water + 10% methanol). Such a combination can ensure a pot life of ~ 50 minutes, thus making the industrial application of phenosolvan pitch feasible.

The use of complexing agents such as caprolactam did not have any noticeable effect on the pot life of the above glue–mix. Acetone was also employed but it was found to be less effective than that of methanol.

2.17 THE PREPARATION OF EXTERIOR GRADE PARTICLE–BOARD (PB) FROM PHENOSOLVAN PITCH–BASED ADHESIVES

Formulations based on phenosolvan pitch very similar to the ones tested for plywood were initially tried for the preparation of particleboard (PB) samples (Table 2.28). The phenosolvan pitch, as well as resins based on it, i.e. Resin 4C which is based on Sasol 1(S1) phenosolvan pitch and Resin 2 which is based on Sasol 2 (S2) phenosolvan pitch, were fortified with different compounds such as wattle tannin extract, pure PF and UF resins, raw polymeric 4,4′–diphenylmethanediisocyanate (MDI) and resorcinol. Wood chips were sprayed with the above glue–mixes at a level of 12% resin solids on dry solid wood and one–layer boards with the densities indicated in Table 2.29 were prepared. Contrary to plywood, the PB internal bond strength (IB) results which were obtained during the formulation scanning phase (Table 2.29) are generally low in the dry test whereas most of the samples fell apart after 2 hrs in boiling water. The best results were given by the samples fortified with either PF resin (sample 5), or MDI (samples 7,9,12,13). Resin 2 (sample 11) also showed promising results. Some glue–mixes were also used for the preparation of 3–layer boards (Table 2.30). 3–layer boards are generally stronger as the surface layers that are made of fine wood particles tend to increase dimensional stability and breakage resistance of the board. This is demonstrated by a comparison of the IB strengths of samples 5 and 7 (Table 2.29) with those of samples 8 and 7 (Table 2.31) correspondingly. The MDI/S1 phenosolvan pitch (30/70) sample improved from 0.45 MPa to 0.69 MPa and the PF/S1 phenosolvan pitch (20/80) sample from 0.18 MPa to 0.26 MPa. The increase in IB strength, however, is also partially due in part to the higher board density.

The results of Table 2.31 indicate that the PF resin is not a successful fortifier for the S1 phenosolvan pitch (samples 6 and 8). A combination of the PF resin with pitch Resin 2, however, brings about a drastic improvement of the resin; from 0.19 MPa (sample 4) to 0.54 MPa (sample 5).

MDI seems to be the best fortifier of S1 phenosolvan pitch and, therefore, several boards were prepared in order to investigate the potential of such a combination (Table 2.32). The results suggest that relatively strong boards can be obtained when the MDI is added at the 30% level. However, if the amount of MDI is reduced to 20% or the amount of glue–mix is decreased from 12% to 9% on wood chips basis, a marked drop in the board strength is observed. It seems that the ability of the MDI to act as a cross–linking agent is enhanced, thus giving better results, when the phenosolvan pitch is firstly resinified i.e. Resin 4C (samples 2 and 7). Reasonably high dry IB values (0.74 MPa) can be obtained with 30% MDI as a fortifier of S1 phenosolvan pitch when 12% glue–mix is used to prepare 3–layer boards (sample 4). According to the previous observation this value can be improved even further if the plain S1 phenosolvan pitch is substituted with either Resin 4C or Resin 2.

In conclusion, reasonably high dry IB results can be obtained either by Resin 4C or Resin 2 fortified with MDI or by Resin 2 fortified with PF at the 20% level. The results obtained, however, showed that all the phenosolvan pitch–based resins (Table 2.29) fail when exposed to boiling water and thus cannot be classified as exterior grade weatherproof boards. These results are in opposition to those obtained for plywood where similar glue–mixes gave weather resistant products. This difference in the results implies that the phenosolvan pitch–based resins are not fully water proof and the greater exposure of the resin to water attack in the case of PB makes it likely to fail whereas in the case of plywood, the resin being protected by the outside veneers and being exposed to water only at the edges of the sample, weather resistance is achieved by both glue and the construction of the panel. From the results obtained up to now, it seems that a considerable improvement in the water resistance of the phenosolvan pitch–based resins is necessary before they can be employed in the preparation of exterior grade

PB. Interior application of such boards, on the other hand, seems highly unlikely since the UF resins that dominate this field have several important advantages such as relatively low cost, white colour, no smell, and they require only short pressing times to give excellent dry strength results.

2.18 RELATIVE KINETICS

It would be of interest to be able to follow the reaction of the phenolic components constituting the phenosolvan pitch by kinetic means. Considering the great number of phenolic compounds present in the material the most usual approach would dictate that each single compound be separated and its characteristic reaction with paraformaldehyde be followed by kinetic techniques. The standard equation for second rate reactions i.e.

$$KT = \frac{2.303}{C_A^o - C_B^o} \log_{10} \frac{C_A \; C_B^o}{C_A^o \; C_B}$$

could then be applied and the rate of reaction of each component would be determined. However, the great number of different compounds present makes such a study very difficult and troublesome to carry out as exact percentages of each compound are not known, the variability of the raw material would indicate different behaviour with each batch and because the competitive interferences of each of the various phenols with the others will not be reproduced by single phenols kinetics.

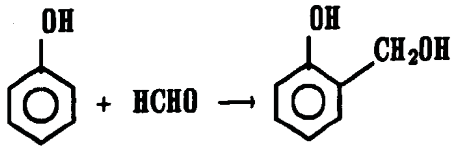
It was then decided to see if any information could be gained by performing kinetic work on the mixture of compounds, mainly on the reaction of the phenosolvan pitch itself with paraformaldehyde, and to follow the variations in relative quantities of the relevant chemical groups with time i.e. relative kinetics, by instrumental techniques. This was considered both an easier and more manageable approach as well as an approach of greater significance as regards the "real" industrial situation in which the reactions have to take place. It was not known if instrumental analytical techniques could give enough information to allow a kinetic study of the reactions to be carried out. It is understandable that this was a difficult analytical undertaking.

