RECORD
of the
1985 ANNUAL CONVENTION
of the
BRITISH WOOD PRESERVING ASSOCIATION

Cambridge
June 25th – 28th, 1985

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R. P. MARSHALL
President of the British Wood Preserving Association

The British Wood Preserving Association

PREMIER HOUSE, 150 SOUTHAMPTON ROW
LONDON WC1B 5AL

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BRITISH WOOD PRESERVING ASSOCIATION

The British Wood Preserving Association is a scientific and advisory association.

It is a body which collects information on the preservation and fireproofing of timber and the methods of applying preservatives and fire retardants; it sponsors scientific research into the use of preservatives and fire retardants, and makes available to all enquirers the results of its researches by the publication of leaflets, a technical advice service and specialist lectures. It is completely impartial in its outlook and in the advice it gives. Among other objects it aims at making known the advantages of using preserved timber in the interests of the consumer and the national economy.

MEMBERSHIP: Amongst the members are

Learned societies and research bodies at home and overseas.
Architects, surveyors, builders, etc.
Manufacturers of all types of preservatives and fire retardants.
Users of timber.
Firms operating all forms of treating plant.
Specialists in the remedial and curative treatment of timber *in situ*.
Manufacturers of plant.

COMMITTEES

In the working of its committees close liaison is maintained with Government Departments, as well as with the principal consuming industries.

On the Council there are representatives of learned societies, scientific bodies, principal consumers, architects and consultants, as well as manufacturers and those who specialise in preservative treatment of timber.

Other Committees deal with technical matters, finance, membership and environmental problems.

On several of these Committees there are representatives of the nationalised industries, consuming industries, and organisations such as Princes Risborough Laboratory, T.R.A.D.A. and the Health and Safety Executive.

SERVICES

It offers a free advisory service on all problems connected with timber preservation.
It issues leaflets dealing with practical problems and the latest developments in research.
It holds an Annual Convention at which specialist papers are presented by experts from all over the world.
It publishes in book form a Record of the Annual Convention containing copies of the papers, etc.
It issues free of charge to all members a News Sheet.
It maintains a panel of lecturers whose services are available on request.
It organises exhibitions to show the value of preservation.
It arranges visits to the works of manufacturers and treaters.
It represents the industry on a number of international committees connected with timber preservation.

FINANCES

It should be appreciated that the Association depends entirely on subscriptions and special contributions from its members. This, of course, enables it to remain completely independent and at the same time to maintain its impartial and scientific approach to all problems.

CONTENTS

OPENING ADDRESS BY THE PRESIDENT
R.P. MARSHALL

Ladies and Gentlemen,

Once again it is my very great privilege and pleasure to welcome you to Cambridge for our 36th Annual Convention and a particular welcome to those attending for the first time. I hope you all have an enjoyable and interesting stay in Cambridge, that you will be the catalyst by which our traditional (i.e. cool and wet) English summer changes for the better and thus enable you to benefit to the maximum during the informal parts of the Convention.

As you will no doubt have noticed we are housed for our programme of papers in a brand new location, the Peterhouse Theatre. To some extent this movement has been forced upon us by the non-availability of our usual location at the University Lecture Rooms in Bene't Street, but I hope that if we find Peterhouse Theatre satisfactory (and I am sure we will) then we shall have a base for our Convention for many years ahead.

May I also say how pleased Council and Officials of B.W.P.A. are to see the continued excellent support which this Convention receives. Again this year we have no fewer than 274 delegates and guests, of whom 62 have come from 13 overseas countries.

I would, before starting the Convention proper, like to make a few remarks about the activities of the Association over the past year. Whilst much steady and important work has been done by the Technical Committee in connection with Standards and Codes and Practice; by the Remedial Treatment Section in consolidating the pre-eminence of B.W.P.A. membership for this sector of our Industry; and by the Pretreatment Committee in promotional activities and movement towards a quality assurance scheme, the year has been dominated by the introduction of legislation to change the voluntary P.S.P.S. (Pesticides Safety Precautions Scheme) to a statutory basis.

The Association has spent much time and effort in discussions with Government, Members of Parliament, kindred Associations, and other interested parties to ensure that matters of vital interest to our Industry are not overlooked during the passage of the Food and Environment Bill through Parliament. The basic problem has been to make sure that all concerned understand that other industries besides the agrochemicals industries use pesticides and that the criteria for effective control is not necessarily the same. We feel as an Association that we are already well to the fore in promoting and operating the safe and efficient use of pesticides in our Industry and we will support any additional reasonable proposals arising from the Bill. We have been promised continued consultation during the drafting of the Regulations which will implement the Bill, but we will not know how successful our campaign has been until the final Regulations are issued, probably later this year.

One further point of concern has been the increased environment pressure against pesticides in general and certain pesticides in particular. We in Wood Preservatives use a very limited range of products and whilst we continue to support and promote work to discover new and safer products and systems, the loss of any of our existing 'portfolio of products' is a serious matter. I am not sure that the pressure groups who advocate the ban on pesticides recognise that the effect could be a more unsatisfactory situation that the present careful approach of training, safe practice, and compliance with existing statutory controls.

So you will see that the Association is very active on behalf of its Members and I recommend you read the Annual Report for a much more detailed account of the work of the Committee, and of the full-time Officers. On this latter point I shall have more to say at the end of the Convention.

Turning now to the Convention, I look forward to the usual assembly of interesting papers and probably what is of equal importance a lively and useful discussion period at the end of each presentation. I therefore have great pleasure in declaring the 36th B.W.P.A. Annual Convention under way.

As is traditional I as President have the pleasure of chairing the first paper and I would ask Dr. Janice Carey to join me on the platform.

B.W.P.A. ANNUAL CONVENTION 1985

DEVELOPMENTS IN THE ASSESSMENT OF JOINERY PRESERVATIVES

by Janice K. Carey and A.F.Bravery
Department of the Environment, Building Research Establishment, Princes Risborough Laboratory

Summary

The paper describes the development of a method for assessing joinery preservatives using destructive examination of simulated joinery components (L-joints). Criteria for assessing the performance of treatments are derived from determination of the fungi colonising the samples and the related changes in the porosity of the timber.

On Scots pine sapwood five per cent pentachlorophenol (P.C.P.) treatments by dip and double vacuum are giving a better performance than one per cent tri-n-butyltin oxide (Tn.B.T.O.) treatments, whereas on spruce P.C.P. and Tn.B.T.O. are giving a broadly equivalent performance. The relative performance of these treatments is beginning to show a good correlation with results, assessed by failure through decay, from similar long-term field trials established previously. It is anticipated that data obtained by destructive examination early in exposure will be capable of forming a basis for predicting the likely service life of new preservative treatments for use on external joinery.

Introduction

The need for preservative treatment of external joinery manufactured from non-durable timber species is now well established and the problems of decay and the introduction of preservative treatment have been documented (Savory and Carey, 1979). The suitability of particular wood preservatives for the treatment of joinery was originally assessed in the U.K., in terms of initial toxicity to wood decay fungi, by comparison with a pentachlorophenol (P.C.P.) standard (Forest Products Research Laboratory, 1967) using data from laboratory tests according to the B.S.838:1961 test method. This practice has continued for products containing active ingredients not already listed in B.S.5707:Part I (1979). However, this approach whilst meeting a short term need can be criticised for lack of realism. For instance, the fully impregnated test block used in B.S.838 differs in several respects from the dip or double vacuum treated joinery member, particularly in that there is no untreated core to be protected. Test blocks containing an untreated core have been subjected to labora tory tests (Savory and Carey, 1976) which indicated that many treatments complying with British or B.W.P.A. Standards might not afford protection. However, the test conditions are particularly severe in providing near optimum conditions for the fungus, including a nutrient food base from which to colonise the test blocks. In an alternative and less severe approach in which basidiospores deposited directly on the test blocks were used as the source of infection, it was shown that the levels of preservative required to prevent attack were similar to those using mycelium established on a food base (Savory and Carey, 1976). Other alternative approaches to making laboratory tests more realistic have been attempted, for example the polythene bag technique of Amburgey and Behr (1979) but at P.R.L. a model L-joint system has been favoured.

