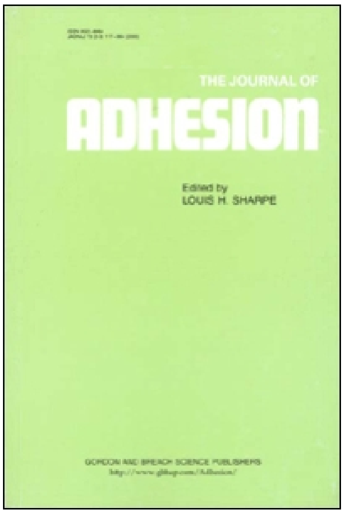

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Hydrogen Peroxide as a Resin Cure Accelerator

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Hydrogen Peroxide as a Resin Cure Accelerator †

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The reaction of hydrogen peroxide with conventional resin adhesives was sufficiently exothermic for the heat to accelerate and improve resin cure in the hotpress. As a consequence, pressing times for medium density fibreboard, particleboard, and plywood could be reduced by up to 30% and, in some cases, better resin cure permitted a reduction in binder level. Differences in the interaction of hydrogen peroxide with various adhesives were observed and a catalyst was found to enhance the exothermic effect.

The behaviour of hydrogen peroxide in combination with a tannin-based binder and wood fibre was studied over a wide temperature range. Below 60°C the system was stable. At 70°C the initial reaction was endothermic followed by a slow exothermic reaction. At hotpressing temperatures the exothermic reaction was rapid but controllable. It was concluded that the hydrogen peroxide-tannin-fibre system does not impose an additional safety hazard on medium density fibreboard plant operation.

KEYWORDS: Accelerator, fibreboard, hydrogen peroxide, particleboard, plywood, resin cure.

INTRODUCTION

A problem in commercial production of reconstituted wood panels is that of long pressing times, especially for thick panels, because of the

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time necessary for the occurrence of heat transfer to the core of the panel. This has been overcome by utilising the heat produced *in situ* from the exothermic reaction of hydrogen peroxide with the binder. The addition of small amounts of hydrogen peroxide to the binder system leads to the evolution of a considerable amount of heat which results in more rapid heating of the material in the hotpress and significantly increased core temperatures. The exothermic reaction has been recorded with all of the commonly used binders and the result has been significant reductions in pressing time for particleboard, plywood, and medium density fibreboard.

EXPERIMENTAL

1. Medium Density Fibreboard

Urea-formaldehyde resin (8.5% on O.D. fibre unless indicated) or *Pinus radiata* bark tanin extract solution (12% extract solids on O.D. fibre) was added to the fibre at the refiner blowline and the resulting fibre was collected after passing through the dryer. Hydrogen peroxide or an equivalent amount of water was added at a laboratory blender specially designed to handle fibre. Mats, 490 mm by 390 mm, were pressed in a laboratory hotpress at 165°C to give panels of 725 kg/cu. m nominal density at 10% moisture content and thickness after sanding of 12 or 25 mm. Duplicate mats were pressed for each set of conditions. A thermocouple inserted into the centre of each mat prior to hotpressing enabled the core temperature to be recorded.

In addition, a series of tannin-containing mats, half with hydrogen peroxide (1% on O.D. fibre) and half without, were prepared. Those mats not containing hydrogen peroxide had an equivalent amount of water added. The mats thus prepared were cut in half and recombined so that one half (245 mm by 390 mm) contained hydrogen peroxide and the other half did not. The matched pairs were pressed at platen temperatures of 45, 55, 70, 105 and 165°C and a press opening of 13.8 mm which gave a nominal mat density of 650 kg O.D. matter/cu. m. Duplicate mats were prepared for each set of conditions, the only difference being that the positions of the peroxide and non-peroxide half-mats in the press were reversed between press loadings. The time to stops was less than 20 seconds.

2. Particleboard

Single layer 300 mm square panels of 12.2 mm nominal thickness were made from *P. radiata* flakes. Target density was 700 kg/cu. m at 8% moisture content. Hydrogen peroxide (1% on O.D. flakes) was sprayed onto one lot of flakes as a 40% aqueous solution. An equivalent amount of water was sprayed onto another lot of flakes in lieu of hydrogen peroxide as a control. Tannin-based resin (10% on O.D. flakes) was sprayed onto both lots of flakes separately. The moisture content of the mats was 18.3%, the platen temperature was 170°C and the pressure was 4 MPa with the time to stops 0.5 minutes. The panels were pressed at maximum pressure for 2.5 minutes and the pressure was then released gradually over a further 1.0 minute. The temperature at the centre of each panel was measured as a function of time using a thermocouple connected to a datalogger.

