Additives and modifiers can contribute useful properties to phenolic resins used for wood gluing. Multipurpose additives are the aminoresins, urea–formaldehyde and melamine–formaldehyde polymers as well as dimethylol urea, trimethylol melamine, and hexamethylol melamine. The amounts of these additives vary from 5 to 15% of phenolic resin solids and they improve resin tack and prepressing, increase long assembly time tolerance, shorten pressing times, and enhance resin functionality. This results in stronger bonds.

Formaldehyde in liquid solution or solid form, and formaldehyde generating compounds, are also used as phenolic resin additives which improve functionality and decrease curing times. Paraformaldehyde is the most frequently used. Significant effects are obtained when 3 – 5% is added, based on phenolic resin solids. Further reduction in curing time is possible if 1 – 2% resorcinol or natural extractives such as wattle–tannin extract is added. This is usually mixed with paraformaldehyde and added to the liquid phenolic resins glue mix. The lignin residues from wood, pulp production are also receiving attention as phenolic resin additives. Substituted phenols, such as cresols and xylenols, have been used as glue mix additives for phenolic adhesive resins to improve assembly–time tolerance.

Some common complexing additives are the soluble salts of boron, chromium, zinc, cobalt, lead, manganese, and other. Some of these compounds have been successful in reducing pressing times and improving prepress performance [6] when added to phenolic resin adhesives. Mixed borate salts are very effective as preservatives of wood products against fungi and most insects. However, the application of these borate–based treatments to green hardwood veneer inhibits bonding with phenolic adhesives after veneer drying. However, very dilute aqueous solutions of borates (i.e. 0.25%) applied to softwood veneers in their green state decrease their thermal degradation during high temperature drying and preserve their reactive sites for bonding with phenolic adhesives.

1.3.5 Plywood Glue Mixes

Some of the most important factors for the preparation of plywood adhesives glue mixes are:

1. The maintenance of phenolic solids in the glue as high as possible (preferably 30 – 40%).
2. The incorporation of a cellulosic filler, such as nut shell flour, in about 20 – 40% of phenolic solids.
3. Alternatively, to add about half this amount of unrefined starchy material, such as wheat flour.
4. To add at the most only 1 – 2% alkali to disperse and stabilize the starchy material.
5. Addition of the minimum amount of water required to drop the viscosity of the glue mix to a level that can be handled by the gluing equipment. The preferred viscosity range is 1500 – 2500 cp at 25°C.
6. Addition of surface active agent (0.1–2.5% on resin solids), to ensure proper wetting of the veneer by the glue film.

The surfactant improves the wetting of the veneer by the glue film, and displaces air from the veneer surface, thus, maximizing adhesive contact. It also limits the depth to which liquid glues are absorbed, thus concentrating adhesive solids more effectively on the glue line.

1.4 PLYWOOD

1.4.1 Variables in Plywood Manufacturing

The following are factors of particular importance to plywood manufacture.

1. Adhesive Application

   The double–roller spreader is the most frequently used plywood adhesive applicator world wide. Glue spreads are in the range 150 – 250 g/m^2 single glue line. The veneer thickness and the properties of the glue determine the exact weight so as bleeding and blistering are avoided as much as possible.

2. Assembly

   The assembly involves the alternate lay–up of veneers spread with glue and those without glue. Assembly–time is very important for gluing dense and difficult hardwood. Lengthened assembly time is necessary, to allow the liquid glue lines to lose water, and become tacky, high–solids films before pressure is applied. Minimum top panel assembly time of 15 – 30 min and bottom panel assembly time of 45 min to 1 hr is recommended.

3. Prepressing

Phenolic wood adhesives, usually have high concentration of resin solids and they are therefore inherently tacky and develop satisfactory prepress bonds. A top panel stand time of 10 – 15 min. is required for these bonds to develop before prepressing. Prepressing can be improved and the required stand time can be shortened if starchy materials are added to the resin. The development of temporary bonds, between most wood veneers usually requires a prepressing cycle of 10 min. at about 5 – 7 Kg/cm^2. It is also possible to manufacture plywood without prepressing.

4. Pressing Temperatures

Phenolic plywood adhesives require a much higher minimum heat input than do urea resin adhesives in order to cure. Some water must be present on the glue lines to permit liquefaction, flow and transfer before curing. This is especially important for soft–wood phenolic adhesives. Loss of water and drying out occurs more rapidly at intermediate pressing temperatures for high–heat– activated phenolic cure. Under these conditions, phenolic glue films dry out and develop inferior, water–sensitive bonds. Plywood bonded with phenolic adhesives should be hot pressed at the highest practical temperatures possible for equipment performance and without causing too many steam blisters.

5. Pressure

The minimum platen pressures for proper bonding for dense hardwoods and medium–density softwood are 14 and 12 Kg/cm^2, respectively. For rough veneer surfaces or extremely dense wood, a pressure of 16 Kg/cm^2 is the minimum required.

The hot press should reach full pressure in 1 min. or less, preferably 30 sec., to minimize the effects of precure on outer glue lines.

6. Panel Construction

The preferred thickness for easy drying, minimum handling losses, and maximized strength should be between 2 and 4 mm. If the veneer is thicker it tends to become rough and deeply cracked, drying times become too long, and chances of overdrying increase. If the veneer is less than 2 mm thick, handling losses increase substantially. This plies promote excessive blistering on adjacent glue lines when they are used in the interior of a panel. Phenolic adhesives can handle almost any normal plywood lay–up to about 50 mm total thickness. However, the thicker the panel, the higher the press temperatures must be to ensure that the heat rise on the center glue lines is enough to produce proper cure instead of dry–out.

Very thin decorative hardwood veneer faces should not be bonded with phenolic adhesives because of their dark colour when cured and the risk of bleed–through. Liquid phenolic adhesives can be used successfully if the glue mix contains a starchy filler. Glue spreads should be carefully controlled to minimum levels consistent with good adhesion and be allowed a top panel stand time of 15 – 30 min. before hot pressing.

1.4.2 Wood–Related Factors

The following comprise the principal wood–related factors that affect the bonding of wood veneer with phenolic adhesives:

1. Density and Porosity

The effect of density is more physical than chemical. The liquified adhesive is confined to the immediate glue line for longer time by dense, nonporous wood surfaces. This causes the adhesive solids to move too much to areas of minimum contact or pressure, which results in poor bonding. Liquid glue lines on lower–density woods lose water into the wood more quickly and become high–solids films before heat and pressure are applied. In this form, they flow less and present a more concentrated layer of adhesive solids which produces stronger, more uniform phenolic adhesive bonds. Conversely, excessively thin glue mixes used on softwoods, show overpenetration of the whole adhesive solution into the veneer. Much longer assembly times are needed on very dense wood surfaces to immobilize liquid glue lines and to obtain a tacky, concentrated adhesive layer.

On exposure to water or weathering, dense hardwoods, develop stronger mechanical separating forces on the glue line than do softer species. Bonds are more easily ruptured by these cross–growth expensive forces in the case of dense wood because the extent of wood failure tends to be shallow.

2. Extractive Content

Most wood species contain various substances which become concentrated on the surfaces of wood veneer through drying thus presenting both physical and chemical barrier to bonding. They can seriously interfere with normal adhesive behaviour and bond development.

3. Drying Conditions

Temperature, time and humidity under which hardwood veneers are dried can have a profound effect on bonding. High temperatures, low humidity, and long heat exposure can cause overdrying and destroy bonding sites of the wood surfaces and thus reduce adhesion.

4. Freshness

The older the veneer, the poorer the adhesion. The loss of wood failure after 6 months of storage can be as much as 15 – 20%. This poorer adhesion could be due to two factors. One is a series of reactions between atmospheric oxygen and the cellulose, lignin, and sap constituents causing the loss of surface functionality, and the other is bacterial or fungal action which occurs if the veneer is stored green.

5. Veneer Surface

Surface smoothness is particularly important for high–density hardwood veneers since they do not crush readily and the gaps are not easily eliminated. Where there is no contact, there can be no adhesion.

If the wood surfaces are covered by damaged wood cells, the adhesive may do a good job, but never quite reach the sound wood underneath thus resulting in weak bonding.

Veneer surfaces should also be kept clean to promote the development of strong adhesive bonds.

1.4.3 Types of Plywood [19]

1. Decorative Plywood

Decorative plywood is greatly valued and utilizes richly toned, highly figured hardwoods from deciduous or broadleaf trees such as oak, walnut, cherry, mahogany etc.

Hardwood veneer–plywood may be as thin as 3.0 mm and is very often uniformly selected for grain printing, completely hiding the annual wood grain pattern. Plywood is used for wall panels and door skins and it is also used in laminated block flooring, chairs, tables, television sets, musical instruments, kitchen cabinets etc. Approximately 80 percent is composed in part of hard–wood plywood. Most of these types of plywood are bonded with adhesives requiring interior–dry exposure.