Using the destructive assessment of painted simulated joinery units (L-joints) it has been shown that the colonisation of joinery by micro-organisms takes the form of a sequence involving bacteria, bluestain fungi, soft rot fungi and culminating in the Basidiomycetes, the fungi which ultimately cause the failure of joinery through decay (Carey, 1980, 1983). In addition, the technique has highlighted the potential rôle of fungi present in joinery but not ultimately responsible for causing decay (e.g. bluestains, soft rots) in influencing the performance of a preservative treatment. For example it has been shown (Sutter and Carey, in preparation) that three *Phialophora* species can induce detoxification of tri-n-butyltin oxide (Tn.B.T.O.). There are clear grounds therefore for proposing that tests intended to provide a realistic evaluation of preservatives for joinery use should, at an early stage, involve exposure to the complete range of micro-organisms ultimately likely to be encountered in service (Carey, 1982). This is of course the principle involved in conventional field trials (Purslow and Williams, 1978) but the time to failure through decay is too long to permit the use of such trials in lieu of laboratory tests. However, the work with L-joints has shown that the rate at which the sequence of colonisation by micro-organisms progressed was changed by preservative treatments. Additionally, microbial activity has been shown to bring about changes in the porosity of the wood, and these findings have provided new criteria which can be detected early in the process and which may be related to service performance (Carey, 1982).

To develop and assess the predictive capability of the technique a phased series of L-joint trials have been established which extend the test parameters to include double vacuum treatments, preservatives other than Tn.B.T.O. and P.C.P., other timbers (largely spruce but also hemlock and red lauan), other coating systems and the effects of sealing the end grain exposed within the joint, to restrict water uptake. This paper concentrates on the comparisons of Tn.B.T.O./P.C.P., dip/double vacuum and Scots pine sapwood/spruce.

Materials and Methods

Method

The nature of the L-joint test sample, and the general methods of handling, exposure and assessment have been described already (Carey, 1982). Essentially the L-joint consists of two members, each 38 × 38 × 203 mm joined by a bridle joint with the tenon in the horizontal member (Figure 1). After various exposure periods, replicate sets are sawn to yield blocks for moisture content and porosity studies and for sampling the microbial population at predetermined points.

Timber

Scots pine sapwood *(Pinus sylvestris)* — British grown, kiln dried:
Spruce *(Picea* species) — unsorted Russian whitewood:
Hemlock *(Tsuga heterophylla)* — selected from packaged hemfir:
Red lauan *(Shorea* species) — timber merchant.

Preservatives

Tn.B.T.O. — 1 per cent in Shellsol E* or a commercial solvent:
P.C.P. — 5 per cent in Shellsol E containing 10 per cent by weight of dibutyl phthalate as co-solvent:
Acypetacs zinc — 14.5 per cent solution containing 3 per cent zinc:
Tn.B.T.N./Xyligen B — 0.9 per cent tri-n-butyltin naphthen-

*Shellsol E is an aromatic hydrocarbon solvent, distillation range 153–193°C

ate, 0.38 per cent ai Xyligen B plus 0.18 per cent dichlofluanid and 4.8 per cent resin:
P.C.P.L. — 5 per cent pentachlorophenyl laurate plus 0.5 per cent gamma H.C.H.:
Xyligen B — 0.84 per cent ai Xyligen B plus 6 per cent resin:
I.P.B.C. — 0.5 per cent 3-iodo-2-propynyl butyl carbamate (Troysan Polyphase)

Treatment
The ends of the L-joint tenon members remote from the joint were sealed with two coats of P.V.A. glue (Evostick Resin W) prior to treatment to prevent unrealistic end grain absorption of preservative solutions. The components were dried for a minimum of four weeks prior to assembly and coating; the end seal was removed after drying.

Coating
After assembly, unless otherwise indicated, a proprietary pure alkyd paint system, consisting of primer, undercoat and gloss finish, was applied to each L-joint, at the manufacturer's recommended rate of coverage. After labelling, the end grain surfaces remote from the joint of both members were sealed with two coats of Hevikote**. Finally the paint seal across the joint was broken by separating and reassembling the two members so that water could enter all the joints immediately, rather than at a variable time dependent on the durability of the paint film.

Sampling
The system of conversion used for the destructive sampling and assessment of the tenon member of the L-joints is shown in Figure 1. The four moisture content and porosity sample blocks were weighed to establish moisture content at the time of sampling, then dried to constant weight at 50°C prior to being dipped in dekalin for 10 sec and uptake assessed as a measure of porosity. Finally, after evaporation of the dekalin, the blocks were dried at 103°C and the moisture content calculated.

The fungal population was sampled within six small areas of each L-joint tenon member, three close to the joint and three along the remaining length. At each sampling point, three media, each selective for a different part of the fungal population, were used in an attempt to isolate a high proportion of the fungi present.

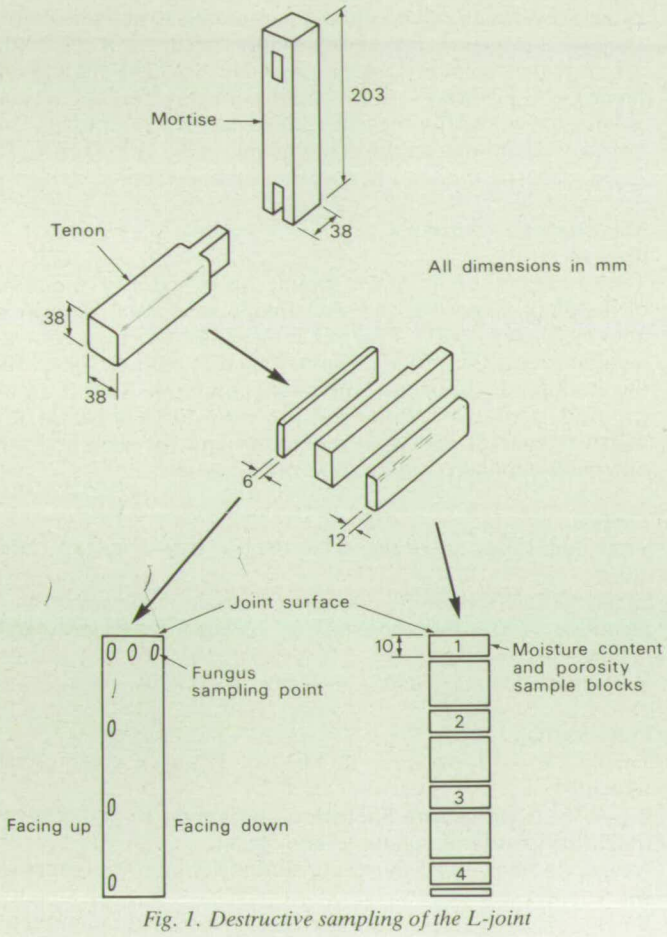

Fig. 1. Destructive sampling of the L-joint

**Hevikote is a two pack product combining epoxy resin and modified coal tar pitch.

TABLE 1
Preservative Treatment Schedules

Timber species	*Immersion time*	*Double vacuum schedule*
Scots pine sapwood	3 min	1 –0.33 bars 3 min 2 atmospheric pressure 3 min 3 –0.67 bars 20 min
Spruce	10 min	1 –0.83 bars 10 min 2 2 bars 15 min 3 –0.67 bars 20 min
Hemlock	not tested	as pine
Red lauan	not tested	as spruce

1 Initial vacuum
2 Pressure stage
3 Final vacuum

TABLE 2
Chemicals other than Tn.B.T.O. and P.C.P.
(Results after 4 months exposure)

Timber	*Treatment*	*Preservative uptake* l/m^3	*Mean % porosity*	*Number of fungal isolates*
Scots pine sapwood	Untreated	—	77.8	39
	Acypetacs zinc	76.4	126.6	6
	Tn.B.T.N./ Xyligen B	62.3	75.5	4
	P.C.P.L.	81.9	95.3	24
	Xyligen B	80.6	77.8	5
Spruce	Untreated	—	127.5	30
	Acypetacs zinc	79.3	118.6	7
	Tn.B.T.N./ Xyligen B	74.9	116.7	8

RESULTS
The schedules for the preservative treatments used are recorded in Table 1; details of preservative retentions are included in Tables 2–5.

The mean moisture contents for Scots pine sapwood L-joints over two year exposure period are presented in Figure 2 and for spruce over one year, in Figure 3. Variation in the distribution of moisture along the length of the tenon members for both timbers is shown in Figure 4.