Infra red (IR) spectroscopy was the technique finally chosen as being able to give, rapidly during the course of the reaction, significant information on the increase and decrease of certain chemical groups which could definitely be assigned to particular molecular species. To this purpose during the preparation of resin 4C (c.f. experimental paragraph 2.4.2.3) samples were taken at 10 minutes intervals and 1R spectra taken. On examination of the spectra (spectra 9–15) the bands at 740, 770, 800, 815, 930, 1020, 1080, 1105, 1235 and 2900 cm^{-1} were found to vary consistently with the reaction time. Table 2.34 shows the peaks depth observed for 30 minutes reaction time for resin 4C. In Table 2.33 the assigned significances to specific chemical groups present in the material are listed. The most indicative IR bands can be assigned on the basis of the appearance and disappearance during the reaction of aromatic nuclei of different levels of substitution. Thus, the bands at 800 and 815 cm^{-1} do represent the relative reaction as a function of reaction time of 1,4–disubstituted and 1,2,4–trisubstituted aromatic nuclei respectively. The two bands at 740 and 770 cm^{-1} represent the variation during the reaction of 1,2–disubstituted and 1,2,3–trisubstituted aromatic nuclei respectively. The band at 930 cm^{-1}

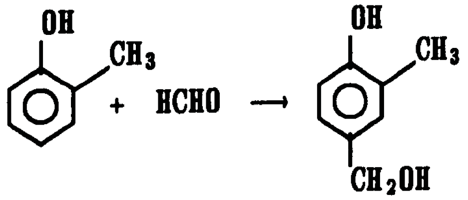
indicates quite clearly the decrease of formaldehyde during the reaction. The band at 1105 cm^{-1} is characteristic of methylene ethers $-CH_2-O-CH_2-$ formed during the initial ambient– temperature stage of the reaction and their decrease during the higher temperature period, this being due to their instability. This instability is demonstrated by the corresponding curve in Fig.2.5. The 1020 cm^{-1} band is instead representative of the methylol group and this band shows the increase in methylolation of the mixture of phenolic compounds as the reaction with formaldehyde proceeds. The band at 1080 cm^{-1} is characteristic of 1,3–disubstituted aromatic nuclei; it is then, for phenosolvan pitch, characteristic of the variation in the reaction of m–cresol. The 1235 cm^{-1} band is characteristic of the $>C-O-$ bond in phenols while the 2900 cm^{-1} band, although it is not too variable, is also an indication of the variation of the formaldehyde content in the reaction mixture. The 1460 and 1500 cm^{-1} bands are respectively an indication of $-CH_2-$ and CH_3- groups (the 1460 cm^{-1} band) and of $-CH_2-O-$groups (the 1500 cm^{-1} band). While the 1460 cm^{-1} band does not appear to give any reliable or interpretable variation there appears to be some significant variations for the 1500 cm^{-1} band. The presence of the small bands at 1360 and 1340 cm^{-1}, although their variation is not present or vary very little indeed, indicate in the mixture and in the resin that isopropyl groups are present as side chains of some of the phenolic species in the phenosolvan pitch although their amount appears to be very small; there are probably present as side chains of some of the phenolic species in the phenosolvan pitch although their amount appears to be very small; there are probably present on some of the higher molecular weight C_3 phenols (c.f. Table 2.33). The band at 1225 cm^{-1} is of particular interest, not to follow the reaction with formaldehyde, but because this band is characteristic of a C–O–C grouping indicating that (i) phenoxy–

coupling of reactive phenols is present in the 40% higher molecular weight fraction of unknown nature and that (ii) at least part of the 40% unknown fraction is composed of phenolic material in small polymers state and polymerized by phenoxycoupling in the original phenosolvan pitch. This is confirmation, by a different route than the applied behaviour of the pitch, that polymeric compounds may well be present in the 40% unknown fraction.

The variation during manufacture of resin 4C, of the different compounds is illustrated graphically in Figures 2.5; 2.6; 2.7. It is important, however, to observe here that the increase or decrease during reaction of trisubstituted and disubstituted species is not a direct indication of the reaction of single well defined compounds. For instance, during reaction 1,2–disubstituted compounds both form and disappear as a consequence of the reaction with formaldehyde. Thus phenol reactivity with formaldehyde will contribute to the promotion of 1,2 ortho disubstituted aromatic nuclei, while o–cresol will contribute to the decrease of the 1,2 ortho disubstituted aromatic nuclei as it transforms itself to trisubstituted aromatic nuclei; in short graphically



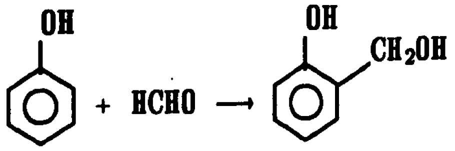
increase amount and IR band
of disubstituted aromatics



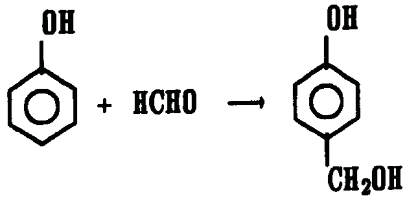
decrease amount and IR band
of disubstituted aromatics

From this the conclusion is that many of the curves presented in Fig.2.5 are composite of the two effects, one adding and one subtracting to the intensity of the respective IR bands. In the example illustrated it is logical that the corresponding curve shown in Fig.2.5 should increase as the reactivity of phenol towards formaldehyde is higher than that of o–cresol. This is indeed the case. Such reasoning is appropriate for most, but not all, of the curves presented in Fig.2.5.