2. Structural Plywood

The structural use of plywood implies a dependence on its strength and adhesive–wood bond durability under stressful conditions. In such structural applications aesthetics may not be of any significant importance. As an engineered wood product, plywood has great versatility in manufacture with a wide range of applications modified to best suit the intended use.

Hardwood and softwood plywood are used in structural applications and most often where specific physical properties are important to its performance. This applies for plywood in tennis rackets, golf club heads, hockey sticks, and other sporting equipment uses.

The use of plywood for subflooring, decking, and siding has revolutionized light frame building construction. Structural and construction plywoods usually are made of softwood from evergreen or needle–bearing trees such as pine, Douglas fir, spruce, and hemlock. However, in the recent years plywood plants are also utilizing medium–density hardwoods, such as sweetgum and yellow poplar, for structural plywood.

The use of structural plywood can be extended by modifying the surfaces. Brushed plywood is used for paneling, displays, and exhibits; high–density overlay plywood is used for highway traffic control signs, concrete forms, store fixtures and storage tanks; medium–density overlay plywood is suitable as a paintable surface for cabinets and marine uses; and marine exterior plywood is made with plies of highest grade and adhesive bond quality.

3. Mechanical Properties

The changes in mechanical properties, as compared to solid wood, that are brought about by gluing thin veneers at right angles to the grain of adjacent plies (cross laminated) into wide plywood panels give plywood some inherent properties that have made plywood a popular and reliable structural material for engineering and architectural applications.

Wood is much stronger along the grain that it is across the grain. This is also true for veneers. However, by alternating the direction of the grain 90 degrees with each successive wood layer or ply of veneer, many strength properties are equalized, producing plywood with properties across the width more nearly equal to those along the length. This arrangement of crossbonding prevents plywood from splitting easily, in contrast to wood, which is readily split along the grain. Plywood also has superior built–in resistance to racking, twisting, and distortion. With its large flat sizes reducing air infiltration and versatile strength properties, plywood yields many economic benefits for utilization of wood. Large flat plywood panels, for example, are easily attached over large areas so a building can be enclosed readily.

Dimensional stability (shrinkage or swelling) is another important feature of plywood. Whereas wood may change dimension up to 12 percent across the grain and 1 percent along the grain, plywood changes of dimension along or across the grain of the phase ply rarely exceed 1 or 2 percent. In thickness, plywood acts essentially like wood in dimensional stability. The greater the number of crossplies, the closer the equalization of strength in the two directions, parallel and perpendicular to the grain of the face plies, and the better the distribution of load across the panel. However, three–ply is a more popular and economical assembly.

Solid wood is always stronger and stiffer than plywood parallel to the grain of face plies and weaker than plywood perpendicular to the grain of the face plies. For example, the strength and stiffness of three–ply 9.5 mm plywood panels perpendicular to the face grain are twice as great as that of solid wood. Therefore, plywood performs much better than wood where plate action or shear in the plane of the panel is involved, because of the degree of equalization of properties parallel and perpendicular to the face grain.

1.5 PARTICLEBOARD MANUFACTURE

Phenolic resins that are used for plywood can also be employed in the manufacture of particleboard. However, one would have to account for the different conditions of application. During the manufacture of industrial three–layer boards a maximum pressure of 23 – 27 Kg/m^2 is reached as fast as possible after press closure (i.e. 35 – 50 sec.). Contact with the gauge bars is made after 60 – 120 sec. from the start of the press closure. After approximately 1¼ – 2 min. of maximum pressure, the pressure is slowly decreased until the final pressure on the panel is as low as 2 – 3 Kg/cm^2.

This takes place toward the end of the cycle, just before press opening. Many different pressing procedures and diagrams are available. The above pressing conditions produce a board with high–density face layers, and the shortest possible pressing time, at a given temperature and a low power consumption. The main properties of panels with high–density face layers are the stiffness of the panel; better warp resistance; high dimensional stability; hard, glossy, and shockproof surfaces; and narrow thickness tolerances.

Considerable variations in the properties of the final board can be obtained by varying the moisture contents of surface and core layers, and by using faster resins in the core layer and slower reacting resins in the surface layer. This can be achieved by varying geometry and sizes of the wood chips, the density of the board, and so on.

In many cases a light water spray is applied to the top surfaces of the board before pressing to shorten the pressing time. The water on the surface is vaporized when it comes in contact with the hot caul sheet of the press and migrates towards the core of the panel causing a faster increase in temperature and faster cure.

Small variations in the manufacture and characteristics of the phenolic resin used do not affect the properties of the finished particleboard as extensively as do the above factors.

The normal temperature for 12 – 13–mm–thick board glued with phenolic adhesive are 170 – 200°C and the pressing time is 5 – 5½ min.

Resols–glued particleboard show no bond formation at 120°C. At 130°C the resol–glued panels show internal bond strengths of 0.55 – 0.7 MPa.

One of the more common problems in the manufacture of pine plywood and particleboard is adhesive dry–out. This problem is associated with the high liquid absorbancy of pine sabwood. This problem can be overcome either by using phenolic resins modified through reaction with alkylated phenols, especially 3,4–xylenol, or by the manipulation of synthesis procedures used in preparing a standard phenolformaldehyde resin. Such a resin can be prepared by coreacting a prepolymer, prepared by reacting formaldehyde and phenol in the molar ratio 2.6:1.0, and a prepolymer obtained by reacting formaldehyde and phenol in a molar ratio of 1:1. The two prepolymers are then mixed in 50:50 proportions by mass and coreacted.

1.6 RESORCINOL–FORMALDEHYDE WOOD ADHESIVES

In the world practice, resorcinol has been widely employed for the synthesis of resin modifiers and of resorcinol–formaldehyde adhesives for the manufacture of water resistant glued laminated timber constructions. There are various adhesive formulations that can be used for the manufacture of laminated wood beams and finger joints for structural purposes. These formulations include Resorcinol–Formaldehyde, Phenol–Resorcinol–Formaldehyde, Urea–Resorcinol–Formaldehyde, and several other adhesive formulations [10]. All these formulations are based totally or partially on resorcinol. In view of the fact that resorcinol is expensive and in short supply, activated phenols obtained in thermal processing of oil shale [20] can play an important role in these syntheses.

The reactivity of formaldehyde toward Phenosolvan pitch, which is a mixture of phenolic components obtained by SASOL, is very high. Because of this high reactivity the synthesis of phenol–formaldehyde polycondensates in the production of adhesive resins will probably require a new technology. Also, the fact that phenosolvan pitch 1 is a mixture of a great variety of phenolic components (Table 10) whose reactivity toward formaldehyde varies dramatically may cause problems in the synthesis of resins. One way of solving such a problem could be the use of complexing agents that would decrease and equalize the reactivities of different activated phenols in the mixture. Accordingly, the synthesis could be accomplished in the presence of compounds that form molecular complexes with phenols by means of hydrogen bonds.

Studies of the composition and structure of crystalline molecular complexes formed between various phenols and caprolactam [20] showed, for instance, the structure to be endless chains in which caprolactam participates as an associated dimer and the carbonyl groups of the dimer form supplementary hydrogen bonds with the hydroxyl groups of the active phenols. The existence of molecular complexes between resorcinols and complexing agents strongly influence the kinetics of hydroxymethylation and polycondensation reactions: there is a reduction in the rate of formaldehyde decrease and on the rate of viscosity increase during the synthesis. In the systems including phenol and caprolactam or resorcinol and urea, conversely, the rate of hydroxymethylation reaction increases, but in this case the reaction proceeds with an amide component.

CHAPTER TWO

2. DISCUSSION

2.1 INTRODUCTION

The first phase of this research program involved work for the establishment of the feasibility of the phenosolvan pitch as the raw material for the preparation of phenol–formaldehyde(PF)–type resins. The actual nature of the pitch introduced some extra problems in this research work. Such problems are normally not encountered in PF synthetic work involving the use of pure chemicals. Some of the factors that made the use of phenosolvan pitch more difficult are:

(i) the phenosolvan pitch is a mixture of a large number of chemicals that vary greatly in reactivity.

(ii) the identity of a big fraction (40%) of the pitch is not known.

(iii) there is a considerable difference in viscosity and reactivity between pitch samples from different batches, and

(iv) to our knowledge no successful chemical investigation of this material was done before as regards their use as PF resins for wood adhesives.