The changes in porosity during the exposure periods,

TABLE 3
Time to First Incidence (in months) of the Various Groups of Fungi (Scots Pine Sapwood)

Fungus type	*Untreated*	*Tn.B.T.O.*		*P.C.P.*	
		Dip	*Double vacuum*	*Dip*	*Double vacuum*
Bluestain	3	3	3	3	8
Soft rot	3	3	3	8	8
S. brinkmannii	8	3	8	18	ni
Decay	3	24	ni	ni	ni
Preservative uptake l/m^3		31.9	62.3	40.8	71.1

ni — Not isolated in exposure periods of up to 24 months

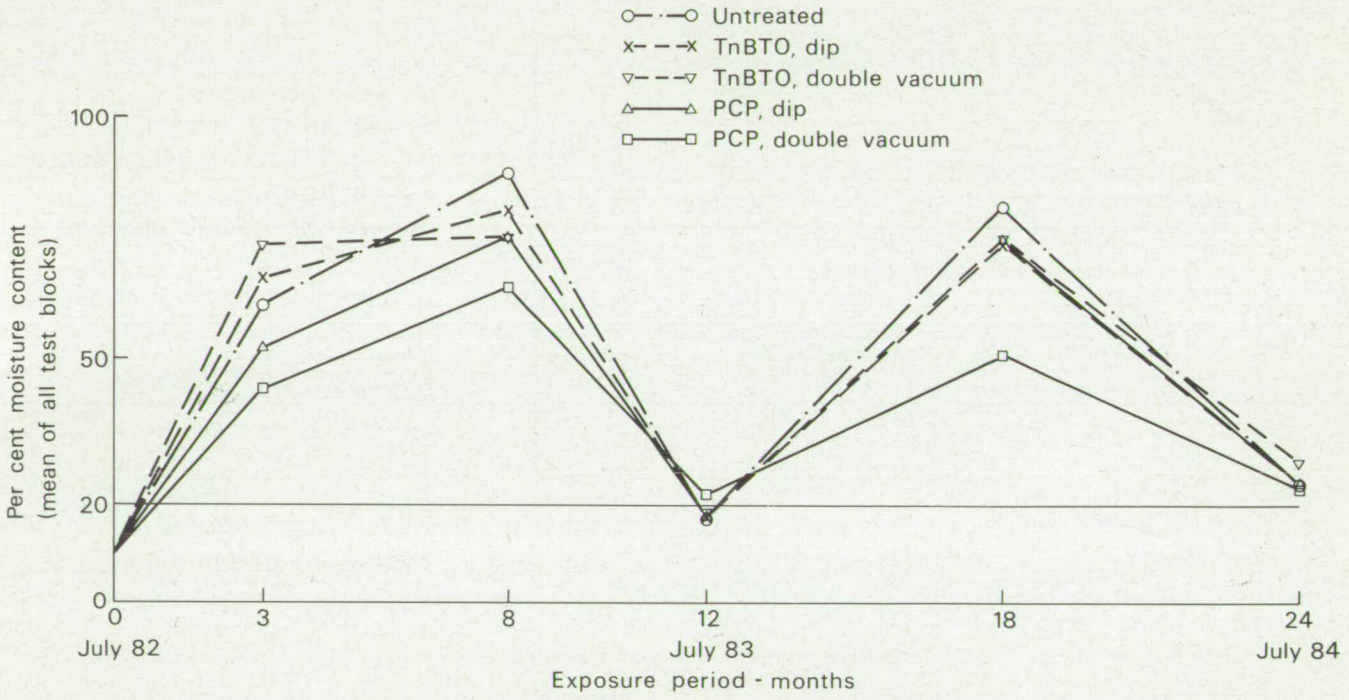

Fig. 2. Moisture content in Scots pine sapwood L-joints

expressed as the mean of all the sample blocks, are presented in Figure 5 for Tn.B.T.O. and P.C.P. treated Scots pine sapwood and in Figure 6 for equivalent treatments using spruce. Data for both timbers treated with a range of alternative fungicides are recorded in Table 2.

The number of different fungi from each isolation position of each replicate L-joint have been summed to give the incidence of fungi. These data are presented in Figure 7 for Tn.B.T.O. and P.C.P. treated Scots pine sapwood, Figure 8 for equivalent treatments on spruce, and Table 2 for alternative fungicide treatments.

The majority or fungal isolates have been categorised as moulds, bluestains, soft rots, *Sistotrema brinkmannii* or decay fungi. The occurrence of these groups in Scots pine sapwood treated with Tn.B.T.O. and P.C.P. is shown in Figure 9 and summarised in Table 3. Data collected over shorter time periods for spruce are presented as Figure 10 and Table 4, and for the alternative fungicides in Figure 11.

The incidents of *S. brinkmannii* and decay fungi in a range of timbers, both untreated and treated by double vacuum with one per cent Tn.B.T.O., is recorded in Table 5.

The influence of a range of coating materials on moisture content and the incidence of both *S. brinkmannii* and the decay fungi is given in Table 6.

Discussion

The L-joint trials described in this paper are part of a phased, on-going programme. Results comparing the effectiveness of one per cent Tn.B.T.O. and five per cent P.C.P. applied by three minute dip or by double vacuum treatment to Scots pine sapwood are already available for periods up to two years, the trial having been established in July 1982. Results with equivalent treatments in spruce are available for periods up to one year, the trial having been initiated in August 1983.

Moisture relations

Although moisture contents were only sampled at infrequent intervals, the pattern in Scots pine sapwood (Figure 2) clearly displays the annual fluctuations established in previous exposure trials (Purslow and Williams, 1978); a similar pattern appears to be developing in spruce (Figure 3), but with markedly lower moisture contents. This difference can be attributed to the relative impermeability of spruce. The distribution of moisture itself within the L-joints is also quite

different for the two timbers. With Scots pine sapwood (Figure 4), the highest moisture contents were generally recorded close to the joint (position 1) with a gradual decrease towards the remote end. Where sampling occurred following a dry period, the highest values were recorded at position 2 indicating probable drying via the joint surfaces.

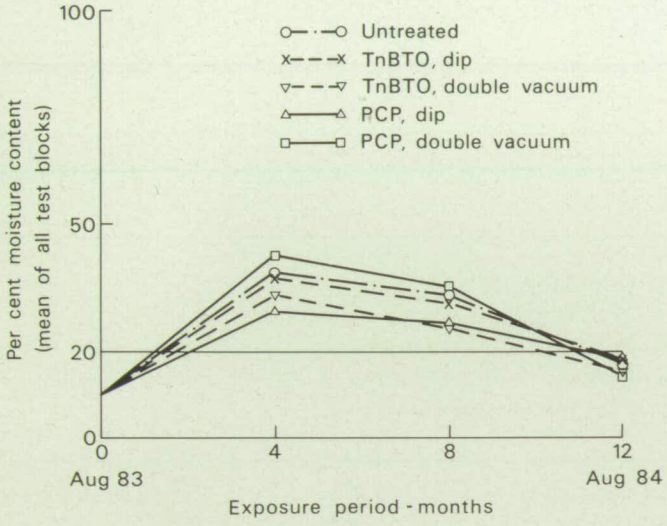

Fig. 3. Moisture content in spruce L-joints

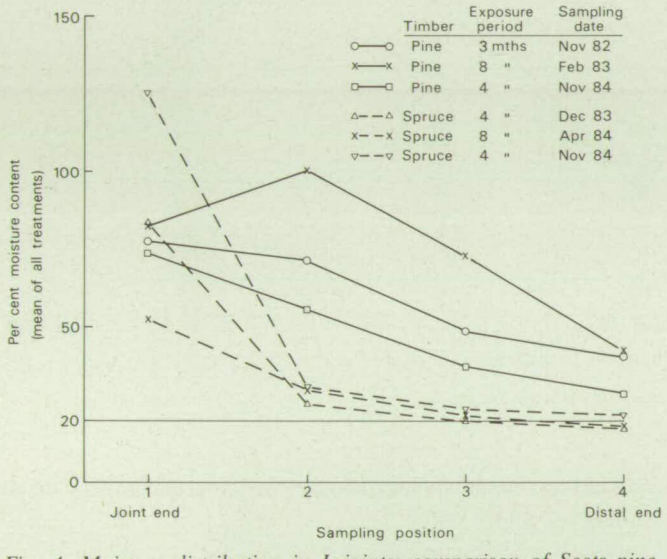

Fig. 4. Moisture distribution in L-joints; comparison of Scots pine sapwood and spruce

With spruce, although high moisture contents were recorded close to the joint (Figure 4), little water had moved along the L-joint members. Thus, moisture contents recorded in the spruce L-joints were lower overall than for Scots pine sapwood, although in the vulnerable joint region they were as high or even higher. Therefore, in both Scots pine sapwood and spruce, conditions suitable for microbial growth occurred within three–four months of exposure, though the zone at risk in spruce was restricted to that immediately adjacent to the joint. Since this is the area in which drying can take place most rapidly, it is possible that microbial growth will also be arrested more easily, as moisture contents fall below 20 per cent. These responses to wetting may have important consequences in determining the eventual performance of both treated and untreated spruce.