3. Plywood

The plywood panels were made up of ten 3.2 mm thick *P. radiata* veneers with the core veneers parallel laminated. The veneers were 300 mm square. Each 300 mm square set of veneers was cut in half to give two 150 mm by 300 mm sets. The veneers in one of the sets were sprayed with measured amounts of a 40% aqueous solution of hydrogen peroxide on one surface and spread with adhesive on the other before being laid up in the conventional manner. The veneers in the matching set were sprayed with an equivalent amount of water to compensate for the hydrogen peroxide solution before they were coated with adhesive and laid up as for the hydrogen peroxide-treated veneers. Hydrogen peroxide was applied at rates of 6, 12 and 18 g/m^{2}DGL. The adhesives used were a commercially available phenol-formaldehyde plywood resin and one based on *P. radiata* bark tannin extract. The gluespread was 450 g/m^{2}DGL in all cases. The time between spraying the hydrogen peroxide onto the veneers and spreading the adhesive was denoted the peroxide residence time. Three different time periods were used—10 minutes, 1 hour and 24 hours.

Thermocouples were inserted into the centre of each panel and the matching panels were prepressed as a pair of 1.0 MPa for 10 minutes before being hotpressed at 1.2 MPa and 150°C for 18 minutes. The temperature at the centre of each panel was recorded as a function of pressing time. The resulting plywood was 31 mm thick. Each press loading was duplicated except that the positions of the peroxide-treated and control panels in the hotpress were reversed between loadings.

RESULTS

1. Medium density fibreboard

The exothermic behaviour of hydrogen peroxide with urea-formaldehyde on 25 mm thick medium density fibreboard is illustrated in Figure 1. Both levels of hydrogen peroxide addition reduced the time for the core temperature to reach 100°C relative to that for the conventional panel. The time for each of the core temperatures to reach 100°C and the maximum core temperatures attained are recorded in Table I for comparison. The higher the level of hydrogen peroxide the greater the rate of core temperature increase and the higher the maximum core temperature attained.

The interaction between hydrogen peroxide and the binder depended on the binder level as illustrated for urea-formaldehyde in Table II and on the chemical character of the binder. Comparison of the mats

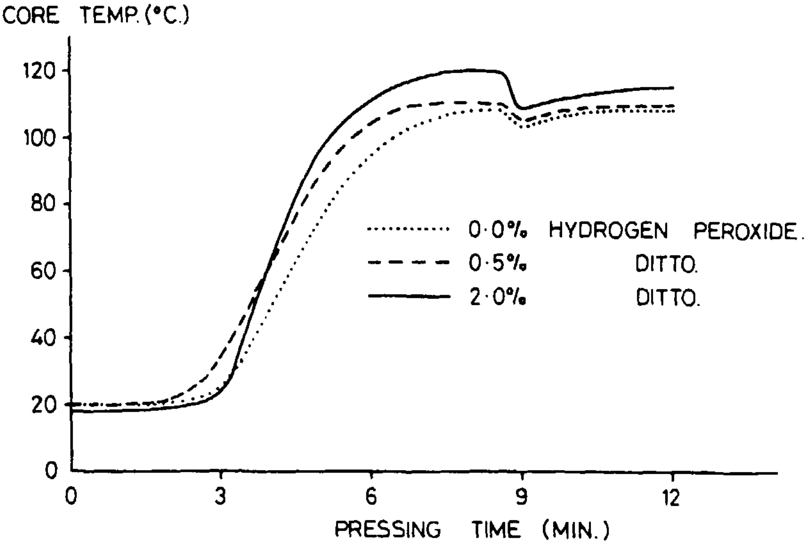

FIGURE 1 The exothermic effect of hydrogen peroxide on medium density fibreboard bonded with urea-formaldehyde resin.