Analysis of the Sasol 1 Phenosolvan pitch by means of gas chromatography (GC) revealed the presence of a great variety of phenolic components in this pitch (Table 2.1). The components shown in the table comprise the distillate which is only 60% of the Phenosolvan pitch. The remaining 40% residue is pitch with R × B softening point of 88°C. The identity of this fraction could not be revealed because of the high molecular weight of its components. Nevertheless, even the reactivity of the known components is very difficult to predict as their exact structure is not known. For example, a C_3 phenol can be as unreactive as the 2,4,6 trimethylphenol which has both the ortho and the para positions blocked and therefore is very unreactive (cf.1.1.1). However, a C_3 phenol can be much more reactive such as the case of 3–methyl–5–ethylphenol.

As the complexity of the material makes its analysis and any predictions about its reactivity very difficult, the synthetic approach was chosen as the best method to investigate the feasibility of the phenosolvan pitch in the development of phenolic–type resins that can be used as wood adhesives. In this synthetic approach the phenosolvan pitch was treated as a mixture of monomeric phenols comprising the 60% of the material and the remaining 40% was assumed to consist of higher molecular weight phenols but mainly of dimers and trimers which could be the products of phenoxy coupling between highly reactive resorcinolic and/or orcinolic components. This theory is supported by the low percentage content of orcinol and the total absence of resorcinol from the monomeric constituents that are present in the 60% known fraction. It is also quite logical to assume that phenoxy coupling polymerization would start with the more reactive phenols. Therefore, according to the above theory, the unknown fraction of the phenosolvan pitch would consist of oligomers with high reactivity toward formaldehyde. Highly exothermic reactions between phenosolvan pitch and paraformaldehyde, under the right conditions, appear to indicate that such a theory could well be true.

2.2 INITIAL INVESTIGATION OF THE REACTIVITY OF SASOL 1 (S1) PHENOSOLVAN PITCH

The field of wood adhesives has been dominated by two main classes of adhesives: aminoplastic and polyphenolic adhesives. The reactivities of urea, in the first case and phenol, in the second class, toward formaldehyde are utilised in the formation of the resins. Therefore, the initial investigation of the reactivity of the phenosolvan pitch was directed toward investigating its reactivity with formaldehyde.

Firstly, the assumption made earlier that highly reactive phenolic components are concentrated in the 40% unidentified fraction was investigated. If such a theory was correct, one would expect a high reactivity of the pitch toward formaldehyde, similar to that of resorcinol, thus leading to fast–setting resins. The first reactions of the phenosolvan pitch with paraformaldehyde were performed at room temperature and sodium hydroxide was used as a catalyst i.e. aiming at resol–type resins. Low reactivity was first indicated by long curing periods. However, when more sodium hydroxide was added and the pH of the resin exceeded the 10.4 mark the whole scenario changed and very fast–setting resins were obtained (Table 2.2). These results infer that the theory about the presence of highly active prepolymerised phenols could be correct. The highly exothermic reaction of the phenosolvan pitch with formaldehyde at room temperature is much more exothermic than what would be expected from the analysis of the mixture of monomeric phenols contained in the 60% known fraction. A very vigorous and highly exothermic reaction takes place under strongly alkaline conditions (Fig.2.1). As the pH increases, the curing of the resin becomes considerably faster. At pH values between 12 and 13, for example, a hard plug is obtained within 10 to 15 minutes indicating the presence of fast reacting, but very bulky phenolic components.

2.3 CHARACTERISTICS OF THE PITCH–FORMALDEHYDE "COLD SETTING" RESINS

2.3.1 Trigger pH: as mentioned above, the phenolsolvan pitch can react with paraformaldehyde at room temperature to give hard cured resins. The curing rate which is indicated by the pot life (Tables 2.2; 2.3; 2.4; 2.5; 2.9; 2.10; 2.11) is determined by the alkalinity of the resin. However, an important characteristic of this resin is the sharp change in its reactivity within a very narrow pH range. The first batch of S_1 phenosolvan pitch, for example, has a pot life longer than one day at pH 10.3 whereas the pot life is less than one hour at pH 10.4. The value of pH 10.4 was named "trigger pH" since it triggers such a high reactivity (Fig. 2.2). However, there is an inherent disadvantage in this characteristic of the material in concern. Such a drastic change of the reaction rate over such a narrow pH range would make it virtually impossible to control the hardening time, and pot life, of the resin through pH manipulations.

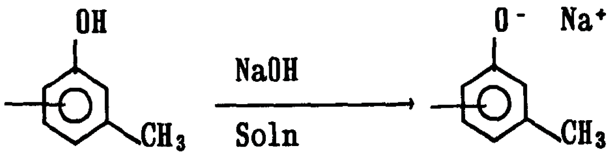
2.3.2 **Material inconsistency**: the viscosity of phenosolvan pitch can vary considerably between samples from different batches. Such samples also exhibit different reactivity toward formaldehyde (Tables 2.2; 2.3; 2.4; Figs. 2.2; 2.3). Such a difference in reactivity between samples of the same material could pose serious problems on application of the material since its pot life could vary considerably from sample to sample. Inconsistency is a common characteristic of waste by–products and it usually comprises the stumbling block that may prohibit the utilization of most of such materials. It is therefore important that a system is used to buffer the reactivity of the different samples of phenosolvan pitch.

2.4 THE PHENOSOLVAN PITCH RESIN IS NOT A TRUE COLD SET

The whole scenario about the cold–setting ability of the phenosolvan pitch resin changed dramatically once the resin was applied on wood strips. When a resin with a very short pot life (~ 20 minutes) was applied on wood strips, it took several days before the resin could cure completely. This infers that the pitch resin is not a real cold set but a thermoset which cures when it occurs in bulk quantities as the high exotherm that is released by the reaction causes temperature increase (Fig. 2.1) and consequent curing of the resins without the necessity of heat application from an external source. For instance, the temperature of 35.0 g of S1 phenosolvan pitch at pH 11.0 increases to 99°C within 2 minutes from reaction initiation. However, in applications where the resin is applied in the form of a thin film such as the case of wood adhesives, the cooling effect of the substrate eliminates the exotherm thus resulting in very long curing time. This situation can be improved with the addition of resorcinol (Table 2.12). In order to obtain acceptable setting times, however, the resorcinol content must reach very high levels thus making the resin economically non–viable because of the high cost of resorcinol. Thus, application of the phenosolvan pitch as a cold–setting wood adhesive is not likely to succeed without extensive modifications of the raw material. This, however, was not the task of this research program.

2.5 THE EFFECT OF WATER ON THE REACTIVITY OF PHENOSOLVAN PITCH

Although it is originally extracted from an aqueous medium, the phenosolvan pitch is insoluble in water. Under highly alkaline conditions, however, it becomes highly compatible with water. This is probably due to the enhancement of the polarity of the pitch components as a result of ionization under alkaline conditions.



An oligomeric
Pitch component

The water, however, has a strong retarding effect on the reactivity of the phenosolvan pitch (Table 2.14; Fig. 2.4). This could be due to the formation of molecular complexes with the phenolic components of the pitch by means of hydrogen bonds as well as due to the dilution effect of water. Formation of such complexes minimizes, and most importantly equalizes, the reactivity of the different components. Thus, water can be used as a means of control of the reaction rate between phenosolvan pitch and formaldehyde. The pot life of the phenosolvan pitch resin can be extended to an acceptable time length even under highly alkaline conditions. This can be done simply by adjusting the water content of the resin. This is of great importance as it can determine the applicability of this material for industrial use; pot life must be long enough to allow preparation and application of the glue mix before any major changes in its chemical or physical characteristics take place. As mentioned earlier, it would be difficult to control the reaction rate through pH manipulations only. High pH values that give the desired fast curing thermosets also yield very short pot life whereas low alkalinity results in relatively slow setting resins. Also, an appropriate intermediate pH value that could give a resin with reasonably long pot life and relatively short gel time is not feasible because of the inconsistency of the material. At pH 10, for example, some pitch resins will exhibit reasonably long pot life whereas other pitch resins with lower trigger pH will show unacceptably short pot life.

The water, however, does not only inhibit the reaction of the phenosolvan pitch resin at ambient temperature but also under thermosetting conditions. This is indicated by long gel times that are observed when the water content of the resin is high enough to provide acceptable pot lives. This lengthening of the gel time as the water content increases implies that on its application the resin would require longer to reach complete curing. Thus, the performance of the resin under standard conditions is expected to drop since not enough time will be available for the resin to set. The introduction of longer pressing times in the case of wood laminates, for example, could eliminate the above problem but such an approach is undesirable as it would increase the cost of production of the final product.