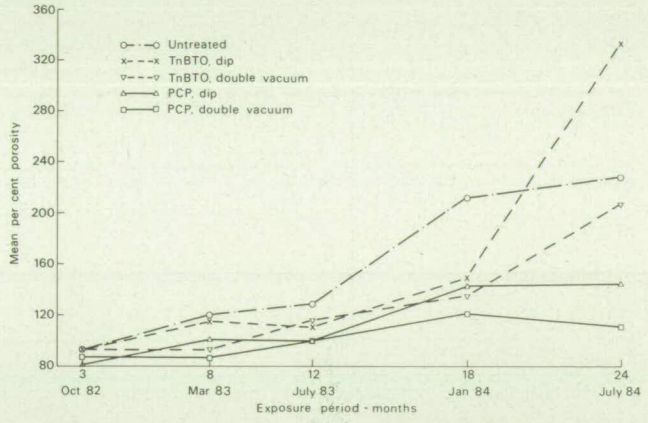

Fig. 5. Increase in porosity of Scots pine sapwood L-joints

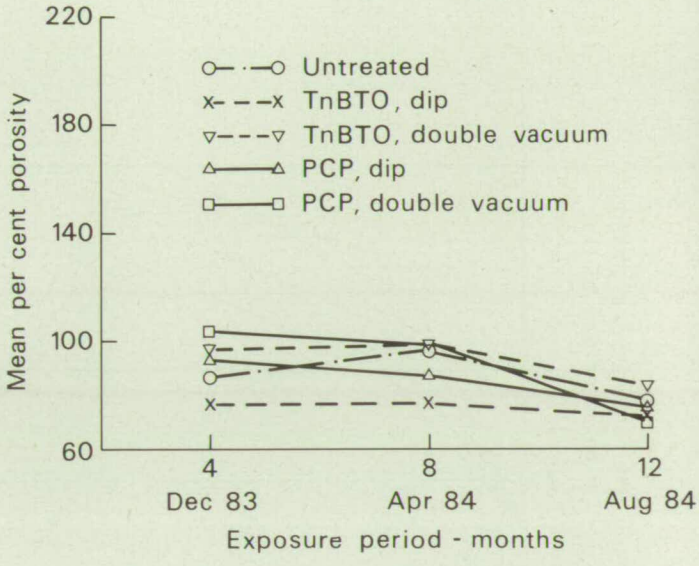

Fig. 6. Change in porosity in spruce L-joints

Porosity

The initial porosity of the timbers used in these L-joint trials, as measured by the uptake of dekalin, has been found to vary widely between individual L-joints. It has therefore proved necessary to sample each L-joint before any treatment is applied, to establish a base line against which the values obtained after exposure can be assessed, after corrections have been made for the effects of preservative, coating and moisture. For this reason, the data are expressed as a percentage and values above 100 per cent are considered to be significant and can be attributed to the effects of microbial activity. This method has been used successfully over some years with Scots pine sapwood; use with other timbers is less well tried and it will only be possible to judge the true significance of the results after more experience has been gained.

Scots pine sapwood: In untreated L-joints significant increases were first recorded close to the joint and subsequently along the complete length of the tenon members resulting in a gradient from the joint to the remote end. The porosity values continued to increase during exposure (Figure 5) the rate becoming more rapid between 12 and 18 months. Tn.B.T.O. treatments reduced the rate of increase over the first 18 months but there was a marked increase between 18 and 24 months with the dip treated exceeding the values recorded in untreated L-joints; the reason for these high values

is not certain at present. P.C.P. treatments have allowed a slow rate of increase with values in dip treated L-joints being generally higher than those in double vacuum treated L-joints. The greater effectiveness of P.C.P. in limiting increases in porosity has been shown previously (Baker et al, 1979).

With other fungicides (Table 2) results are available only after four months and it is too early to assess the significance of the differences in porosity between the treatments. It is likely that at this stage the direct measurement of the number of fungal isolates is a better indicator of potential performance than porosity which measures their activity.

Spruce: Increases in porosity in untreated and treated spruce have been sporadic and the overall values (Figure 6) suggest a slight downward trend. However, as observations extend over a limited period it seems likely that they indicate no significant change at this stage.

Fungal Colonisation

Data from isolation work can be considered in two ways. Firstly, total numbers of isolates can give indications of the comparative susceptibility of different timbers and treatments. Secondly, by grouping the isolates according to the different types of fungi, an indication can be gained of the stage in the colonisation sequence that has been reached in any given treatment. As indicated previously the expected colonisation sequence is bluestain fungi, followed by those capable of causing soft rot and finally the Basidiomycetes. Within this last group, *Sistotrema brinkmannii* is identified separately because of its early arrival and high incidence but more importantly because it is apparently unable to cause decay of timber. Mould fungi are generally of rather low and erratic incidence and are of lesser significance because they are known to be present in the timber prior to exposure.

Scots pine sapwood: In terms of the numbers of fungal isolates (Figure 7), untreated L-joints were rapidly colonised. Experience suggests that 50–60 isolates is the maximum number which can be successfully separated by the techniques used and this level was reached after 12 months exposure. P.C.P./double vacuum treatment has proved the most effective in reducing colonisation though only a few more fungi were present in the P.C.P./dip treatment. On this basis the Tn.B.T.O. treatments have proved much less effective than P.C.P.: whereas after 18 months barely 20 isolates were obtained from the P.C.P./dip treatment, over 30 were obtained from the Tn.B.T.O./double vacuum treatment and nearly 60 from the dip treatment.

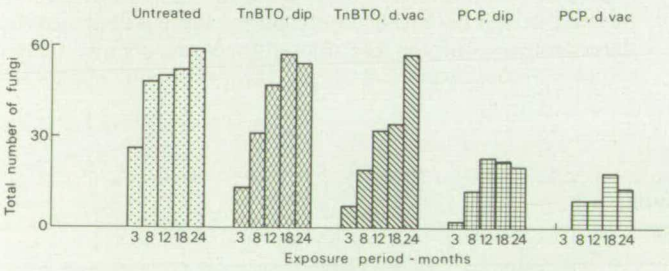

Fig. 7. Incidence of fungi in Scots pine sapwood L-joints

Evidence from the colonisation sequence (Figure 9) confirms that P.C.P./double vacuum treatment was most effective in that even after 24 months there was still no consistant occurrence of soft rot fungi nor any decay inducers. P.C.P./dip treatment was somewhat less effective and Tn.B.T.O./double vacuum was much less effective again. Tn.B.T.O./dip treatment was least effective with the first decay-inducing fungi already recorded at 24 months. These differences are summarised in Table 3.

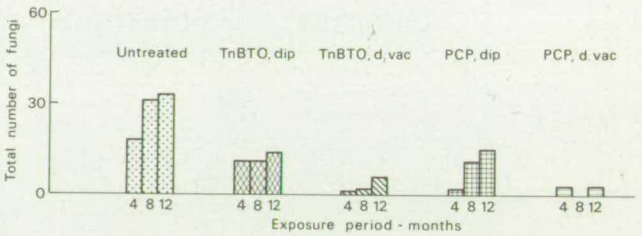

Fig. 8. Incidence of fungi in spruce L-joints

Spruce: The number of fungal isolates from untreated L-joints increased gradually from 4–12 months (Figure 8) but at a slower rate than with Scots pine sapwood (Figure 7). Both Tn.B.T.O. and P.C.P. applied by double vacuum reduced colonisation dramatically and though the dip treatments were less effective they nevertheless reduced colonisation compared with untreated samples. Interestingly, at this stage Tn.B.T.O. in spruce was apparently of similar effectiveness to P.C.P.

The progress of the colonisation sequence in spruce (Figure 10) shows interesting differences from pine. With untreated spruce, the preponderance of fungi fall into the soft rot category, *S. brinkmannii* has yet to be isolated and the decay fungi are much less common. This implies that the spruce used in this trial (probably all heartwood) is inherently more resistant to colonisation than is Scots pine sapwood. However, evidence from unpainted T-joint trials (P.R.L.,unpublished data) indicates this is not always the case.

The types of fungi isolated from the preservative treated spruce L-joints (summarised in Table 4) emphasise the superior performance of the double vacuum treatments which generally resisted soft rot fungi, whereas the dip treatments have permitted some colonisation by *S. brinkmannii* after 8–12 months.