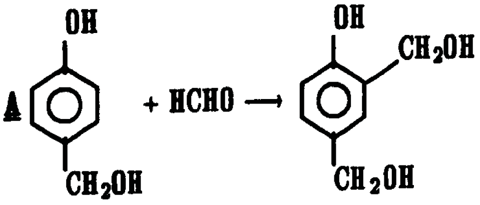
There is no doubt that mathematical manipulations of the raw data in conjunction with the knowledge of both the composition of the 60% known fractions of the pitch and of the likely reactivity of each of the monomeric phenols present in the same fraction will allow the determination of approximate rate constants for some, if not for all, of the reactions while occurring in the phenosolvan pitch/formaldehyde system. The possible reactions in the system are as follows:

1) 

1,2 disubstituted -----→ 4)

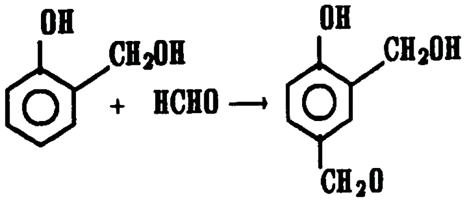
2) 

1,4 disubstituted -----→ 3)

3) 

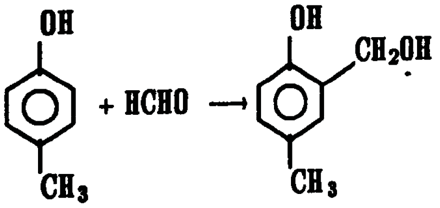
1,2,4 trisubstituted -----→ 8)

4) **B**



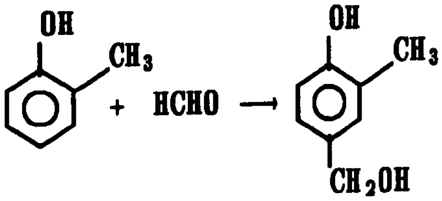
1,2,4 trisubstituted -----→ 8)

5) **C**



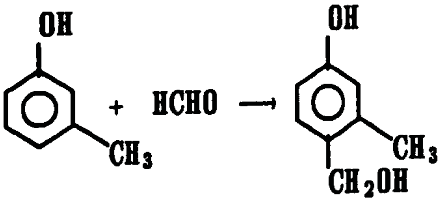
1,2,4 trisubstituted -----→ 8)

6) **D**



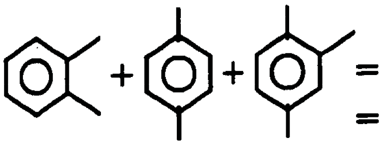
1,2,4 trisubstituted -----→ 8)

7) **E**



1,2,4 trisubstituted -----→ 8)

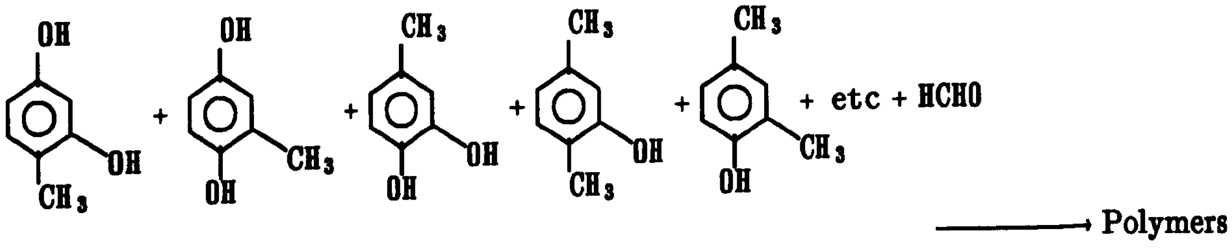
if at time = 0; CH_2OH band = 14 and



= 8 + 6,5 + 6.0
= 20 . 5

and

8) Band of 1,2,4–trisubstituted = 6.0 depths; then



Reactions 3,4,5,6 and 7 are truly a set of parallel reactions. Thus, if F = formaldehyde

$$A + F \longrightarrow G$$
$$B + F \longrightarrow G$$
$$C + F \longrightarrow H$$
$$D + F \longrightarrow I$$
$$A + F \longrightarrow J$$

$$\frac{dC_{G_1}}{dt} = Kg_1 [A][F]$$
$$\frac{dC_{G_2}}{dt} = Kg_2 [B][F]$$

$$\frac{d(C_{G_1} + C_{G_2})}{dt} = (Kg_1 + Kg_2).[A][B][F]^2$$
$$\frac{dC_G}{dt} = Kg_2 [A][B][F]^2 \text{ with } Kg = Kg_1 + Kg_2$$

For this we have to assume that the areas of the bands and hence their depths are proportional to the concentration of the compounds. This may well not be the case, but no better approximation can be thought with such a complex system. Therefore, taking the depth of the respective bands as

[A] = 6.5 squares
[B] = 8 squares
[F] = 12.5 − 2 = 10.5 squares
$[F]^2 = 110.3$

Compounds A and B will definitely be exhausted after 25 minutes of reaction, while the depth of the band of the formaldehyde F varies from 12.5 squares at time = 0 to 2 at time = 25 minutes. Then

$\Delta A = [A] = 6.5 \text{ squares} - 0 = 6.5$

$\Delta B = [B] = 8 \text{ squares} - 0 = 8$ and

$\Delta F = [F] = 12.5 \text{ squares} - 2 \text{ squares} = 10.5$ squares, thus

$[F]^2 = (10.5)^2 = 110.3$

ΔC can be measured by the increase of the band of 1,2,4 trisubstituted phenols as it can be assumed that most of the reactive trisubstituted phenols existing at the beginning of the. reaction are already reacted to polymers. The unreactive ones will remain unaffected and the increase in trisubstituted phenols will thus mainly be due to the reaction of the monomethylol phenols to 1,2,4 trisubstituted phenols. As the band at 815 cm^{-1} increases from 6.0 squares to 15 squares in 25 minutes (1500 seconds). Thus,

$$\frac{\Delta C}{\Delta t} = Kg[6.5][8][110.3]$$

$$\frac{15-6}{1500} = Kg[6.5][8][110.3] \qquad Kg = 1.05 \times 10^{-6} \text{ squares} \times \text{sec.}^{-1}$$

We can then propose that as the maximum theoretical amount of phenol is 1,7% of total phenosolvan pitch (Table 2.1) then the total amount of monomethyol phenols A and B produced at maximum can be 1.7% of total reaction mixture.