Nevertheless, it was found that even a high water content pitch resin can perform very well under highly alkaline conditions when used for the preparation of plywood or particleboard even though it has a very long gel time. This infers that in this particular case the gelling test fails to reveal the true curing rate of the pitch resin. Thus, while the gelling test which is an easy and quick method was successfully employed in the development of fast thermosetting resins, it fails when the water content is high. In a gel time test the water slows down the reaction and long time periods are required for the gelling of the resin even under highly alkaline conditions. The scenario, however, changes dramatically when the resin is used for the preparation of plywood or particleboard. Under the effect of high pressure and temperature that are applied, the water is volatilized and escapes in the form of steam thus leaving behind a drier resin which then cures fast in the absence of water. In the gelling test, however, the water can not escape very easily from the test tube. When the steam reaches the top of the tube which lies outside the water bath, it condenses and falls back into the resin. Thus, the resin does not get rid of the water and therefore long gel times are observed. Furthermore, the activation energy of all formaldehyde resins is lowered when the resin is cured in contact with lignocellulosic materials [21].

Addition of water also leads to the decrease of the viscosity of the pitch thus making the application of its resins feasible. This is very important, especially for particleboard application where the resin is sprayed and therefore a considerably lower viscosity is required. The successful use of water as a solvent for the phenosolvan pitch has the great advantage of eliminating the need to use more expensive solvents such as methanol and acetone. Furthermore it has the advantage that it allows the addition of inexpensive fillers to the resin in plywood formulations leading to a lowering of the cost of the final formulation.

2.6 FORMULATION SCANNING

The first phase of this investigation which involved experimentation with gelling tests, proved the great potential of the phenosolvan pitch as raw material for the development of adhesives for plywood and particleboard. The next phase revolved around the preparation (cf. 3.2) and testing (cf. 3.3) of plywood and particleboard test specimens.

In the first series of test specimen preparation different glue–mixes (Table 2.16) were prepared and the effect of several fortifiers on the pitch–based resin was tested (Table 2.17). These initial results are a clear indication of the great potential of the pitch–based resin for the development of industrial plywood with fully exterior properties (compare results of Table 2.17 with standard values in Table 2.15). Most of the shear strength values obtained are way above the standard specifications for exterior grade plywood [SABS 929 (1986)]. Standard industrial conditions were employed preparation of the test specimens, with the only exception of the glue–spread applied; about 550 g/m^2 double glue line (d.g.l.) were used. Industrial plants employ between 320 and 400 g/m^2 d.g.l. of glue–mix in plywood manufacture. This, obviously, is very important when accounting for production costs and, therefore, the reduction of the glue–spread had first priority in the experiments that followed. The aim was to reduce the glue–spread without any drastic decrease of the strength.

These results, however, helped in the evaluation of the different fortifiers and the selection of the one with the most potential for further experimentation.

2.7 EVALUATION OF THE RESULTS OF THE FIRST SERIES OF PLYWOOD SAMPLES (Table 2.22).

2.7.1 Unfortified phenosolvan pitch–based adhesive.

The first test sample was prepared with a glue–mix where S_1 phenosolvan pitch was used instead of pure PF resin. Based on the assumption that the 40% unknown fraction of the S1 phenosolvan pitch is made up of oligomeric phenolic compounds, the material was treated as an already made phenolic resin. S1 phenosolvan pitch does, indeed, behave like a resol type thermosetting resin that cures under alkaline conditions. The curing mechanism should be similar to that of pure phenolic resin (cf. 1.1.5).

The results obtained show a relatively low wood failure whereas the high strength of the dry and soak tests falls dramatically in the boil test. Although the value of 0.45 MPa is still within the standard specification for exterior grade plywood, it leaves no safety margin for possible variations which always occur, especially on a big scale production where conditions cannot be controlled very precisely. Apart from this, as mentioned earlier, excess glue–spread was used. In order for the pitch–based adhesive to be comparable to the resins currently used in industry the glue–spread would have to be reduced by a considerable amount. However, such a reduction in glue–spread would inevitably decrease the strength of the sample thus causing it to fail.

Panel No.7 of the same table was prepared with Sasol 2 Phenosolvan pitch which has a Ring and Ball (RxB) softening point of 52°C (cf. 3.1.1). Exceptionally high results were obtained in the dry test (0.99 MPa). However, although such high strength can be achieved, the wood failure is very low. This could be attributed to the high molecular weight of the components of the RxB 52°C pitch. During the preparation of an RxB pitch sample with relatively high softening point, the more volatile components are distilled off and the remaining sample contains a much higher proportion of the higher boiling temperature components. These are the components which are supposed to be largely high molecular weight monomers and oligomers. Some of these oligomers occur in the untreated pitch whereas others may be formed during the distillation process. Because of their large size the molecules of the pitch with relatively high R×B softening point are likely to not be able to penetrate very easily and get into the structure of the wood, thus resulting in low percentage of wood failure.

Although the dry test gives such a high strength, this value becomes very marginal in the boil test suggesting that the material does not have a very good water resistance.

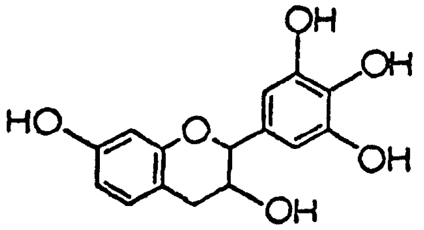
Another disadvantage of using S2 RxB 52°C phenosolvan pitch–based adhesive would be the probable higher cost of the final glue–mix due to the extra process necessary for the preparation of the RxB pitch except if the distillate is of high enough value to cover the extra cost. Contrary to S1 phenosolvan pitch the S2 sample has very low viscosity probably due to low content of oligomeric material and high content of monomers. Thus, it cannot be used in its unprocessed form to provide a pitch–based adhesive. A different approach in finding a way to utilise S2 phenosolvan pitch is to use it as the basic material and synthesize a resin that could be used as a wood adhesive. Such a resin, "Resin 2", was developed (cf. 3.4.2.2) and used in panel No.13 (Table 2.16). The test results obtained (Table 2.17) appear to be quite promising but not as good as those of S1 pitch or S2 RxB pitch–based resins.

In conclusion, S1 phenosolvan pitch appears to be the most promising raw material for the development of pitch–based wood adhesives. It does not require any processing prior to its use, i.e. it can be used as a premade resin. Also, another factor that favours the promotion of the S1 phenosolvan pitch is the fact that it is more readily available than S2 phenosolvan pitch.

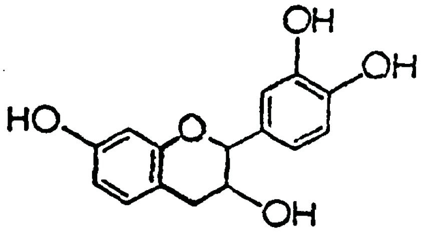
However, further improvement of the S1 phenosolvan pitch–based adhesive is necessary to improve its performance in the boil test. Such an improvement was attempted by means of fortification. Different compounds were used as fortifiers, some of which resulted in marked improvements of the material.

2.7.2 Fortification of phenosolvan pitch–based adhesives for exterior grade plywood by means of wattle tannin.

Phenol–formaldehyde resins extended with small quantities of tannin extracts have been used commercially during the last almost 40 years [22]. The tannin is used to accelerate cross–linking by reacting with the available methylol groups of the phenol–formaldehyde resin. Its function is both as partial hardener and accelerator. Both actions are due to the high reactivity of the tannin towards methylol groups under strongly basic ($pH > 10$) conditions. This reactivity is due to the resorcinol A ring of the flavenoid analogues.



I



II

The above two flavonoids comprise the 95% of the tannin extract of which the 70% is flavonoid I and 25% flavonoid II. The remaining 5% of the tannin constitutes of two different flavonoids with phloroglucinol A rings which also have high reactivity toward methylol groups under alkaline conditions.

The amount of tannin extract used as an extender of PF resins has to be kept low because of two main reasons: (i) large amounts of wattle tannin extract shorten the usable pot life of the mixture at high pH, and (ii) wattle extract needs a considerable amount of water to maintain a usable viscosity and the water required for large amounts of tannin cannot be tolerated by the PF resin [23].

A wattle: S1 phenosolvan pitch (20:80) combination resulted in a considerable improvement of both strength and wood failure especially in the wet tests, i.e. improving the water resistance of the resin thus increasing the chances for a final product with fully exterior properties (Table 2.17, panel No.2). This improvement is most probably due to increased amount of cross–linking introduced by the tannin.

Whereas the fortification with wattle tannin introduced a marked improvement of the S1 phenosolvan pitch, it essentially had no effect on the S2 RxB 52°C sample (panel No.8). This could mainly be due to two reasons: (i) tannin and probably the components of the RxB pitch sample are of large molecular size and therefore large hollow spaces are probably created when the two are combined and cured together, and (ii) for a cross–linking agent to be successfully incorporated into a system, its reactivity must be of an order of magnitude comparable with that of the system, which might not be the case here.