TABLE I
The effect of hydrogen peroxide on the core temperature of 25 mm density fibreboard bonded with urea-formaldehyde

Hydrogen peroxide (% on O.D. fibre)	0	0.5	2.0
Maximum core temperature (°C)	106	109	120
Time to 100°C core temperature (sec.)	390	345	315
Density (kg/m^3)	684	690	664
Internal bond (kPa)	555	440	110

TABLE II
The effect of urea-formaldehyde binder level on the exothermic behaviour of hydrogen peroxide in 12 mm medium density fibreboard

Binder level (% on O.D. fibre)	0	5.5	8.4	9.0
Hydrogen peroxide (% on O.D. fibre)	1	1	1	0
Maximum core temperature (°C)	120	119	122	115
Time to 100°C core temperature (sec.)	153	140	130	152
Density (kg/m^3)	675	701	711	722
Internal bond (kPa)	110	300	585	845

hotpressed in the presence of hydrogen peroxide alone and those containing urea-formaldehyde without any added hydrogen peroxide shows that the use of 1% hydrogen peroxide on O.D. fibre did not affect the time taken for the core temperature to reach 100°C. It was the interaction of hydrogen peroxide with the binder rather than the fibre which caused the exothermic behaviour.

The interaction between hydrogen peroxide and urea-formaldehyde resins leads to a loss in bond quality as shown in Table II. This reinforces the conclusion that the hydrogen peroxide reacts with the binder rather than the fibre.

Hydrogen peroxide has been used to bond wood[1–4] but it seems that either high panel densities or the concurrent use of a polymerisable crosslinking agent are necessary to achieve satisfactory bonding.[5–8] In order to determine whether hydrogen peroxide would give a significant improvement in bond quality at the levels employed to achieve resin cure acceleration, the internal bond and the modulus of rupture of the panels made solely from fibre and hydrogen peroxide at a standard density of 725 kg/m^3 were measured. The internal bond and the modulus of rupture of these panels made using 1% hydrogen peroxide without urea-formaldehyde binder were 110 kPa and 8.8 MPa respectively, values which are insignificant compared to the internal bond for the panels made with 9% urea-formaldehyde resin and no hydrogen peroxide of 1225 kPa and typical modulus of rupture figures for urea-bonded medium density fibreboard of 40–45 MPa. As well, the panels swelled excessively in cold water and disintegrated in water at 70°C. On the basis of these results it was concluded that interfibre bonding induced by the oxidative effect of hydrogen peroxide did not contribute to the bond quality of medium density fibreboard made using conventional resin adhesives in conjunction with hydrogen peroxide as a resin cure accelerator. At least 6% hydrogen peroxide is necessary for significant oxidative bonding in medium density fibreboard. Even then a commercially acceptable product could not be produced.

Reactions of hydrogen peroxide may be enhanced by the use of catalysts. As the exothermic effect of hydrogen peroxide with urea-formaldehyde resins is less than with other binders, catalytic amounts of ferrous sulphate were sprayed onto the fibre after hydrogen peroxide addition. The results are shown in Table III. At the two lower levels of ferrous sulphate addition, there was no effect but at the highest level, corresponding to a ferrous sulphate/hydrogen peroxide mole ratio of 0.002 : 1.0, there was an increase in maximum core temperature and likewise a decrease in the time to a core temperature of 100°C. There are two consequences of this. First, the potential resin cure acceleration is greater for a given amount of hydrogen peroxide using a catalyst. Second, a given level of resin cure acceleration can be achieved using less hydrogen peroxide thereby improving the economics of the technique.

Recently, a tannin-based extract from *Pinus radiata* bark specifically formulated for use as a particleboard binder became commercially available in New Zealand. It was felt that being phenolic in character the tannin would be better suited to react with hydrogen peroxide

TABLE III

The effect of ferrous sulphate on the exothermic behaviour of hydrogen peroxide and urea-formaldehyde resin

Hydrogen peroxide (% on O.D. fibre)	0	1†	1	1	1
Fe SO_4 $7H_2O$ (% on hydrogen peroxide)	0	0	0.017	0.17	1.7
Maximum core temperature (°C)	115	122	121	121	126
Time to 100°C core temperature (sec.)	152	129	133	130	118

† Mean of four mats, others duplicates.