Other fungicides: This work is at an early stage and only results after four months exposure are available (Table 2). The greatest number of fungal isolates was found in untreated pine with somewhat fewer in spruce. There was also a rather large number (24) in the pentachlorophenyl laurate treatment among which two have been confirmed as decay inducing fungi (Figure 11). This is in contrast to the four to six isolates from the other treatments in pine. As with the porosity determinations, it is considered too early yet to attach significance to differences between the treatments.

Effect of timber on preservative performance

The combined evidence of the porosity studies and the fungal isolation studies allows the Tn.B.T.O. and P.C.P. treatments in pine to be ranked in the following order of effectiveness:

most effective –	five per cent P.C.P./double vacuum
	five per cent P.C.P./three minute dip
	one per cent Tn.B.T.O./double vacuum
least effective –	one per cent Tn.B.T.O./three minute dip

Although the equivalent spruce experiment is still at a relatively early stage in exposure, it would appear that the order of effectiveness is different. The double vacuum treatments are giving an equivalent performance with the two preservatives and are more effective than the dip treatments which are also giving an equivalent performance. Therefore, both Tn.B.T.O. treatments are performing better on spruce than on pine. This is supported by recent data in the long-term L- and T-joint trials in which 0.5 per cent Tn.B.T.O. applied by three minute dip has performed better on 'whitewood' than on Scots pine sapwood (P.R.L., unpublished data). One possible reason for this better performance by Tn.B.T.O. is that it may be inherently more toxic in spruce; recent work gives indications that this is true but no more so for Tn.B.T.O. than for other preservatives so far tested. Alternatively it is

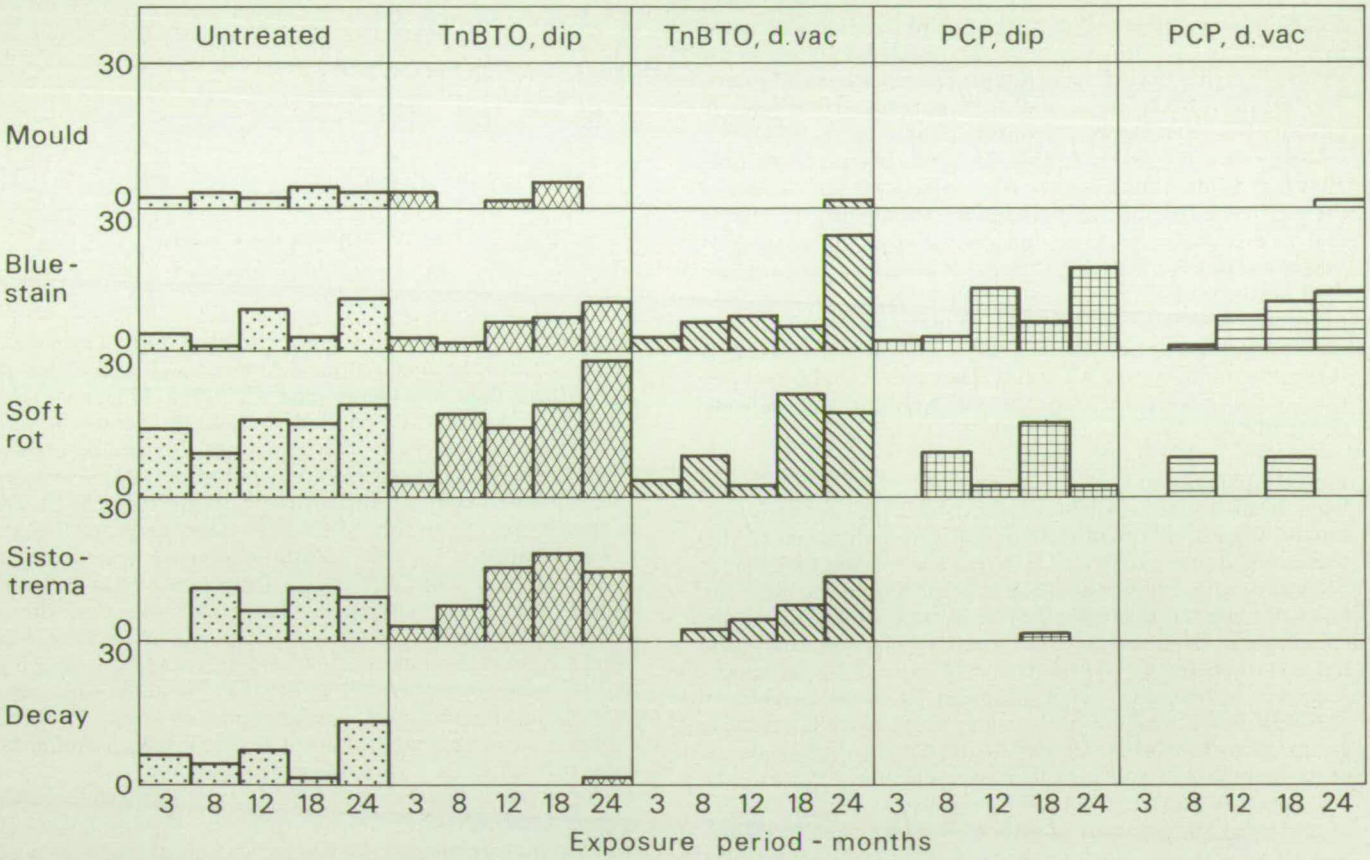

Fig. 9. Fungal colonisation of Scots pine sapwood L-joints

known that *S. brinkmannii* is highly tolerant to Tn.B.T.O. (P.R.L., unpublished data) and has an ability to degrade the chemical (Orsler and Holland, 1982). In the absence of significant colonisation by *S. brinkmannii* in spruce L-joints, this possibility for removal of Tn.B.T.O. does not exist and a greater proportion may thus remain to confer protection.

Trials are already in progress using hemlock and red lauan in addition to Scots pine sapwood and spruce. Although detailed results are not yet available for inclusion in this paper, some preliminary indications can be given of the incidence of Basidiomycetes in untreated timber and following double vacuum treatment with one per cent Tn.B.T.O. (Table 5). Within eight months untreated pine and spruce were well colonised. Treatment delayed colonisation of pine and generally prevented colonisation of spruce. Colonisation of both untreated hemlock and that treated by a redwood schedule (Table 1) occurred by 24 months. Red lauan has proved inherently more resistant to colonisation than the other timbers, no colonisation having occurred within 24 months.

Effect of coating material on preservative performance

The L-joint trials have in general, used a 'standard' coating system of an alkyd paint chosen as the finish traditionally applied to joinery in the United Kingdom. However, a range of other coating materials has been used. These have been found to influence the moisture contents recorded in the L-joints, so that for example, the less permeable finishes, such as alkyd paint, resulted in generally higher moisture contents (Table 6) because water entering via the joint was unable to escape through the finish. Interestingly, there is evidence that the coating also influences colonisation of preservative treated samples by Basidiomycetes (Table 6). No coating completely

TABLE 4
Time to First Incidence (in months) of the Various Groups of Fungi (Spruce)

Fungus type	*Untreated*	*Tn.B.T.O.*		*P.C.P.*	
		Dip	*Double vacuum*	*Dip*	*Double vacuum*
Bluestain	4	4	4	4	4
Soft rot	4	4	12	12	(4)
S. brinkmannii	ni	12	ni	(8)	ni
Decay	(8)	ni	ni	ni	ni
Preservative uptake l/m^3		7.3	73.0	7.0	78.6

ni — Not isolated in exposure periods of up to 12 months
() — Not isolated after longer exposure periods