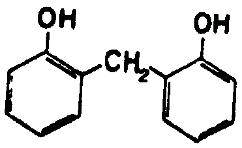
In conclusion, large molecular size and/or reactivity incompatibility are probably the main factors why wattle tannin fortification of the high

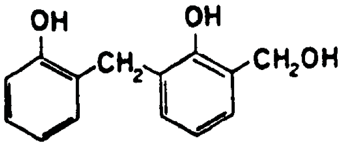
RxB pitch sample does not increase the amount of cross–linking and consequently no improvement of the strength of the cured resin is achieved.

2.7.3 Fortification of phenosolvan pitch–based adhesives for exterior grade plywood by means of phenolic resins.

A low condensation, water soluble phenolic resin which is compatible with the phenosolvan pitch solution and is able to fortify it without hardening is what is required. The hardener function, in the mixture, can be fulfilled by additional formaldehyde, in the form of paraformaldehyde, added to the glue–mix just before use.

The phenolic resin prepared and used as a fortifier, has an average molecular size of about two phenolic rings bound together with a methylene bridge:





As the P:F molar ratio was of 1:1.8 a high amount of methylol groups are available in the PF resin for reaction and copolymerization with the phenosolvan pitch.

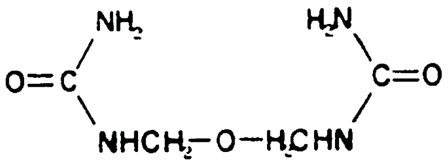
The methylol groups and the free active sites of the phenolic rings can function as cross–linking sites by forming covalent bonds with the PF components of the pitch (c.f. 1.1). The copolymerization of the phenolic oligomers and phenosolvan pitch by the further addition of formaldehyde gives, under suitable conditions of pH, heat and pressure, a cured resin that constitutes a good bond for exterior grade plywood (Table 2.17, panel No.3). The PF:S1 phenosolvan pitch (20:80) combination that was tried resulted in a remarkable increase in wood failure and good improvement of the water resistance of the resin. This improvement could be attributed to increased cross–linking introduced by the PF dimers and trimers and also to the fact that the PF resin itself is an excellent wood adhesive.

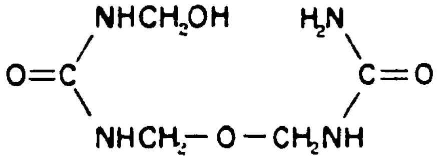
The slight decrease in strength in the dry test is not very important since the results in this test are well above the standard specifications. However, the increase in the boil test is of great significance since it brings the sample at a safe distance from the standard specification level.

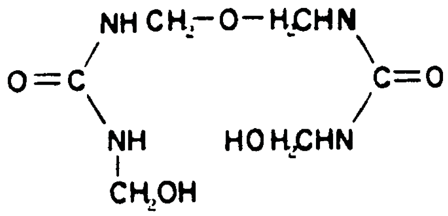
The above also apply to the PF as a fortifier of the S2 RxB 52°C pitch–based resin. The most remarkable feature is the increase of the wood failure from about zero per cent to almost 100 per cent.

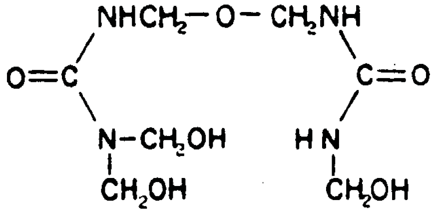
2.7.4 Fortification of the phenosolvan pitch–based adhesives for exterior grade plywood by means of aminoplastic resins.

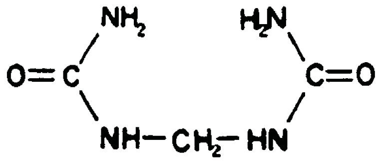
The fortification of the phenosolvan pitch–based adhesives by means of aminoplastic resins is based on the same principle as the fortification with phenolic resins. A urea–formaldehyde (UF) resin is a mixture of methylene– and methylene ether–bridged ureas and methylol ureas:

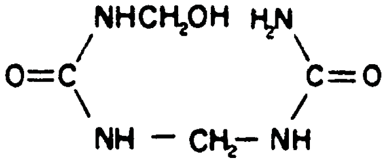


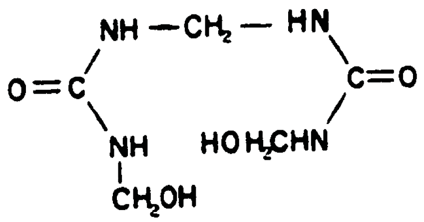


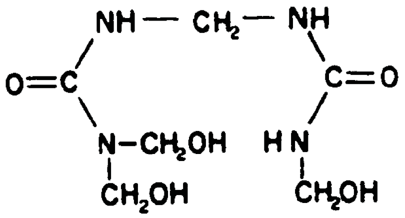












The methylol groups of these compounds can react with the highly reactive phenolic components of the phenosolvan pitch in the same way as the phenolic methylol groups. Thus, the result of the fortification of the phenosolvan pitch resin with UF is expected to be very similar to that of the PF fortification. Nevertheless, there is a significant difference between the two resins; the UF fortified resin fails catastrophically in the boil test (Table 2.17 panel No.4 and 10) whereas PF fortification results in a completely boil proof pitch resin.

The UF fortified phenosolvan pitch resin was prepared by mixing commercial UF resin with phenosolvan pitch at a 20:80 ratio. As it is well known, UF resins are not weather resistant although under certain conditions they can be protected from water attack by the phenolic component of the copolymer [24] The results obtained suggest that this drawback of the UFs is passed onto the phenosolvan pitch resin when UF is used as a fortifier, thus causing failure in the boil test. Also, there is a considerable drop in the strength of the resin in the soak test but not a complete failure. Considering the fact that a pure UF resin is very vulnerable to water attack, the results of Table 2.17 suggest that there is some blending of the properties of UF and phenosolvan pitch resins, thus making the UF less susceptible to water. This observation is of great importance and it opens a new field of research for optimization of the UF: phenosolvan pitch ratio as well as experimental conditions in order to synthesise a UF fortified exterior grade phenosolvan pitch resin. The feasibility of this approach is revealed by a simple comparison of the results of panel No.3 against those of panel No.1 in Table 2.26. PF:S1 phenosolvan pitch (20:80) resin was used in both cases with the only difference that commercial UF was added to the glue–mix of panel No.3 at the 7% level. Almost identical results were obtained by the two panels even in the wet tests (soaking and boiling). This is a clear indication that small amounts of UF resin can copolymerize with the phenosolvan pitch resin in such a way that they are sufficiently protected against the effect of cold and boiling water. Future experimentation should therefore be concentrated on partial and, if possible, complete substitution of the pure PF by UF as a fortifier of the phenosolvan pitch resin. The advantage behind such a substitution is twofold:

(i) economical: UF resins are of much lower cost than PF resins, and

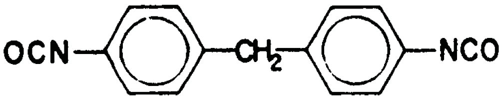
(ii) pot life extension: the S1 phenosolvan pitch–based resin is characterized by a very short pot life, the extension of which will be absolutely necessary for a successful application of the resin. It has been observed that some lengthening of the pot life is introduced by the fortifier. In this respect, UF is more desirable as it renders the phenosolvan pitch resin of longer pot life than the PF does.

In conclusion, even if complete substitution of PF by UF fails, the addition of a small amount of UF (7 per cent by mass on resin solids basis) might still be desirable for the lengthening of the pot life of the resin i.e. use the UF as an extender. The feasibility and extent of this approach will be determined by the relative cost of UF in comparison to that of other possible extenders.

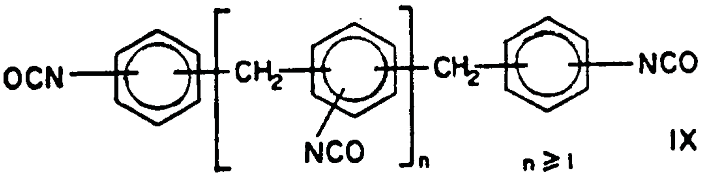
2.7.5 Fortification of phenosolvan pitch–based adhesives for exterior grade plywood by means of polymeric 4,4′–diphenylmethane diisocyanate (MDI).

Diisocyanates are a relatively new synthetic resin for use for panel products. Diisocyanates have been used industrially with success for more than 10 years. Advantages of the diisocyanates are: high reactivity, good binding qualities for exterior–grade panel products, and no formaldehyde emission potential after curing. Furthermore, diisocyanates do not contain hygroscopic salts like phenolic resins. Disadvantages of diisocyanates are the higher price and higher toxicity of the uncured glue in comparison with other wood adhesives [25]. However, its low vapour pressure (~ 10^{-5} mm Hg) contributes to its safety of use. Commercial MDI contains about 40% 4,4′–diphenylmethane diisocyanate, see formula below, and the remaining

60% comprises higher molecular weight isocyanates of a degree of polymerisation up to 6.