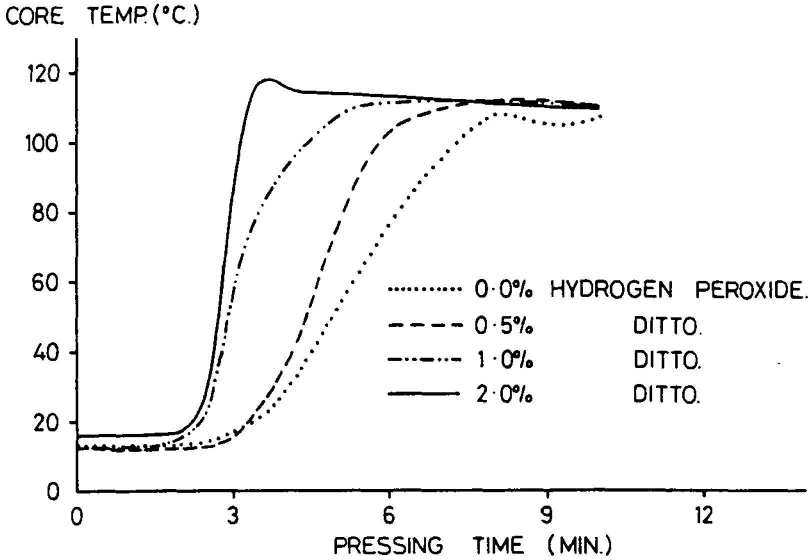

FIGURE 2 The exothermic effect of hydrogen peroxide on tannin-bonded medium density fibreboard.

TABLE IV
The effect of hydrogen peroxide on the core temperature of 25 mm medium density fibreboard bonded with tannin-formaldehyde.

Hydrogen peroxide (% on O.D. fibre)	0	0.5	1.0	2.0
Maximum core temperature (°C)	108	111	112	117
Time to 100°C core temperature (sec.)	425	345	270	190
Density (kg/m^3)	741	731	745	733
Internal bond (kPa)	1170	1140	1210	995
Internal bond retention (%)†	32.5	46.3	38.7	29.4
Permanent swell (%)†	4.6	4.4	4.0	6.2

† 2 hr boil, 1 hr cold soak, 24 hr dry at 105°C

than urea-formaldehyde. This proved to be so and the results are summarised in Figure 2 and Table IV. At 2% hydrogen peroxide addition, the time taken for the core temperature to reach 100°C was 45% of the value measured for the peroxide-free control panels compared to 81% for the urea-formaldehyde bonded example in Table I.

Nonetheless, the greater reactivity of hydrogen peroxide with tannin did not detract from the stability of the hydrogen peroxide-tannin-

TABLE V

The effect of the time between the application of hydrogen peroxide/tannin to the fibre and hotpressing (peroxide assembly time) on the core temperature of 12 mm medium density fibreboard

Peroxide assembly time (hours)	0	1.0	3.5
Maximum core temperature (°C)	127	127	124
Time to 100°C core temperature (sec.)	80	78	76
Density (kg/m^3)	710	696	695
Internal bond (kPa)	1260	1260	1315
Internal bond retention (%)†	40.2	39.4	27.6
Permanent swell (%)†	8.3	4.2	5.5

†2 hr boil, 1 hr cold soak, 24 hr dry at 105°C.

fibre system under ambient conditions. The time between blending the hydrogen peroxide (2% on over dry fibre) and tannin with the fibre and hotpressing the mats was varied up to 3.5 hours and the effect of this time on the heating rate and core temperature is shown in Table V. The hydrogen peroxide-tannin-fibre system was stable under ambient conditions for the 3.5 hours of the experiment.

It was also found that, for a given binder system, the effect of the peroxide-induced exotherm was greater the thicker the mat. Thus for 12 mm panels the time for the core temperature to reach 100°C was reduced by around 40% compared with the 55% reduction noted above for 25 mm thick panels.

2. Particleboard

Similar effects were observed for hydrogen peroxide with particleboard. The hydrogen peroxide-tannin system on 12 mm particleboard made with 1% hydrogen peroxide on oven dry flakes was typically exothermic (Figure 3). The time taken for the core temperature of the boards made with hydrogen peroxide to reach 100°C was 14% less than the time for the boards made without hydrogen peroxide. As well, the maximum core temperature in the peroxide-treated mats was 10°C higher. For thicker boards the effect of the peroxide-induced exotherm on the time taken for the core temperature to reach 100°C could be expected to be correspondingly greater as with the medium density fibreboard.