(Total reaction mixture = 33.3g pitch + 3g paraform. + 1g NaOH solution + 7.5g methanol = 44.8g).

Thus, phenol concentration on total mix will be

0.017 (1.7% phenol) × 0.60 (60% fraction) × 33.3g = 0.3397g

$$\text{Concentration} = \frac{0.3397g \times 1000g\ \ell^{-1}}{94.11g\ mol^{-1} \times 44.8g} = 0.0806 \text{ molar}$$

As 0.0806 molar can at maximum form 0.0806 moles of the two monomethylol phenols A and B and such components are certain to have progressed to trisubstituted nuclei at 25 minutes of reaction, then assuming a parallel reaction between phenol and paraformaldehyde, 12.5 – 2 squares = 10.5 squares could be equivalent in proper units to 0.0806 moles of compound; on this basis the approximate Kg would thus be of the order of

$$Kg = 0.0806 \times 1.05 \times 10^{-6}/10.5 = 8.06 \times 10^{-9}\ \ell mol^{-1}.sec^{-1}$$

This is a very approximate representation of the reaction, in such a mixture, thus with all the interference of the other phenolic material, of the two monomethylol phenols to 1,2,4 trisubstituted aromatic nuclei. The rate constant of monomethylol phenols in their pure state to form trisubstituted nuclei are respectively (c.f. Table 1.1)

p—monomethylol phenol → 2,4 disubstituted phenol $K = 7.5 \times 10^{-6}$
p—monomethylol phenol → 2,6 disubstituted phenol $K = 7.3 \times 10^{-6}$
o—monomethylol phenol → 2,6 disubstituted phenol $K = 8.7 \times 10^{-6}$
$\ell \times mol^{-1} \times sec^{-1}$

Considering the heavy approximation taken, the above still indicates that the reaction of the monomethylol phenols is much slower in the multicomponent mixture of phenosolvan pitch. This is probably due to the much faster reaction of the faster phenols with formaldehyde. It is interesting, however, to compare the Kg value obtained above with those of cresols the measurement of which just follows.

The calculations can become slightly more accurate in the use of the group of cresols where the concentration of the sum of the three cresols is known from the analysis of the phenosolvan pitch.

As approximate relative kinetics can be calculated also on the appearance and disappearance of differently substituted aromatic nuclei not only on the basis of the concentration of compounds present, we can postulate for the other reactions that H = I = J = G (cresols going to tetrasubstituted aromatic nuclei which are not detected by IR) and that only the reactions of compounds C,D and E exist at time = 1st period (time = 0 for these reactions).

Thus $C + F \rightarrow G$

$D + F \rightarrow G$

$E + F \rightarrow G$ then

$$\frac{\Delta C_G}{\Delta t} = K_g\,[C][D][E][F]^3$$

because the number of squares at the beginning of the reaction for the three cresols are

m – cresol = 14 squares = 49.1%

0 – cresol = 8 squares = 28.1 %

p – cresol = $\underline{\text{6.5 squares}}$ = 22.8

total = 28.5 IR band squares

But the concentration in the total mixture of the monomeric cresols is 8.5% on the 60% known fraction of the pitch thus 5.1% on total pitch and the total mixture is 44.8g for 33.3g pitch. The concentration of the cresols would then be 3.79% of which 1.86% is m–cresol, 1.06 is 0–cresol and 0.87% is p–cresol. Their molar concentration in the mix will then be

$$\text{m–cresol} = 1.86\% = 18.6\text{g } \ell^{-1} = \frac{18.6\text{g}\ell^{-1}}{108 \text{ g mol}^{-1}} = 0.172 \text{ mols } \ell^{-1} \text{ m–cresol}$$

$$\text{o–cresol} = 1.06\% = 10.6\text{g } \ell^{-1} = \frac{10.6\text{g}\ell^{-1}}{108 \text{ g mol}^{-1}} = 0.098 \text{ mols } \ell^{-1} \text{ o–cresol}$$

$$\text{p–cresol} = 0.87\ \% = 8.7\text{g } \ell^{-1} = \frac{8.7\text{g}\ell^{-1}}{108 \text{ g mol}^{-1}} = 0.081 \text{ mols } \ell^{-1} \text{ p–cresol}$$

$$[\text{HCHO}] = \frac{3}{0.0448} = 66.96\text{g } \ell^{-1} = \frac{66.96\text{g}\ell^{-1}}{30.03\text{g mol}^{-1}} = 2.23 \text{ mols } \ell^{-1} \text{ HCHO}$$

$$\frac{\Delta C_G}{\Delta t} = \text{Kg } (0.172 \times 0.098 \times 0.081 \times [2.23]^3)$$

In 25 minutes (1500 seconds) the m–cresol band changes from 14 squares to 2.5 squares. As no meta substitution is present in the formation of monomethylol phenols this band should only vary with the reaction of concentration of m–cresols as it reacts. If the $[E_0]–[E_t]$ = 14 squares – 2.5 squares = 11.5 squares, it means that the concentration of m–cresol has passed from 0.172 mols ℓ^{-1} to 0.0307 mols ℓ^{-1}. Thus,

$$\frac{\Delta C}{\Delta t} = \text{Kg[m–cresol][HCHO]}$$

$$\frac{(0.172 - 0.0307) \text{ mols } \ell^{-1}}{1500 \text{ sec}} = \text{Kg } 0.172 \text{ mols } \ell^{-1}\ 2.23 \text{ mols } \ell^{-1}$$

$$\text{Kg} = 2.46 \times 10^{-4}\ \ell \text{ mol}^{-1} \text{ sec}^{-1} \quad \text{m–cresol}$$