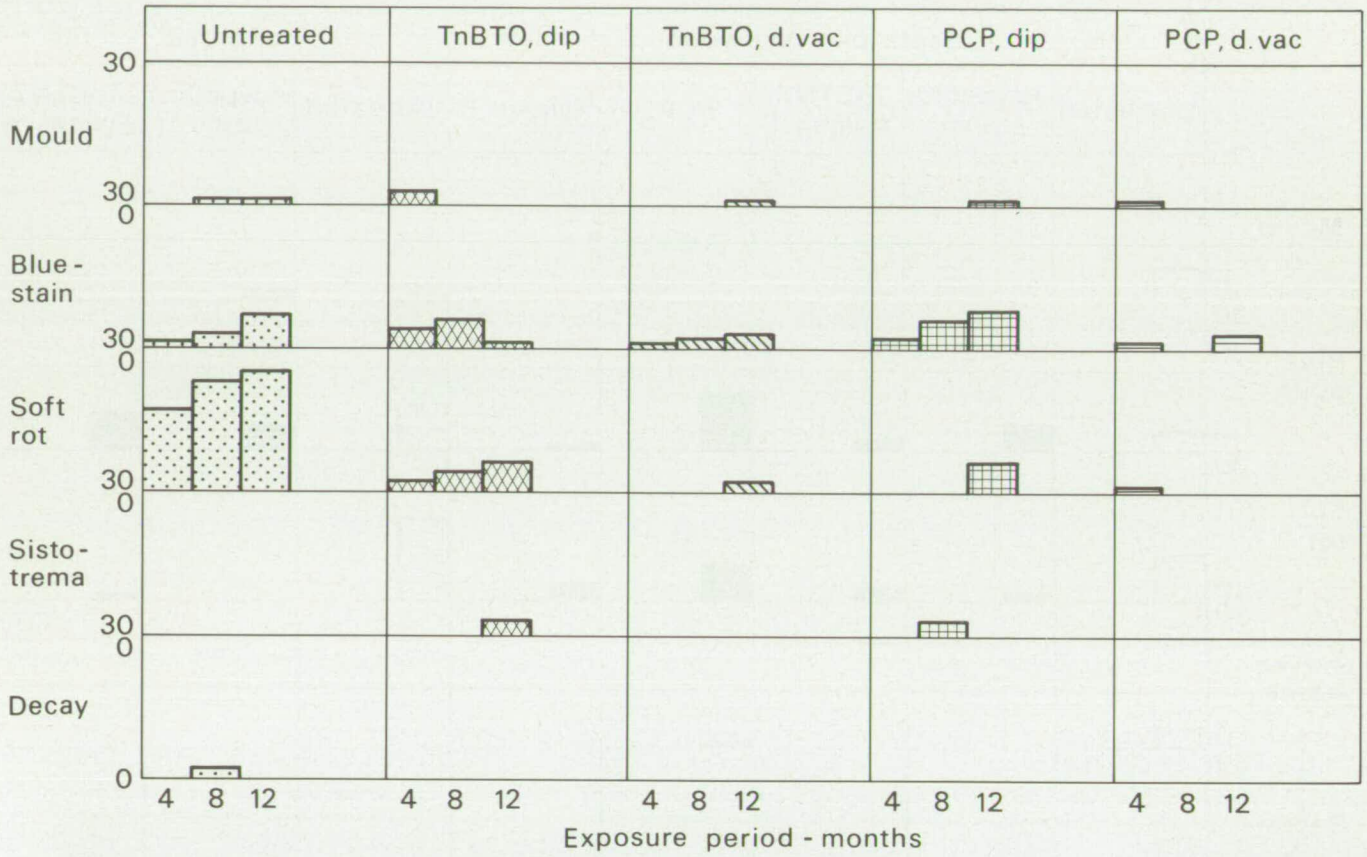

Fig. 10. Fungal colonisation of spruce L-joints

prevented colonisation by both *S. brinkmannii* and decay fungi but the best allowed only a single isolate; however, others of the same type (low build exterior wood stains) were less effective. Indeed variation in resistance to colonisation was as great within types as between them. This evidence suggests that preservative treatments may perform less well under some coating systems than under a traditional paint finish.

Predicting long-term performance

One possible method of using the data generated by the destructive assessment of L-joints to predict the likely service life of similarly treated joinery has been discussed previously (Carey, 1982). The method depends on establishing a relationship between the 'induction' phase, that is the time prior to colonisation by the decay fungi, and the period between colonisation and the ultimate occurrence of visible decay (the 'decay' phase). To establish this relationship it is necessary to have results from long-term trials in which various treatments have failed. Replicates for long-term exposure have been included in all the trials reported, but results from these will not be available for many years. However, similar trials, last reported by Purslow and Williams (1978), are now well advanced. One

TABLE 5
Basidiomycete Incidence in a range of Timbers

Timber	*Exposure period (months)*	*% occurrence**						*Preservative uptake l/m³*
		Untreated			*1% Tn.B.T.O. (double vacuum)*			
		Sb	*Decay*	*Total*	*Sb*	*Decay*	*Total*	
Scots pine sapwood	8	28	50	78	0	2	2	20.7
	24	0	17	17	40	4	44	
Spruce	8	17	17	28**	0	2	2	26.8
	24	0	17	17	0	0	0	
Hemlock	8	0	0	0	0	0	0	21.3
	24	0	28	28	10	2	12	
Red lauan	8	0	0	0	0	0	0	20.2
	24	0	0	0	0	0	0	

*Number of isolation positions yielding Basidiomycetes expressed as a percentage of the total number of such positions.

**One point yielded *S. brinkmannii* and a decay fungus.
Sb = *Sistotrema brinkmannii*

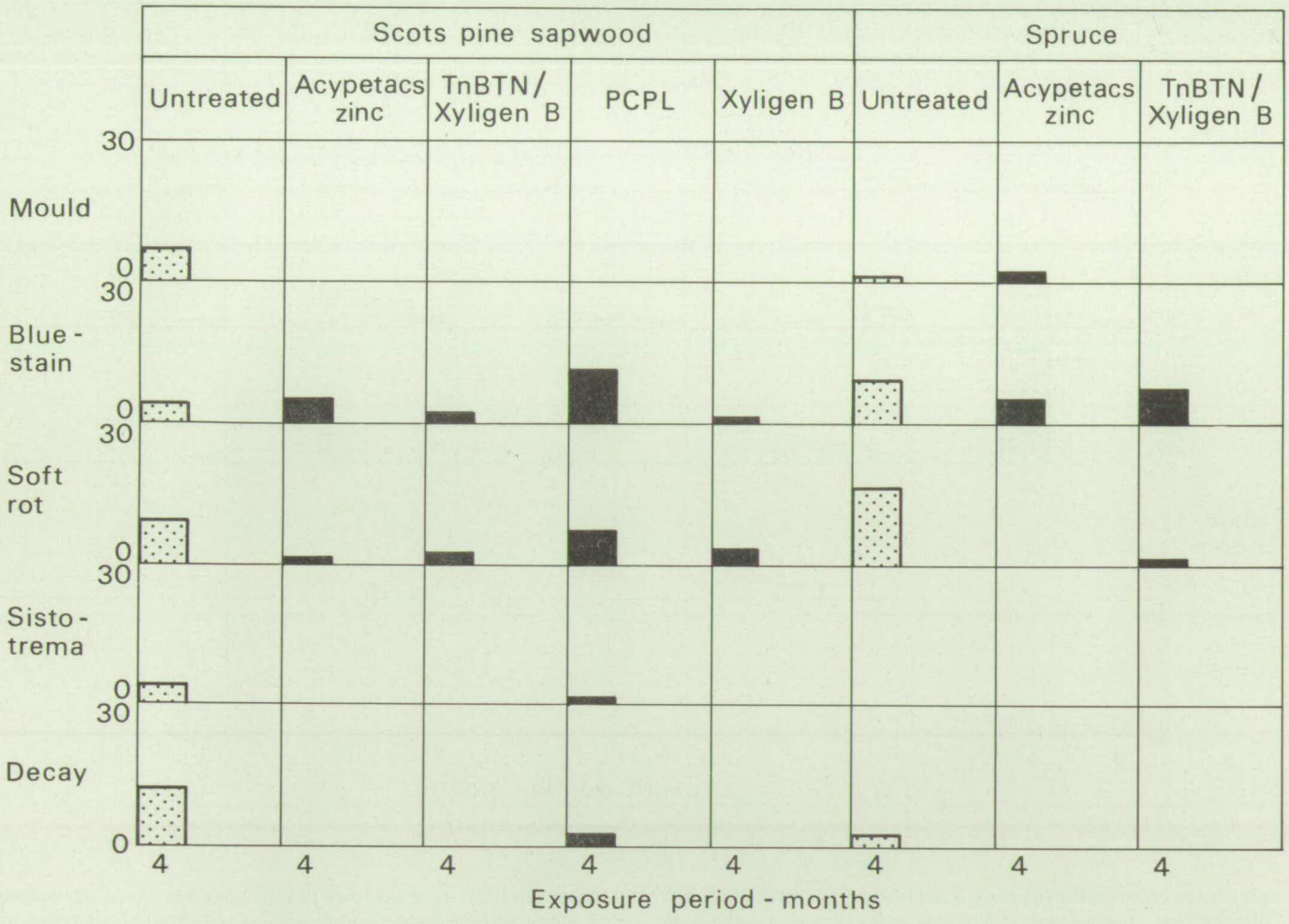

Fig. 11. Fungal colonisation of L-joints (other chemicals)

complete series of untreated, painted pine sapwood L-joints has failed giving a mean life of 8.1 years. This indicates a similar hazard situation to badly designed joinery in service which commonly needs replacing in six–eight years. The first failures of painted L-joints treated with one per cent Tn.B.T.O. applied by three minute dip have now occurred 11 years after exposure; no failures have occured in double vacuum treated L-joints after the same period. Five per cent P.C.P. has only been tested in unpainted T-joints which are proving somewhat less severe than L-joints; no failures have occurred within the first 16 years of exposure following three minute dip treatment. So far the predictive capability of the destructive L-joint tech-