3. Plywood

By spraying hydrogen peroxide onto one veneer surface and spreading adhesive on the other in each glueline to produce the exothermic

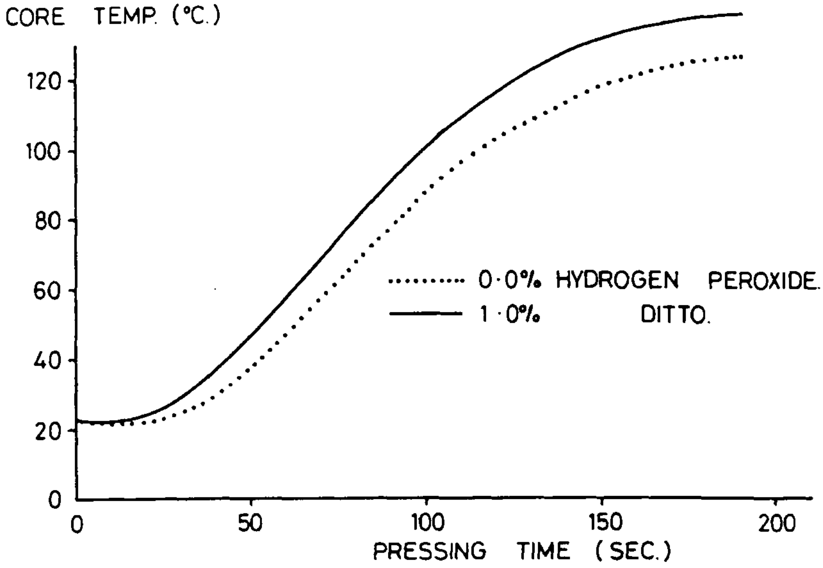

FIGURE 3 The exothermic effect of hydrogen peroxide on tannin-bonded particleboard.

reaction of the hydrogen peroxide with the adhesive in the hotpress, significant reductions in pressing time were achieved for plywood, especially for thick panels. Very good results were achieved using tannin-formaldehyde (Figure 4) and phenol-formaldehyde adhesives. For 31 mm thick softwood plywood bonded with tannin-formaldehyde or phenol-formaldehyde the core temperature reached 100°C up to 40% faster when hydrogen peroxide was present. In contrast to the results for medium density fibreboard and particleboard, little or no difference in maximum core temperature was observed.

The hydrogen peroxide-adhesive systems were reasonably stable during the assembly and prepressing operations; slightly more so for the tannin-formaldehyde resin as shown by the small temperature difference between the peroxide-containing panel and the control at zero pressing time (Figure 4) than for the phenol-formaldehyde resin. The greater reactivity of the phenol-formaldehyde resin with hydrogen preoxide was insufficient to cause precure and no decline in plywood bond quality was detected in panels made with hydrogen peroxide relative to those made without.

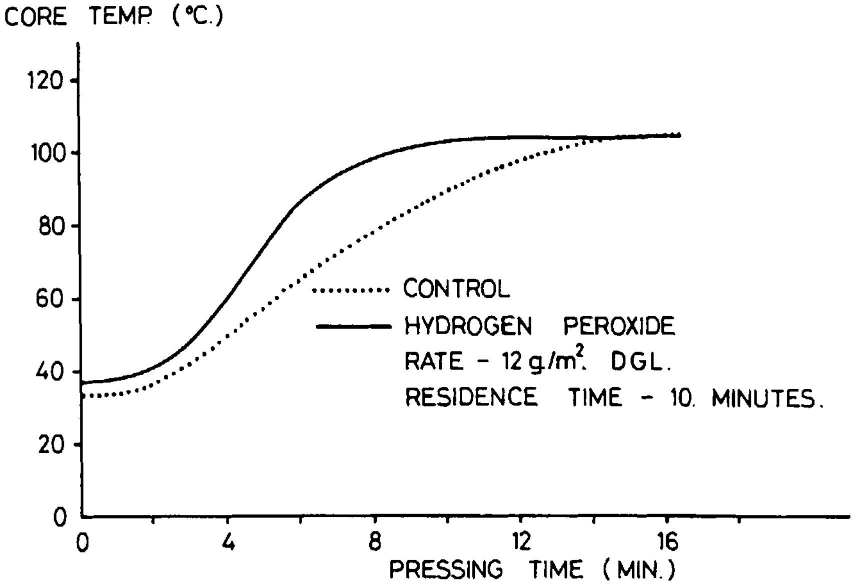

FIGURE 4 The effect of hydrogen peroxide on the core temperature of tannin-bonded plywood—10 plies, 31 mm.