MDI
4,4'-diphenylmethane-diisocyanate

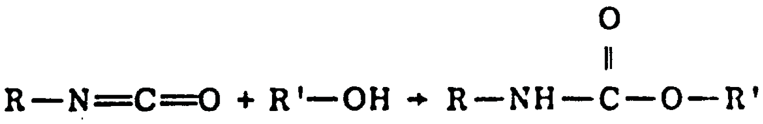


IX

"*polymeric*" *MDI*

Although the use of diisocyanates as wood adhesives is relatively new, they have been used for at least 40 years for the manufacture of polyurethane resins. Commercial manufacture of diisocyanate–bound particleboard was the result of the pioneering work of Deppe and Ernst [26,27].

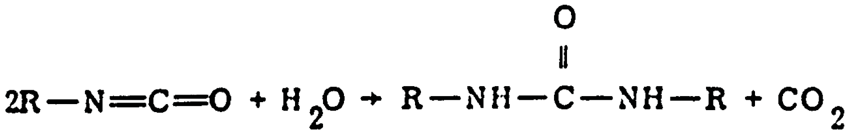
The chemistry of the reaction of isocyanates and diisocyanates with wood is inextricably bound with the chemistry of preparation of polyurethanes. The two most important reactions in the preparation of polyurethanes are the reactions between isocyanates and hydroxyl–containing compounds and the reaction between isocyanate and water. The former is the basic reaction for the formation of urethane groups.



$$R{-}N{=}C{=}O + R'{-}OH \rightarrow R{-}NH{-}\overset{O}{\overset{\parallel}{C}}{-}O{-}R'$$

(R' = alkyl or aryl)

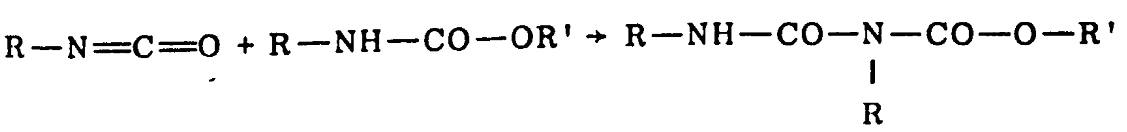
The second reaction takes place with liberation of carbon dioxide and with simultaneous formation of substituted urea groups.



$$2R{-}N{=}C{=}O + H_2O \rightarrow R{-}NH{-}\overset{O}{\overset{\parallel}{C}}{-}NH{-}R + CO_2$$

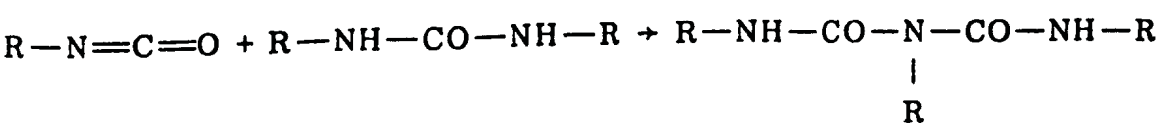
Other reactions that lead to branching and cross-linking and can be used for wood adhesives are the reaction of the isocyanate group with amines and the formation of allophenate and biuret linkages by reaction with urethanes.

$$R{-}N{=}C{=}O + R'{-}NH_2 \rightarrow R{-}NH{-}CO{-}NH{-}R'$$



$$R{-}N{=}C{=}O + R{-}NH{-}CO{-}OR' \rightarrow R{-}NH{-}CO{-}\underset{\underset{R}{|}}{N}{-}CO{-}O{-}R'$$

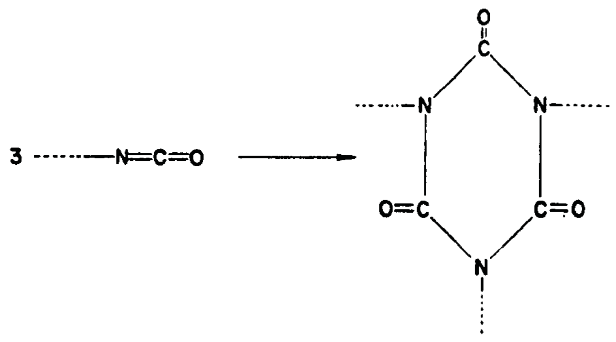
allophanate



$$R{-}N{=}C{=}O + R{-}NH{-}CO{-}NH{-}R \rightarrow R{-}NH{-}CO{-}\underset{\underset{R}{|}}{N}{-}CO{-}NH{-}R$$

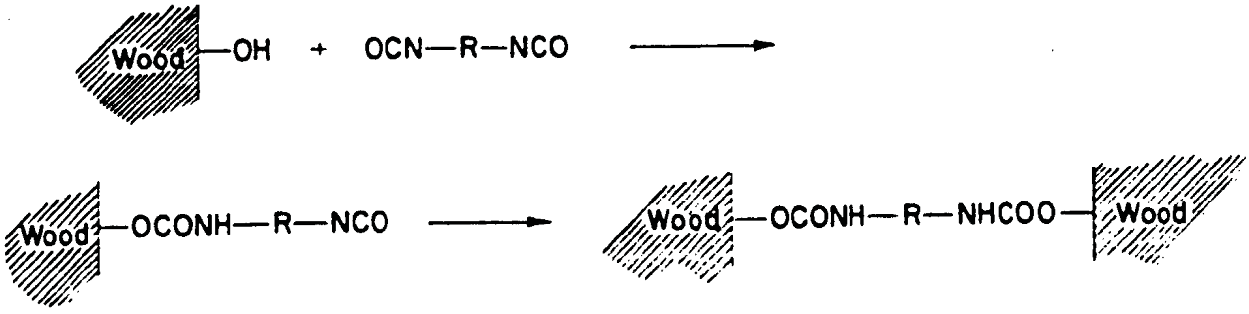
biuret

Another cross–linking reaction is trimerization, leading to the formation of isocyanurate rings which are hydrolytically and thermally very stable.



Thus several reactions of the isocyanate group are useful to bond wood with diisocyanates. Molecules presenting two–N=C=O groups i.e. diisocyanates, are necessary to form bridges of various lengths with the alkyl and phenolic hydroxy groups of wood cellulose and lignin, respectively.

1. Reaction with Cellulose and Lignin Hydroxy Groups



2. Polyurea Formation

$$\mathrm{OCN{-}R{-}NCO} + \mathrm{H_2O} \xrightarrow{\mathit{slow}} \mathrm{H_2N{-}R{-}NH_2} + \mathrm{CO_2}$$

$$n\,\mathrm{OCN{-}R{-}NCO} + n\,\mathrm{H_2N{-}R{-}NH_2} \xrightarrow{\mathit{fast}}$$

$$\longrightarrow \mathrm{OCN}\left[\mathrm{R{-}NHCONH}\right]_n\mathrm{R{-}NCO}$$

$n > 1$

polyurea

The polyurea formed when terminal–NCO groups are still present will then react with wood in the same manner as a diisocyanate. Thus, through the formation of polyureas, a certain variation in the diisocyanate polymer length is introduced which contributes to successful wood bonding. If too much water is present, however, too high an amount of diisocyanates is deactivated, too much polyurea with no –NCO terminal groups is formed, and the system loses considerably in adhesive efficiency, as not enough urethane linkages between the adhesive and the wood can be formed.

Since many of the reactions of the diisocyanates which have been described may be too slow, catalysts can be employed to bring about faster reactions rates and to complete the reactions, resulting in an adequate cure of the glue line. Completion of cure results in maximum strength properties and maximum chemical and weathering resistance. Diisocyanate adhesives for particleboard do not require the use of catalysts due to the high temperatures used in this process.

MDI exhibits high reactivity toward phenosolvan pitch. Simple mixing triggers a vigorous and highly exothermic reaction which leads to an almost instantaneous solidification of the mixture which has the appearance of a polyurethane foam. An application problem is therefore introduced as the two components cannot be mixed together to form a single glue–mix. On a first approach, this problem was overcome by separate application of the MDI and the phenosolvan pitch glue–mix. In the first samples the MDI was combined with phenosolvan pitch on a 30:70 ratio (Table 2.16). The results (Table 2.17) show a considerable improvement of the resistance of the phenosolvan pitch resin to boiling water. This improvement, however, is not as good as that brought about by wattle tannin or PF fortification. Also, the use of MDI is economically unfavourable because of its high cost in comparison to tannin and PF resin and also because of the application problem introduced by the high reactivity of the MDI towards the phenosolvan pitch. Thus, MDI does not appear to be a suitable fortifier. An important observation,however, is that when MDI is used as a fortifier, the bleed–through is greatly reduced. Bleed–through is associated with most industrial wood adhesives to a certain extent but in the case of the phenosolvan pitch–based adhesives the problem is more acute because of the black colour of the pitch and of the higher glue spread which was initially used. During pressing, the phenosolvan pitch is squeezed through the outside veneers and reaches the surface of the panel thus giving a black, motley appearance to the final product (c.f. 2.12.0). This can impose serious limitations on the application of phenosolvan pitch based products. Such a panel for example, could not be used for decorative purposes where surface appearance is very important.