TABLE 6
Influence of Coating on Moisture Content and Colonisation by Basidiomycetes*

Coating Type	*Mean moisture content at time of sampling*		*Number of isolates*			
			Tn.B.T.O.		*I.P.B.C.*	
	Tn.B.T.O.	*I.P.B.C.*	*Decay*	*Sb*	*Decay*	*Sb*
Paints — solvent borne	57	64	0	8	0	6
	83	74	0	6	0	4
	26	30	0	6	0	5
Paints — water borne	26	19	4	8	0	3
	33	41	0	2	0	7
Exterior wood stains — low build	17	14	0	7	1	1
	21	17	2	4	0	5
	34	18	0	0	0	1
	21	16	0	12	1	4
	20	16	0	6	0	3
Exterior wood stains — high build	29	20	2	4	0	4
	27	20	0	2	0	2
	18	18	4	5	0	3
Varnish	40	33	0	6	0	3

*All L-joints were Scots pine sapwood treated by double vacuum and had been exposed for 2 years.
Sb *Sistotrema brinkmannii*

nique is concerned, it is encouraging that the least effective treatment (Tn.B.T.O./dip) correlates with that also found least effective in the conventional long-term trials.

This correlation gives grounds for cautious optimism that the technique of destructive examination will be capable of distinguishing between different preservative treatments and aiding prediction of likely ultimate service lives. From the results obtained for pine this could emerge from the first 6–36 months of exposure under realistic conditions. However, until the point of failure is reached in existing long-term field trials, it will not be possible to establish a precise relationship between the changes recorded early in exposure and the ultimate life of the samples.

Results from the present spruce trials are also very encouraging for the relatively better performance of Tn.B.T.O. in spruce is supported by data from the long-term L- and T-joints in which 0.5 per cent Tn.B.T.O. applied by three minute dip has performed better on 'whitewood' than on Scots pine sapwood (P.R.L., unpublished data).

More recently established trials with other preservatives and other timbers are also yielding results in which differences in performance have been detected by the destructive examination procedures. Thus, although more data are still required, the L-joint biological assessment technique gives promise as a method for predicting the performance of preservative treatments for wooden joinery components though at present, it is only possible to assess relative rather than absolute performance.

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DISCUSSION ON PAPER 1

Chairman: The President

THE PRESIDENT: Thank you very much, Dr. Carey for so ably presenting our first paper of the Convention. We now come to the question and answer session. We have a nice balance between presentation and the time for questions and answers. Would Dr. Bravery like to join us on the platform, please, so that we have both the authors of the paper available for questioning.

When you ask your question would you speak up so that we can hear you and would you also announce your name and organisation. That would be helpful for the Conference record. I will declare the session open now for questions. Would anybody like to ask any point on the paper that has been delivered?

PROF. J. F. LEVY (Imperial College): Thank you for a very able presentation, Janice. The question I should ask is, how far does the treatment affect the moisture content of the treated wood. The suggestion from some of those graphs which you were showing was that it might cut down the moisture content and that alone might deter the organisms. A combination of low moisture content and a toxicant could be very effective.

DR. J. K. CAREY: I think there is some evidence in the data that the treatments are reducing the moisture content to a certain extent but most of the systems we have been using are model systems; they do not contain any water repellents and the effect is really quite limited in those. Also the reduction is still keeping the moisture content well within the area where fungi are perfectly able and happy to grow. With water repellent included in the system then I think you might get a far more obvious effect.

DR. D. J. DICKINSON (Imperial College): I was interested in the comparison between lauryl pentachlorophenol and P.C.P. Was this also evident on the porosity determinations or have you not done that?

DR. J. K. CAREY: The results are only available after four months for the test containing the lauryl P.C.P. and therefore really you cannot look for any effect because the increase in porosity, if there is one, will be between that sampling and the next one; the significance of just one value is difficult to determine.

DR. A. F. BRAVERY: I think one thing we do need to bear in mind is that when there are few fungi recorded logically we can regard that as a good sign, but if there are a number of fungi recorded it does not follow that that is a bad sign because it is what the fungi do which matters. So at this early stage there needs to be just an air of caution about interpretation of number of fungi as a parameter in its own right.

MR. D. P. BLOW (Fosroc Limited): I was woundering why the lauryl pentachlorophenol was used at five per cent whereas in British Standard 5707: Part One we are talking about 6.25 per cent. I was wondering if that could be responsible for the relatively poor performance of that.

DR. J. K. CAREY: Yes, I think you may be right there, Derek. In that part of the testing we asked four different chemical companies to supply us with solutions; the five per cent L.P.C.P. was supplied to us and we used it.

MR. A. C. OLIVER (Bucks College of Higher Education): Throughout your most interesting presentation I kept on thinking why is it that we have always thought that spruce was

not a suitable timber for external joinery. I thought that first of all possibly it was not very durable and secondly you could not treat it very well. It may be that this attitude has to change in the light of the sort of results that you are coming up with.

DR. J. K. CAREY: Yes, I think you have a point there. I think in the past we have always tended to compare spruce with Redwood heartwood. In this work, of course, we are comparing it with Redwood sapwood and then it looks very much more favourable. The spruce sample used accepted treatment relatively well and loadings similar to those in Redwood were achieved. If that is the case, then I think it should perform equally as well in practice.

THE PRESIDENT: Could I ask incidentally, are you hearing in the gallery the questions which are asked down below or are you having difficulty hearing? You are having difficulty. Can I ask those below the gallery to speak up so that the people in the gallery can hear you.

MR. L. D. A. SAUNDERS (Fosroc Limited): Following on from the previous question, in view of the current interest in using spruce as a joinery timber and in view of the problems associated with treating spruce by the high initial vacuum impregnation schedules I wonder whether you have any plans to use this obviously very effective technique for assessing the performance of the low initial vacuum impregnation schedules.

DR. A. F. BRAVERY: Well the technique as presented, of course, is being offered, as it were, as a device for assessing preservatives, and it ought to be feasible to use it for assessing treatments because there is good evidence that it can discriminate. What we propose to do is really a question of what resources we can spend and in what directions, but one of the areas of work which is certainly of some prominence at the moment is to look at the assessment of treatments applied to difficult species and spruce is one such. So we would hope that we would be able to use the technique in due time to look at the relative performance of different treatment schedules.

DR. D. G. ANDERSON (Hicksons Timber Products Limited): Could you comment on that point and say whether you have made any measurements of the envelope that you were achieving by this method on these relatively small samples.

DR. J. K. CAREY: We did not do any analysis at all apart from assessing the uptake.

DR. ANDERSON: I raise the question because I would suggest that on small samples like that you may find differences in samples will not be present because you were getting full penetration of the sample.

MR. E. A. HILDITCH (Vice-Present B.W.P.A. and Cuprinol Limited): Could you please relate your porosity measurements to those found with ponded timber?

DR. J. K. CAREY: I think when we first found there were increases in porosity in the L-joints we assumed it was due to the action of the bacteria as in the ponding situation. However, when you look at the relative numbers of bacteria with the T.B.T.O. and P.C.P. dip treatments you find that there are just as many bacteria present in the P.C.P. treatments as there are in the T.B.T.O. treatments. Therefore you do not get a very good correlation between the increases in porosity and bacteria. However, if you look at the numbers of fungi you find that they correlate much better with the increases in porosity and it seems likely that it is the fungi that are causing the increases and not the bacteria. We do know from some laboratory work that some of these fungi are quite capable of causing such increases, particularly *Sistotrema brinkmannii.*

MR. G. EWBANK (Rentokil Limited): You are comparing pine sapwood with spruce which presumably is a mixture of sapwood and hardwood. That would give a slight difference of natural durability of the material that you are testing. Do you think that would affect a comparison of the results.