Figures 5 and 6 indicate the magnitude of reductions in pressing times which were achieved for plywood using hydrogen peroxide with phenol-formaldehyde and tannin-formaldehyde adhesives respectively. For both phenol-formaldehyde and tannin-formaldehyde the exothermic effect increased as the amount of hydrogen peroxide in each glueline was increased. The time the veneers were left after being sprayed with hydrogen peroxide before contacting the adhesive (hydrogen peroxide residence time) was varied between 10 minutes and 24 hours. The peroxide residence time did not affect the extent of the exothermic effect when the phenol-formaldehyde adhesive was used (Figure 5) but with the tannin-formaldehyde adhesive the exothermic effect diminished, initially quite quickly, until after 24 hours the reduction in the time for the innermost glueline to reach 100°C was about 65% of its value at a peroxide residence time of 10 minutes (Figure 6). Hydrogen peroxide in combination with tannin-formaldehyde gave larger reductions in the pressing time than the hydrogen peroxide/phenol-formaldehyde system especially at the two higher peroxide loadings.

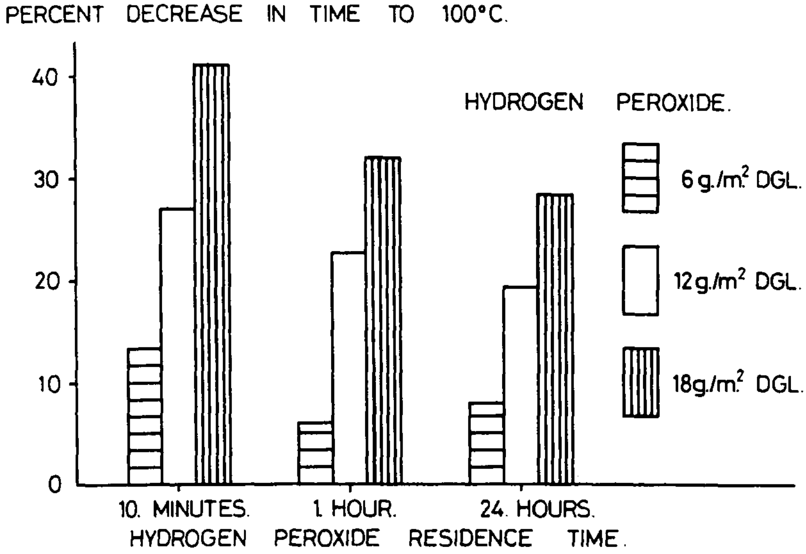

FIGURE 5 The decrease in time for the core temperature of 31 mm phenol-bonded plywood to reach 100°C.

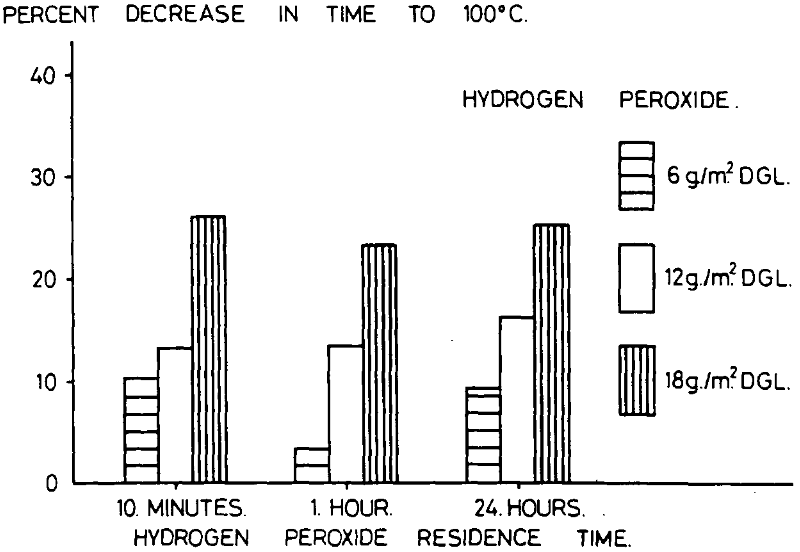

FIGURE 6 The decrease in time for the core temperature of 31 mm tannin-bonded plywood to reach 100°C.