This rate is comparable with values obtained by proper kinetic studies for m–substituted alkylphenols [40] and is well comparable to the phenol Ks (6.2 and 10 × 10^{-6} ℓ mol^{-1} sec^{-1}) of methylolation reactions. The Kg of the 0– and p–cresol cannot be evaluated because of the o– and p–disubstituted benzene rings. Curves attained by IR do not indicate the amount that is reacted at time 1500 seconds.

In conclusion one can see that the reaction of monomethylolated phenols appears to be affected (reduced) by the presence of more highly reactive phenols. Thus the Kg of monomethylolated phenols are of 7.5×10^{-6}, 7.3×10^{-6} and 8.7×10^{-6} ℓ mol^{-1} sec^{-1}. Fast reacting phenols, such as m–cresol, do not appear instead to lose reactivity by interference as the Kg of 2.46×10^{-4} ℓ mol^{-1} sec^{-1} is of similar order of magnitude as that of the pure compound.

The reaction of preparation of resin 4C was repeated at constant temperature. Tables 2.35 and 2.36 represent the change in band intensity as a function of time at constant reaction temperatures (40°C and ambient temperature correspondingly). These changes are also demonstrated by Figures B (40°C) and C (ambient temperature). The rate of change of the concentration of the different components is very similar in all three cases thus implying very little dependence of the reaction on temperature. Whether the reaction is carried out at 40°C or under increasing temperature the curves reach their maxima in about 25 minutes. The rate of change at room temperature is also quite fast with maximum concentrations reached 25 to 30 minutes after reaction initiation. The rate of decrease of formaldehyde (930 cm^{-1}) and 1.3 disubstituted benzene rings (1080 cm^{-1}), however, provide a better evidence of the effect of temperature on the reaction as the temperature increases from room temperature to 40°C to reflux (78°C), the above two graphs reach their minima in 1 to 1½ hour, 25 minutes and 15 minutes correspondingly, thus demonstrating a considerable increase in reaction rate with increasing temperature.

CHAPTER THREE

3. EXPERIMENTAL

3.1 MATERIALS

3.1.1. Phenosolvan pitch

Phenosolvan pitch is a co–product obtained by SASOL in the petrol–from–coal process and it is a mixture of a great number of phenolic compounds. Table 2.1 reveals the composition of the 60% of the SASOL 1 phenosolvan pitch. This is the result obtained by gas chromatography (GC) analysis. The remaining 40% of the material could not be identified probably because of the too high molecular weight of the remaining constituents that comprise this fraction.

Phenosolvan pitch is insoluble in water but dissolves very well under highly alkaline conditions (pH > 10.5). Methanol and acetone are two other very good solvents that have been employed during the course of this research project. The phenosolvan pitch from SASOL 1 (S1) plant is characterized by high viscosity which varies from one batch to another; some samples can flow well at room temperature (~ 25°C) whereas others are in a semisolid state and they can flow only when heated to about 40°C. The phenosolvan pitch from the SASOL 3 (S3) plant has very similar appearance to that of S1 samples whereas the one from the SASOL 2 (S2) plant is considerably different; it is a low viscosity liquid at room temperature. The trend based on the appearance of the three different samples is also followed by their chemical reactivity toward paraformaldehyde. The fast reactions indicated by the pot life and gel time tests (Tables 2.2 to 2.5) are indicative of the high reactivity of S1 and S3 samples. Untreated S2 phenosolvan pitch, on the other hand reacts much slower (Table 2.11). However, when the volatile monomeric components are distilled off, a faster setting time is obtained probably because the remaining sample consists mostly of polymeric components and hence not much cross–linking is required for the material to set. An interesting observation is that when the samples from the three different plants are evaporated to the same "Ring and Ball" consistency, their reactivity is not only increased but also equalized (Table 2.11): at pH 9.8 the gellation time (c.f. 3.3.2) of the S1 and S3 samples is 5 minutes. When the samples are evaporated to 50°C Ring and Ball (RxB) consistency the gellation time is reduced to just 90 seconds. This effect is much stronger in the case of S2 phenosolvan pitch where the gellation time is reduced from over 20 minutes for the untreated sample to only 90 seconds for the RxB 50°C sample. The reactivity pattern is also demonstrated by the infrared (IR) spectra of the different samples. The similarity in the reactivity of the different S1 and S3 samples (Tables 2.2 to 2.5) is implied by their IR spectra which are almost identical (spectra 1 to 4). The different reactivity of the S2 phenosolvan pitch is also demonstrated by its IR spectrum (spectrum 5) which is quite different from the other spectra. Furthermore, the equalization of the reactivity of S1 with that of S2 is also demonstrated by IR spectroscopy; S1 RxB 28°C and S2 RxB 28°C exhibit very similar spectra (spectra 6,7), thus justifying their similar chemical reactivity toward formaldehyde as demonstrated by Table 2.11 (lower RxB samples were used for spectroscopy as they were easier to obtain spectra from). The above IR spectra indicate that the main difference between S1/S3 and S2 phenosolvan pitches is the much higher content of 1,2 (740 cm^{-1}); and 1,4 (800 cm^{-1}) (spectra 1,4 and 5) substituted benzene compounds in the S2 phenosolvan pitch. According to Table 2.1 these components are probably cresols (1,2 and 1,4 disubstituted benzene nuclei). These compounds act as diluents rendering the S2 pitch its low viscosity and slow reactivity toward formaldehyde. When some of these components are removed, the remaining S2 phenosolvan pitch exhibits similar IR spectra and reactivity toward formaldehyde (Table 2.11) to that of S1 and S3 pitch samples. However, the shear strength results in Tables 2.17 and 2.18 demonstrate that whereas S2 RxB 52°C pitch can give strong panels, S1 RxB 50°C cannot. This suggests that the S2 pitch probably contains chemical groups capable of more efficient cross–linking thus increasing the strength of the cured resin.