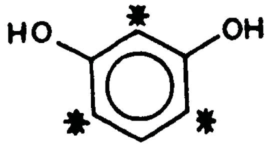
The ability of MDI to reduce the bleed–through is due to its high reactivity toward polyols such as the phenosolvan pitch. When MDI is applied in the form of a thin layer on the inner side of the surface veneers it reacts with and cures the phenosolvan pitch thus not allowing it to penetrate and reach the surface of the panel. The bleed–through is thus greatly reduced and a relatively clean surface is obtained. As the minimisation of the bleed–through appears to be very significant, the experimentation toward a successful employment of MDI as a fortifier of the phenosolvan pitch resin was pursued. The main purpose was the formation of a single glue–mix containing both phensolvan pitch and MDI, with a pot life long enough to allow application on an industrial scale. With a system like that the separate application of MDI and pitch could be avoided thus reducing production costs and making this approach economically more viable.

Solvents like methanol and acetone which depress the activity of phenosolvan pitch were employed in an effort to slow down the reaction between the phenosolvan pitch and MDI, thus making their combination possible. This approach, however, was not successful. Even when great quantities of solvents were used the reaction was still very fast. As a result, the active components of the phenosolvan pitch were consumed before the glue–mix was applied, thus resulting in very weak final products. In conclusion, MDI fortification of phenoslvan pitch, or phenosolvan pitch–based resins can be achieved, for now only if the two compounds are applied separately. Additional experimentation will be required for a successful combination of the two before application.

2.7.6 Fortification of the phenosolvan pitch–based adhesives for exterior grade plywood with resorcinol.

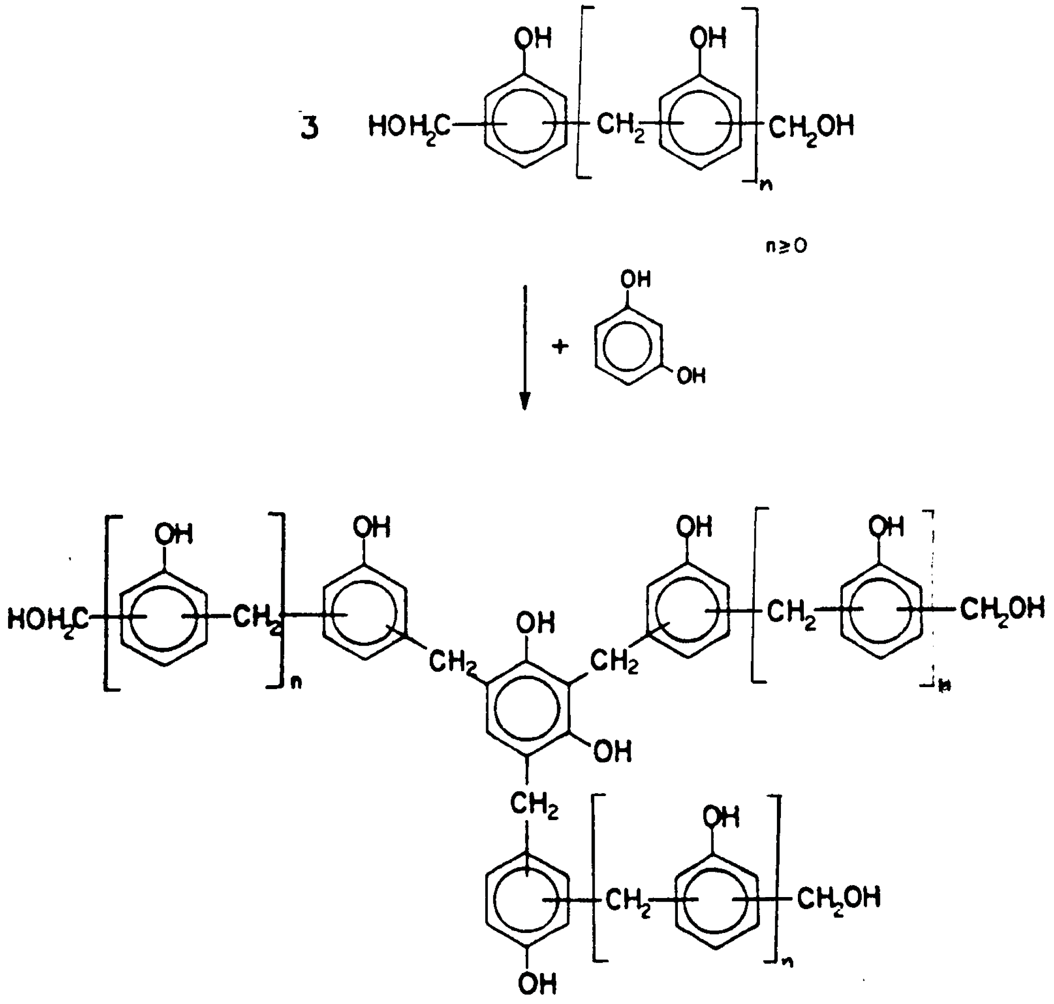
Resorcinol exhibits high reactivity toward formaldehyde and resorcinolic resins can give the strongest and most durable wood adhesives. Phenol–resorcinol– formaldehyde (PRF) adhesives are renowned for their excellent performance and weather resistance. Resorcinol, however, is very expensive and consequently the cost of PRF resins is high.

Because of its high reactivity, resorcinol and also PRF resins have been used in the past as fortifiers especially in the case of slow–reacting or difficult to handle phenolic–type resins. The reactivity of phenols towards formaldehyde is in the order: resorcinol > 3,5–dimethylphenol > m–cresol > o–cresol > p–cresol > phenol. Resorcinol has three reactive sites and it can therefore function as a cross linking agent thus improving the strength of the cured resin.



* POTENTIAL SITES REACTIVE WITH FORMALDEHYDE

Addition of a small amount of resorcinol (5% by mass) to the phenosolvan pitch resin resulted in an improvement of its resisrtance to cold and boiling water (Table 2.17 sample 6). In this initial investigation the resorcinol was added to the glue–mix just before application. However, although resorcinol is characterised by high reactivity, probably the curing time used was not enough to achieve all possible cross–linking. A more suitable improvement of the resin may therefore be likely if the resorcinol is grafted into the phenosolvan pitch in a different way. This could be achieved by synthesizing a resin from phenosolvan pitch using a small amount of formaldehyde for the establishment of methylol groups on the active phenolic components of the pitch followed by the addition of a small amount of resorcinol.



Curing of the above resin can be achieved by the addition of extra paraformaldehyde during glue–mix preparation and the application of high temperature and pressure during sample preparation. Another possibility is that the resorcinol does react with the pitch components thus accelerating the resin (Table 2.12) but it probably does so by increasing the molecular weight of the resin through branching, as shown in the diagram above. However, this does not much improve the strength of the resin since it already contains a relatively high percentage of large molecular weight components. This theory is supported by the fact that although some improvement is achieved by the addition of resorcinol to the unmodified phenosolvan pitch (panel No.6), such an addition has no effect on the high RxB pitch (panel No.12) which contains a greater percentage of high molecular weight components.

2.7.7 Deductions from the formulation–investigation phase

The results obtained during the first phase of this research show that the SASOL phenosolvan pitch has great potential for the development of new, weather–resistant wood adhesives. Fortification proved to be effective. Some fortifiers such as wattle tannin and PF resin, are able to improve the performance of the resin by a considerable degree. The results of Table 2.17 show that the tannin fortification gives better strength results in the dry test than PF fortification whereas the latter one exhibits higher wood failure in all three tests. The strength of the two samples in the wet tests is essentially the same. However, the fortification with PF resins has some important advantages over tannin fortification:

(i) PF addition extends the pot life of the phenosolvan pitch–based resin. This is very important since the resin is characterised by a pot life that is too short to allow application in an industrial scale.

(ii) Further improvement of the final resin is possible by optimization of the conditions of preparation of the PF so as to make it a fortifier more suited to this particular material.

In conclusion, the PF/S_1 phenosolvan pitch combination appears to have the best potential to succeed as a weather resistant wood adhesive. All further experimentation concentrated on the improvement of this resin.