4. Safety aspects

As stated previously, the chemical nature of the adhesive system has a significant bearing on the amount of heat evolved by the hydrogen peroxide. The hydrogen peroxide/tannin-formaldehyde system worked particularly well and its application to medium density fibreboard manufacture was investigated further. In the interests of plant safety it was important to learn more about the behaviour of the tannin-fibre system when it is exposed to hydrogen peroxide under conditions likely to be encountered during medium density fibreboard manufacture. Small amounts of the reactive fibre were shown to be stable under ambient conditions for several hours (Table V) but as heat triggers the exothermic reaction it was important to define as closely as possible the temperature range over which the reactive fibre could be expected to remain stable.

This was done on a laboratory scale by forming half-size mats differing only in the presence or absence of hydrogen peroxide and recombining them so that each mat consisted of two half-mats, one with and the other without hydrogen peroxide. A series of these composite mats was pressed at different temperatures with the core temperatures of each half-mat being recorded and plotted as a function of pressing time (Figure 7). At platen temperatures of 45 and 55°C the hydrogen peroxide had little or no effect on core temperature. At 70°C two features became apparent. First, the core temperature of the peroxide-containing mats was initially lower than for the peroxide-free control mats which is indicative of an endothermic reaction involving hydrogen peroxide. Second, this initial endothermic reaction was followed by the expected exothermic reaction. The exotherm developed slowly and the evolution of heat took place over several minutes. The endotherm was also observed, albeit briefly, when the platens were at 105 and 165°C but it was not detected at 45 or 55°C. The endotherm–exotherm sequence can be connected if it is supposed that the endotherm is due to vapourisation of the hydrogen peroxide–water mixture from the fibre surface. Thus below 60°C vapourisation is negligible, at 70°C it would appear to be controlling the rate of the exothermic reaction and above 100°C it is sufficiently fast to enable the exothermic reaction to proceed rapidly. It can be concluded from this that vapourisation of hydrogen peroxide is a necessary condition for the exothermic reaction to take place. This concurs with thermal analysis data collected by Nguyen *et al.*[9], using milligram quantities

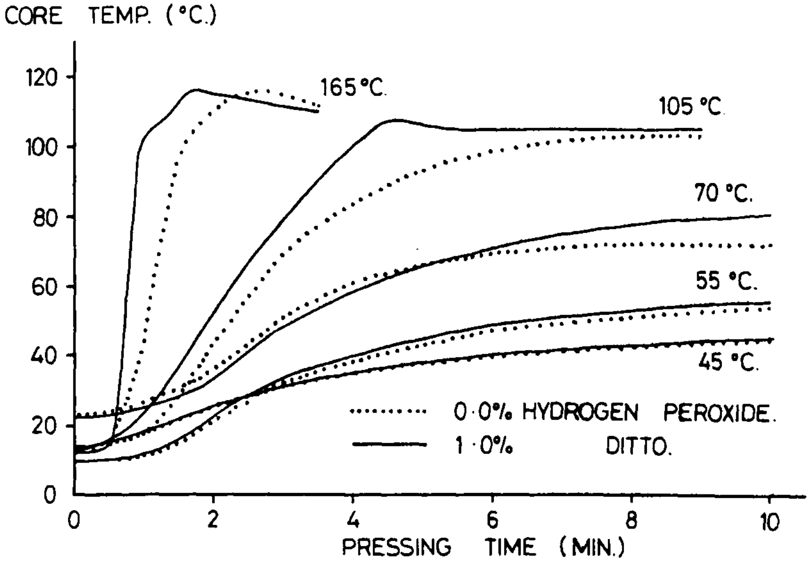

FIGURE 7 The effect of hydrogen peroxide on tannin-bonded medium density fibreboard mats at different temperatures.

of peroxide-treated wood flour in sealed pans with a pin hole to retain the vapourised hydrogen peroxide in contact with the lignocellulosic material. They found that vapourisation of hydrogen peroxide preceded significant reaction of hydrogen peroxide with the wood flour.