High RxB samples i.e. RxB 50°C are solid at room temperature. However, if they are melted by heating and sufficient NaOH solution is added to them while still hot and then allowed to cool they remain liquid and thus easily workable at ambient temperature.

Although all three phenosolvan pitches (S1, S2 and S3) as well as different RxB samples were examined, the main purpose of this research was the utilization of S1 phenosolvan pitch for the formation of a new class of exterior grade wood adhesives.

3.1.2 Benzene derivatives

3.1.2.1 Phenol

M.W. 94.11 g/mol; colourless solid; crystalline form rhombic needles; refractive index 1.54247 at 40.6°C; density = 1.072 g/ml at 20°C; melting point 41°C; boiling point 182°C; infinitely soluble in water from 66°C.

3.1.2.2 Resorcinol

M.W. 110.11 g/mol; density = 1.285 g/ml at 15°C; melting point 110°C; boiling point 276.5°C; solubility in water = 229 g/100 ml at 30°C; ordinary technical grade (purity 99%) resorcinol in the form of flakes was used.

3.1.3 Paraformaldehyde

A white solid with the characteristic irritating odour of formaldehyde. It is a mixture of polyoxymethylene glycols having the type of formula $HO(CH_2O)_nH$, in which the value of n ranges from approximately 8 to 100.

The above represents the accepted chemical definition of paraformaldehyde and corresponds to an HCHO content up to 99%; the balance consisting of combined water. It dissolves in water with depolymerisation and hydration to yield formaldehyde solution. The rate of solution increases with temperature, but decreaseswith increasing molecular weight. The pH of the solvent medium is important. The rate at which paraformaldehyde dissolves in water reaches a minimum in the pH range 3 – 5, but increases rapidly at lower or higher pH values. Paraformaldehyde reacts chemically as formaldehyde at a rate determined by the rate of depolymerisation under conditions of use. Reactivity decreases with increasing molecular weight. On ageing the average molecular weight of a polymer sample tends to increase gradually with a consequent decrease in reactivity. Brands of commercial paraformaldehyde can be roughly divided in relation to reactivity in:

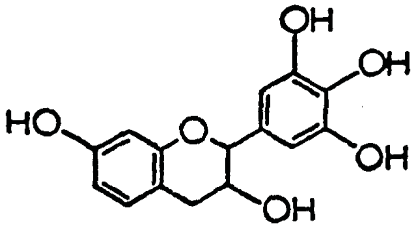
Fast –	examples :	Degussa N	(Germany)	96% powder
		Merck	(Germany)	96% powder
		Synthite	(UK)	90% prills
Medium –	examples :	Synthite	(UK)	97% Q.P.powder
		Celanese	(USA)	95% powder
Slow –	examples :	Campbell	(UK)	88% powder
		Rotex Chemie	(Check.)	95% powder

The brand used in these studies is Degussa N 96% powder; a fast reactivity paraformaldehyde, unless otherwise stated.

3.1.4 Wattle tannin

The extract from Black Wattle (or Acacia Mearnsii, syn. Acacia Mollissima) is readily available in South Africa which is one of the pioneering countries in the use of tannins for the manufacture of wood adhesives. For over ten years now, wattle tannin–based adhesives have dominated the South African market for exterior grade particleboard and plywood after replacing the traditional phenol–formaldehyde resins.

Tannins constitute 60% – 65% of Mimosa bark extract. The preponderant tannins are accompanied in low concentration by a series of flavonoid analogues (phenolic "non–tannins"). The main polyphenolic pattern is represented by flavonoid analogues based on resorcinol A and pyrogallol B, under (I). These constitute about 70% of the tannins. The secondary but parallel pattern is based on resorcinol A and catechol B, under (II). These tannins represent about 25% total bark tannin fraction. Two minor groups of analogues represent the remaining 5% of the tannin fraction.



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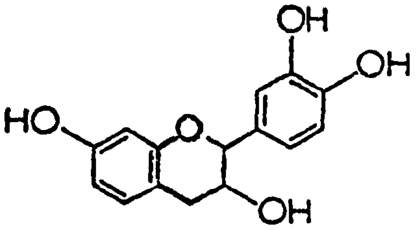


II

3.1.5 Fortifier resins

3.1.5.1 Phenol–formaldehyde (PF) resin

This is the predominant material used as a fortifier of the phenosolvan pitch for the synthesis of wood adhesives. The PF resin consists mainly of two to three phenolic rings joined together through methylene bridges. These oligomers also possess active methylol groups (c.f.1.1).

The PF resin was prepared in the laboratory (c.f.3.4.2.1)

3.1.5.2 Other resins

Commercial urea formaldehyde (UF) resin (65% solids) as well as commercial phenol resorcinol formaldehyde (PRF) resin (~ 60% solids) were employed.

3.1.5.3 Diphenylmethane–4,4′–diisocyanate (MDI)

Polymeric MDI, Desmodur 44V20 (Bayer product) was used.

3.1.6 Complexing agents

3.1.6.1 Caprolactam [Aza–2–cycloheptanone]

M.W. 113,16 g mol^{-1}, assay (6C) > 98%; melting point 69–71°, solubility in water/20°C 820 gl^{-1}; clear colourless.