2.8. OPTIMIZATION OF PF/PHENOSOLVAN PITCH (20/80) RESIN

2.8.1 Optimization of PF Fortifier

Both the effects of the phenol/formaldehyde ratio and of the reflux time of the PF resin were investigated. The results of Table 2.22 indicate that the best performance of the PF resin as a fortifier is attained at a phenol/paraformaldehyde mass ratio 1.7 i.e. molar ratio 1:1.85. The resin was prepared as described in 3.4.2.1. The effect of increasing the reflux time of the resin was also investigated. The results of Table 2.23 suggest that the performance of the resin improves with increasing reflux time of the PF fortifier. As expected, the viscosity of the PF resin also increases with increasing reflux time as more dimers and trimers are formed. However, refluxing for longer than 1 hour results in PF resins characterized by very high viscosity which (a) makes their use difficult, and (b) shortens considerably the shelf life of the resins.

In conclusion, the optimum conditions for the preparation of the PF resin which can serve as a fortifier of the phenosolvan pitch, are a phenol/paraformaldehyde molar ratio of 1:1.85 and a refluxing time of ~ 1 hour. These conditions provide a PF resin with high oligomer content. Those are probably the ones responsible for better cross–linking and consequently higher strength (cf. 2.7.6; 2.9).

Note: the results of Tables 2.22 and 2.23 appear to be much lower than those of Table 2.17. This is due to the fact that much less glue spread was used (only 350 g/m^2 d.g.l. instead of ~ 450 g/m^2 d.g.l. used in the first phase). Further optimization of conditions, however, was expected to increase the performance of the resin above the standard level.

2.8.2 Optimization of the amount of paraformaldehyde in the glue–mix

As indicated by the results of Table 2.24 the resin under investigation i.e. PF/phenosolvan pitch (20/80), reaches its maximum strength when paraformaldehyde powder is added as hardener at the level of 20 per cent by mass of phenosolvan pitch. Addition of further paraformaldehyde hardener does not strengthen the resin further. The performance of UF and PF resins is sometimes improved by the use of excess paraformaldehyde. This approach is used as the last resort by resin manufacturers when they are looking for an easy and quick way to improve low quality resins. Such an improvement, however, is done at the expense of formaldehyde emission from the final products where such resins have been used; the use of excess paraformaldehyde during glue–mix preparation increases formaldehyde emission by the cured resin. This constitutes a health hazard and should, if possible, be avoided as the maximum allowable formaldehyde emission by finished products is strictly controlled in several countries.

The fact that the addition of excess paraformaldehyde to the PF/phenosolvan pitch (20/80) resin does not increase further the strength of the cured resin suggests that the phenosolvan pitch reaches maximum reactivity toward formaldehyde when the latter is added at the 20 per cent level. This could be the reason why addition of extra paraformaldehyde does not force the reaction to proceed further, unlike what happens in the case of pure phenol–formaldehyde and urea–formaldehyde resins. This difference in behaviour can be attributed to the presence of more highly reactive phenolic compounds in the phenosolvan pitch.

2.8.3 The pH effect

High pH phenolic resins i.e. resols, are usually also applied under highly alkaline conditions; a pH of between 11.0 and 13.0 is generally used for these resins.

The results of Table 2.25 emphasize the importance of the pH effect on the resin resulting from the PF fortification of the phenosolvan pitch. It appears that pH is the single most important variable in the performance of the resin; a significant improvement is observed as the pH increases. The same conditions of glue–mix preparation and application were used in all samples of this series. The resin fails badly at pH 10.4 whereas very good results are obtained at pH 12.5. This might be attributed to the higher activation of the phenolic rings (c.f. 2.1.1) of the phenosolvan pitch components. The pH, however, cannot be used as the sole means of improving the resin because of two main limitations:

(i) the pot life decreases with increasing pH, and

(ii) the water resistance of the resin fails at very high NaOH content, (i.e sample 7.)

The optimum pH range for the phenosolvan pitch resin appears then to be between 12.5 and 13.0.

2.9 PLASTICIZATION AND CROSS–LINKING OF PHENOSOLVAN PITCH–BASED ADHESIVES.

Plasticization is required to compensate for the brittle nature of cured phenosolvan pitch–based adhesives. This may be achieved by either including plasticizers which are chemically bound into the adhesive network (internal plasticization) or by simple addition of them. An example of the first type of plasticization is the use of low molecular weight phenol–formaldehyde condensates [28,29] (also used as cross linking agents) which actually take part in the condensation. Polyolefins, vinyl or butadiene polymers of low molecular weight are suggested for the internal plasticization of phenolic adhesives [30]. These are apparently capable of taking up the deformation forces both elastically and reversibly and are able to distribute more evenly glue line stresses. Zinc chloride and boron trifluoride catalyse the reaction of these plasticizers with the phenolic resin [30]. Low molecular weight phenol–formaldehyde condensates proved to be the best internal plasticizers of phenosolvan pitch–based resins. Zinc chloride and zinc acetate catalysts have been employed but no obvious improvement was observed.

In general, no improvements of pitch–based adhesives has resulted from the addition of plasticizers which are chemically unreacted in the polymer network i.e. second type of plasticization. The usual class of chemicals used in this connection are the polyhydric alcohols [31], examples being ethylene glycol, diethylene glycol and teepol. Such plasticizers are usually added to highly polymerized PF polymers to improve resin flow at the hot press. Substituted phenols, such as cresols and xylenols, have been intermittently used as flow promoters, and for improved assembly time tolerance. Substituted phenols can be used to improve flow at a maximum level of 3 to 4% and are incorporated into the resin condensation steps as copolymers [32]. Addition of substituted phenols as flow promotors is not necessary in the case of phenosolvan pitch–based adhesives as the phenosolvan pitch itself contains relatively large amounts of these chemicals; 5.1% cresols and 25.6% xylenols. The fact that the addition of plasticizers to phenosolvan pitch–based resins did not improve the resins can be attributed to such high quantities of substituted phenols in the system. These components can also be held responsible for the excessive flow of the resins during hot–pressing which results in what is described as "bleed–through"; during pressing the adhesive penetrates through the outside veneers and reaches the surface of the panel giving it a spotty black colour. This can impose limitations on certain applications of these panels. A more detailed evaluation of the bleed–through problem is to follow.

The brittleness of unfortified pitch–based adhesives may be due to insufficient cross–linking. In such a case, the plasticizers normally prescribed for thermosetting adhesives would not necessarily have the desired effect on phenosolvan pitch adhesives. The results of Table 2.17 discussed earlier showed that the addition of cross–linking agents i.e. wattle tannin and phenolic condensates, brings about a marked improvement of the resin. This implies that lack of strength of unfortified phenosolvan pitch–based adhesives is probably caused by low amounts of cross–linking; this appears to be due to the formation of the first methylene bridges among large molecular size, more highly reactive phenolic components of the pitch, thus immobilizing the pitch–formaldehyde network which contains gaps too wide to be filled by other methylene bridges. This would render useless further reaction of formaldehyde with the smaller molecular size components of the pitch. Longer, wider molecular weight distribution, cross–linking agents are necessary to fill these gaps, increasing cross–linking and ultimately strength. In view of the fact that the methylene linkages may be too short for the optimum cross–linking, other aldehydes which also have bifunctional character can be used instead of formaldehyde. However, such aldehydes i.e. furfuraldehyde, exhibit slow reactivity toward phenols [33,34,35]. According to Pizzi and Scharfetter [36], however, this problem can be overcome by coupling furfuraldehyde with formaldehyde. Instead, a different and simpler approach was adopted in this research program; the maximum molecular weight and molecular weight distribution of the low phenol–formladehyde condensates was increased simply by adjusting the conditions during the synthesis of the condensates (c.f. 2.9.1).

Compatible reactivity of the phenolic fortifier and phenosolvan pitch towards formaldehyde is also very important for efficient cross–linking, otherwise the fortifier would remain entrapped in the immobilized pitch formaldehyde network without copolymerizing with the pitch components. Resorcinol, wattle tannin and low phenol–resorcinol–formaldehyde condensates have been tried as additional fortifiers of the PF/phenosolvan pitch resin (Table 2.26) but no further improvement of the resin was achieved implying that maximum cross–linking is brought about by the PF fortifier. Contrary to resorcinol and wattle tannin, the phenol formaldehyde condensates consist of components with different molecular weight thus allowing the final resin to contain a whole range of molecular sizes which are more capable of efficient cross–linking; the smaller molecular size phenolics in the PF fortifier, together with formaldehyde initiate the polymerisation and cross–linking between the different components of the phenosolvan pitch, whereas the larger PF constituents i.e. trimers and probably some tetramers in the higher polymerised PFs seem to have the right size to fill the gaps created by the cross–linking between the large molecular size components of the phenosolvan pitch. This appears to reduce brittleness and improve the strength of the resin.

2.10 FURTHER FORTIFICATION OF THE PF/PHENOSOLVAN PITCH (20/80) RESIN.

The results of Table 2.26 show clearly that addition of extra fortifiers apart from the inclusion of the PF resin at the 20% level is not necessary. It seems that as far as sample strength is concerned the addition of pure