The peaks in the core temperature profiles for platen temperatures of 105 and 165°C (Figure 7) mean that the hydrogen peroxide was rapidly consumed in the hotpress at normal pressing temperatures. The exotherm produced during hotpressing of mats can be controlled by controlling the level of hydrogen peroxide addition (Table IV). This, coupled with the brief duration of the exothermic reaction, indicates that the use of 1% hydrogen peroxide on O.D. fibre will not cause excessive heat build-up in the mats during the hotpressing operation and thus special handling procedures at the hotpress are not required.

Figure 8 shows the difference between the maximum core temperature of the peroxide-containing mats and the core temperature of the peroxide-free control mats (recorded when the maximum core temperature was reached in the peroxide-containing mats) as a function of platen temperature for mats containing 650 kg O.D. matter/cu. m. It can be seen that the hydrogen peroxide-tannin-fibre system was stable

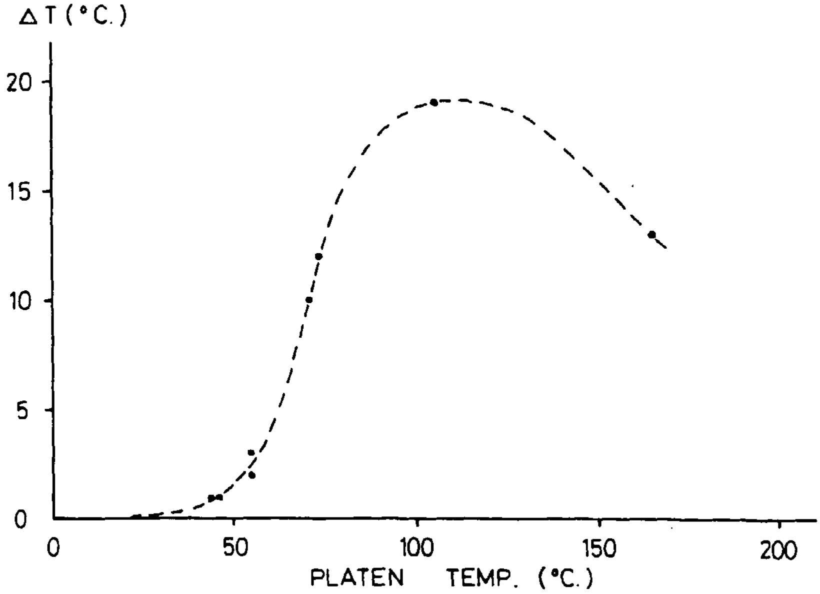

FIGURE 8 The difference between the maximum core temperature of the peroxide-containing mats and the core temperature of the peroxide-free control mats as a function of temperature.

below a temperature of about 60°C. This result was consistent over the density range 230–650 kg O.D. matter/cu. m. This means that during the mat-forming process peroxide-treated fibre can be handled similarly to ordinary resin-coated fibre. The peroxide-treated fibre has the same tolerance to heat as fibre treated with conventional binders and the useful life of the fibre depends only on the resin system employed. The behaviour of bulk quantities of fibre during plant shutdown has yet to be determined. Laboratory data indicate that in practice the interaction of the resin system with plant equipment such as the forming wire will determine how long fibre can be left before it causes handling problems.

CONCLUSION

The feasibility of utilising the exothermic reaction between hydrogen peroxide and conventional resin adhesives to accelerate resin cure has been demonstrated. Potential reductions in total pressing time for thick panels of up to 30% are possible. The ease of spray application of hydrogen peroxide makes the technique particularly suitable for use in the manufacture of medium density fibreboard and particleboard and in situations where increased production is constrained by hotpress capacity it could be of considerable importance.

Scaling up to a full-size hotpress should better utilise the effects of hydrogen peroxide because of less heat dissipation from the larger mats. It is envisaged that this, coupled with the use of catalysts to maximise the exothermic nature of the process, will enable the amount of hydrogen peroxide to be reduced from that required on a laboratory scale, thereby enhancing the economic viability of the technique.

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