3.1.6.2 Urea

M.W. 60.06 g mol^{-1}; melting point 134°C; soluble in water/20°C 1080 gl^{-1}, thermal decomposition above 132°C; bulk density ~ 750 m^{-3}.

3.1.6.3 Acetone

M.W. 58.08 g mol^{-1}; $1\ell = 0.79$ Kg; boiling point 56°C; technical grade acetone was used.

3.1.7 Miscellaneous chemicals

3.1.7.1 Methanol

M.W. 32.04; refraction index 1.3318 at 14.5°C; density = 0.79609 g/ml at 15°C; boiling point 64.45°C – technical grade methanol was used.

3.1.7.2 Ethanol

M.W. 46.07 g/mol; refraction index 1.36242 at 18.35°C; density = 0.7893 g/ml at 20°C; boiling point 78.5°C; technical grade was used.

3.1.7.3 Sodium hydroxide

M.W. 40.0 g/mol; ordinary analar sodium hydroxide pellets were used.

3.1.7.4 Sodium carbonate

M.W. 105.99 g/mol; melting point 891°C; soluble in water/ 20°C 210 gl^{-1}; hygroscopic; technical grade was used.

3.1.8 Wood types for testing purposes

3.1.8.1 South African Pine *"Pinus radiata"*

Density 0.500–0.620 g/cm^3, medium density wood, classified as softwood, distributed throughout the Republic of South Africa. It constitutes 40% of the wood used in particleboard manufacture and in structural timber application. 4mm thick veneers were used for the core and 2mm thick veneers for the surface of the test plywood panels that were prepared throughout this research, except if otherwise specified (3mm thick core veneer and 2.5mm surface veneer were used for samples of Table 2.26 onwards).

3.1.8.2 Patula Pine: *"Pinus patula"*

Density 0.400 – 0.550 g/cm^3, very soft wood; it is the most widely used type of softwood in the country in the particleboard manufacture; it is always used in combination with "*Pinus radiata*" because its low density makes it quite unsuitable for rigid structure particleboard.

3.1.8.3 Okoumé hardwood

Only thin, 1.5 mm Okoumé veneers were employed in this work. They were used as surface veneers in order to demonstrate the effect the density of the wood has on the bleed–through. 4mm thick pine veneers were used for the core.

3.2. PREPARATION OF TEST SPECIMENS

3.2.1 Particleboard

A particleboard panel is composed of wood chips that are bonded under heat and pressure with a thermosetting adhesive.

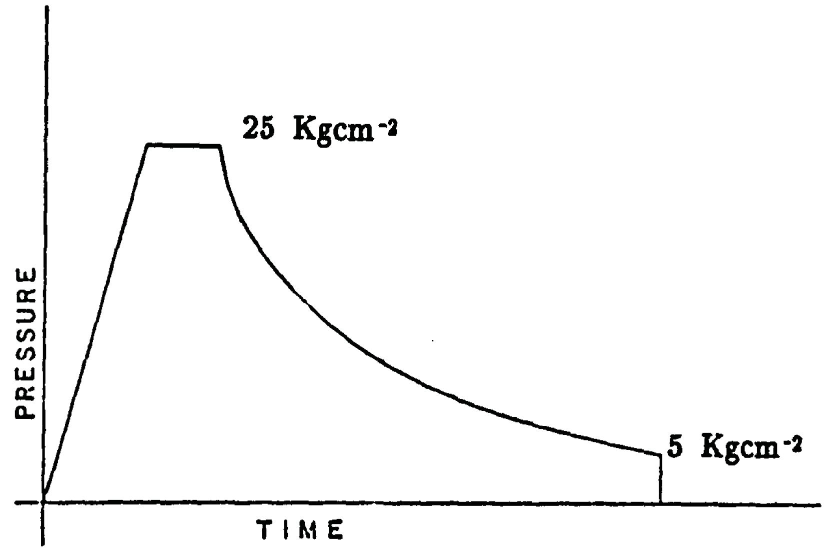
Two types of boards were prepared during this research: one–layer board and three–layer board. The one–layer board is easier and much quicker to prepare than the three–layer one. It is composed of only one layer made up by coarse wood particles which are 1–2 mm thick and 0.5 – 3.0 cm long. The three–layer board is composed of a centre layer of coarse particles and two outer layers of fine wood particles. The centre layer constitutes the bulk of the board. The surface layers give the board a smooth appearance and they also increase dimensional stability and breakage resistance. The particles used for the surface layers are about 0.2 mm thick and about 1 cm long. The particles used for the middle layer are the same as those used in the one layer board.

The particles of both surface and core were passed through a gluing machine in which the glue was sprayed on the wood chips by means of compressed air–operated nozzles. The glued particles were then spread by hand in one or three layers as desired and pressed at 25 Kgcm^{-2} and at 190°C.

A light water spray was applied to the surfaces of the board before pressing. The water spray helped to shorten the pressing time; the water on the surface vaporizes when in contact with the hot caul sheet of the press and migrates in the core of the panel thus causing a faster increase of temperature and consequently faster curing.

The water spray also prevents precuring of the adhesive on the surface of the board during closing of the press before contact with the hot top caul–sheet.

Different pressing procedures can be applied; the one applied in this research is the following: (Fahrni–Novopan system):



This pressing cycle gives a board with high density surface layers and the shortest possible pressing time at a given temperature. The main properties of panels with high density face layers are: stiffness, warp resistance, high dimensional stability in fluctuating ambient humidity, hard and shock proof surfaces requiring less adhesive for veneering, and extremely narrow thickness tolerances.

3.2.2 Plywood

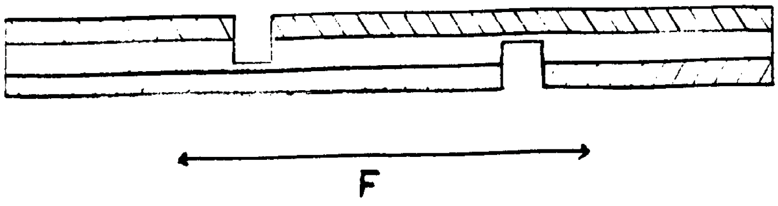
The plywood consists of thin veneers glued together at right angles to the grain of adjacent plies (cross laminated).

Pine, rotary peeled veneers have been used, except in one case where Okoumé hardwood veneers were used, and only three–ply panels were made. An 4.2 mm thick veneer served as the core ply and 2.1 mm veneers were used for the surfaces. The veneers were conditioned in the oven for two days prior to their use and the desired moisture content was obtained (~ 3%).

With the use of a roller, the glue mix was spread on the one side of the core veneer and the surface veneer was attached to the glued side at a right angle to the grain of the core veneer. The same was repeated for the other side. The assembly of the veneers was done as soon as the glue mix was applied, except in the case where the effect of the assembly time on the final product was evaluated. In this test the glued veneers were left with their glued surfaces exposed to the air for the desired length of time (Table 2.27).

After being assembled the panels were pressed at 120°C for 4 minutes. In some cases these pressing conditions were changed and the effect of these changes on the final products was assigned. Where such modifications were made, the exact conditions used are specified. Contrary to particleboard, there is no cycling but a constant pressure is applied in the manufacture of plywood.

Each panel was cut into small pieces 25 mm wide × 150 mm long for the shear strength tests (c.f. 3.3.2.1). These samples provide 750 mm^2 (25 mm × 30 mm) glue line area for testing.



3.3. TESTING METHODS

3.3.1 Viscosity

It is measured in "centipoises" and it gives an indication of the ease of the application of the adhesive. This is particularly important in the case of particle board where the glue is sprayed. The viscosity was measured with a Brookfield viscometer.

3.3.2 Gel time

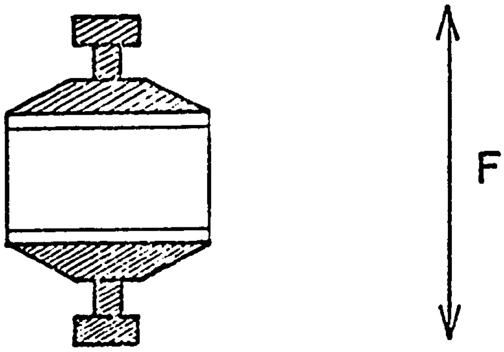
This test indicates the setting speed of the adhesive.

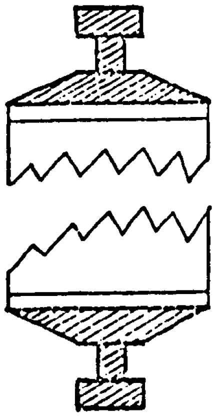
The adhesive solution is mixed with paraformaldehyde in a test tube and stirred with a wire spring while the test tube is immersed in boiling water (95°C). The time required for the adhesive to gel is then measured. This is what is called the gel time.

3.3.3 Particleboard adhesives

3.3.3.1 Perpendicular tensile test

Particle board samples (50 × 50 × 12 mm) are glued with a hot–melt thermoplastic adhesive to two metallic tabs and the breaking stress is measured. This test can be applied to either unweathered samples or after 2 hours boiling.





3.3.3.2 24 hr cold water swelling

Particleboard samples are submerged in cold water for 24 hours. Measuring the original thickness and the thickness after soaking one can measure the percentage swelling in cold water which is one of the most important physical properties indicating the resistance to water and humidity of an exterior grade particleboard.

3.3.4 Plywood

3.3.4.1 Shear strength

The plywood samples were prepared as described in paragraph 3.2.2. and were tested for shear strength and at the same time the percentage wood failure was evaluated.

The shear strength test can be divided into three groups according to the conditioning the samples have been subjected to:

(1) Dry test: the dry samples were tested in a constantly increasing load testing machine. The strength was recorded in Newtons (N) and then converted to Megapascals (MPa) by dividing the force over the surface area which is measured in square millimetres (mm^2).

(2) Cold water soak: the samples were immersed in water at room temperature (~ 20°C) for 24 hours. The samples were tested as soon as they were removed from the water.

(3) Boil test: the samples were immersed in boiling water for 6 hrs. After boiling, the test pieces were cooled to room temperature by quenching in cold water and then tested while still wet.

The minimum values for a Water and Boil Proof (WBP) adhesive are reflected in Table 2.15.

3.3.4.2 Percentage wood failure

This is defined as the percentage of failure in the wood grain over the area of the glue line.

3.4. PHENOSOLVAN PITCH–BASED WOOD ADHESIVES

3.4.1 Initial investigation of the feasibility of phenosolvan pitch for the formation of resol–type resins.

An open beaker was charged with 35.0g S_1 phenosolvan pitch and 2.0g NaOH (28%) solution. Because of the high viscosity of the S_1 phenosolvan pitch, stirring with a magnetic stirrer bar was not feasible and therefore the two components were mixed by hand using a spatula. A marked decrease in viscosity was observed after the intake of the NaOH solution. Thus, the viscosity of the Phenosolvan pitch can be adjusted simply by adding NaOH solution. This has very important practical implications. It can, for example, allow simple spraying of the Phenosolvan pitch in particleboard application. In the same way, the handling of the Phenosolvan pitch for any other possible applications would become much easier without the necessity to use expensive solvents or special techniques.

The pH of the pitch solution was measured with a pH meter equipped with a glass electrode and then 15,0g paraformaldehyde powder were added and mixed with the phenosolvan pitch. A small sample (7.0g) of the mixture was transferred to a glass test tube for the gelling test: a wire spring was inserted in the test tube which was then immersed in a boiling water bath (94°C). The phenosolvan pitch mixture was continuously stirred, with the