DR. J. K. CAREY: No, I do not think so because hopefully we are assessing a realistic sample of spruce. This was a bought in commercial sample of joinery quality. I do not think that there is really that much difference in natural durability. Certainly in terms of graveyard tests with Scots pine sapwood and spruce I think you will find that both have a mean life of about seven years.

MS. J. LE POIDEVIN (Imperial College): You mention briefly about the sealing of the end grain in the joint. I just wondered if this was a possible method for potential improvement in the future. Are you going to spend any time on this idea?

DR. J. K. CAREY: The idea came up from some work in our Finishes Section and it has now been expanded greatly to include four timbers treated and untreated and three coating systems. The results are at about two years exposure and most of the end seal systems within the joints are still effectively preventing major access of water to the timber. Therefore it certainly does look as if, in the future, this type of system can be inbuilt into the joinery it should allow the preservative to provide protection over a greater period of time because it is not going to be put under such pressure from the hazard of the joinery situation.

MR. N. BURGERS (Formerly Western European Institute for Wood Preservation): Do you not think the dipping time for spruce should be longer to make a good comparison with that of pine. Secondly, how many joinery factories in England use end sealing in their normal production.

DR. J. K. CAREY: To answer the first part of your question, I was advised by our preservation section that I should use a ten minute dipping time for spruce. The uptakes are far lower with that than with three minutes with pine and I realise that. I wonder though if a longer dipping time would, in fact, be practicable in the treatment. What it really says is that dipping of spruce is probably not a viable treatment. As to the number of joinery factories which are using end sealing the answer is, of course, "Zero".

DR. C. R. COGGINS (Rentokil Limited): I think that this work has important implications in terms of a variety of treatment specifications. I wondered if the authors would care to comment on perhaps the longer term implications in terms of tying up species with active ingredients and treatment cycles on a very specific basis and perhaps in the shorter term, the future of dipping treatments in general.

THE PRESIDENT: That is a very comprehensive question.

DR. A. F. BRAVERY: I think the reply must be very much along the lines of the reply I gave to Andy Saunders, that we still feel that we are rather at the stage of validating the technique as an assessment procedure because it is going to rely a lot on the results from the long term trials, to enable us to interpret in a practical sense the results that we can get by destructive sampling in the short term. I think that really I can only say that we feel encouraged, that we think we have some indicators, some criteria that can be used to give an early indication of performance, which would otherwise need a very long time to determine. How discriminating the technique can be will become clearer as more parameters are investigated. I think we now have a programme with a good number of parameters, the main parameters, and this is only a fairly early stage with this work. We are barely two years into some of it and only a year into others. We have really got to look at three to five years hence when hopefully we should have a firmer base from which to make the sort of predictions you perhaps would like to see possible through this technique.

THE PRESIDENT: It sounds as though we are going to have a paper at the Convention in five years' time.

DR. C. R. COGGINS (Rentokil Limited): The British Standards will be up for revision again in five years' time. I am not sure whether you addressed the issue of shorter term treatment in general.

DR. A. F. BRAVERY: I would see it as part and parcel of the

same thing. I think to use the technique to set levels of treatment in practice would be a bit premature at the moment. It can form part of an overall appraisal.

MR. J. M. BAKER (Head of Princes Risborough Laboratory): Prof. Levy has indicated the importance of an integrated approach to joinery protection. This is something we are very keen on at Princes Risborough. The concept of end grain sealing is interesting. I remember it being very clearly explained to me by John Savory about 25 years ago in relation to the old lead pigment paints. I think what has happened is that that art or craft was lost sight of and only recently has the importance of blocking the end grain in limiting the uptake of water into the joint and thereby into the joinery as a whole been re-recognised. Limiting the water in that way obviously, as Prof. Levy pointed out, helps in preventing the fungus gaining ground. It also helps to keep a better external coating or paint surface on the joinery as well. So all three factors are working together. That is really by way of comment. The question that I should like to ask is, looking at the ecological picture the authors have presented, do you think there is any chance that one might attack a particular part of the chain and, in particular, is there any possibility of a specific fungicide for *Sistrotrema brinkmannii* which would perhaps stop the detoxification process and allow the T.B.T.O. to remain active against the wood destroyers.

DR. J. K. CAREY: I think the idea of being able to stop the colonisation chain by knocking out one of the earlier components in it is not likely to be effective because the decay fungi are quite capable of getting there anyway in the end. The idea of having a fungicidal system which is active against all components of that colonisation chain is, I think, very important. With T.B.T.O. there are various organisms, the bluestains, the soft rots and *Sistotrema brinkmannii* which are all capable of detoxifying it. Therefore if you are going to use T.B.T.O. as a decay preventative you need something which will prevent growth of the other organisms. So the idea of cocktail preservatives comes into its own. We are already seeing this to a certain extent with the T.B.T. naphthenate/ Xyligen B mixture that we are starting to look at and of course a number of T.B.T.O. preservatives on the market contain Preventol A4 to combat bluestain and I think that this could well be the way forward to a complete protection system, that is to attack all parts of the microbial flora but perhaps by different preservatives against different organisms.

PROF. J. F. LEVY (Imperial College): If I may just interpose a supplementary comment to that, Mr. Chairman. I do not want to anticipate what I am going to say later, but it is the mechanism of the breakdown of T.B.T.O. which might possibly be affected, and there are indications that certain things might make it possible to interfere with the mechanism of that breakdown.

DR. D. J. DICKINSON (Imperial College): I was going to make exactly the same point. I do not think it is necessary to follow the cocktail line if we can understand the mechanism of the degradation of the tin and protect the molecule. This is also another possible line of development.

DR. A. F. BRAVERY: I think there are two points about the cocktail idea though. One was the question of knocking out organisms that might be detoxifiers and there, of course, you are right. Until we know the mechanism of detoxification we cannot assume that it is organisms specific or species specific. However, there is the other factor which Janice's work has shown so clearly, that a porosity change is a feature of the overall process and it appears to be caused by fungi other than the ones which are the ultimate decay inducers.So you might have a chemical which is effective against the ultimate decay inducer but not against the porosity changing organisms, and it could well be that is an important part of the overall protection.

MR. J. DAVID (Catomance Limited and Deputy President, B.W.P.A.): In considering the effectiveness of a fungicide system I think we have to look at certain other properties besides the toxicity. In the physical form pentachlorophenol has the advantage of being volatile, being slight soluble and so it has a wide range physical effect which means that when you try to duplicate it you do not just look at toxicity; you must look for a mixture which gives you a lot of other physical things. Have you taken that kind of thought into consideration? I mean the effective use of an esterification process to block the phenol reduces volatility, reduces solubility, and therefore you tend to get the sort of situations in which water solubility is required, high water content, and the pentachlorophenol ester is not very effective. Can I just make one small point, that 5 per cent and 6.25 per cent are related to weight to weight and weight to volume, and I am not going to get into that one!

DR. A. F. BRAVERY: May I make one point immediately. We are not really in the business in this programme of developing wood preservatives, fungicides or indeed selecting particular fungicides for particular properties, so, no, we have not chosen these materials for the sorts of reasons you have suggested. We are, as I have said before, validating a technique and we want to use realistic current chemicals and combinations in order to try and do that.

THE PRESIDENT: I can take one more question.

MR. B. A. RICHARDSON (Penarth Research International Limited): In the case of Basidiomycete colonisation in treated wood have you considered the distribution of brown rots and white rots on the various preservatives.

DR. J. K. CAREY: With the L-joint trials as far advanced as they are at the moment the only wood decayers that we have isolated from treated or untreated material are white rots. We now have some results from a collaborative trial which has been set up through I.R.G. In Paris, for example, they have a lot of brown rots as early colonisers. In joinery in the U.K. we do get a high proportion of white rots in actual failures whereas on the Continent I think the higher proportion is brown rots. So it looks as if the system is, in fact, picking out those of the natural population that are best able to cope with the situation which varies from location to location.

THE PRESIDENT: It sounds to me as though this question and answer session can go on for a very long time, but I think in order to keep the Convention on the straight and narrow and to break off at this particular point for coffee, I would like on your behalf to thank Dr. Bravery and Dr. Carey very much for fielding the questions that have been asked. I think the questions and answer stage is always the most interesting. A number of vital and relevant points came up and it sounds to me as though there could well be a development, progress or even a final report in three to five years' time, which I think all of us would look forward to with great pleasure and interest. So may I, on your behalf, thank the two authors and the presenter this morning, Dr. Carey, very much for setting off the Convention on such an excellent path. Thank you very much indeed. *(Applause).*

B.W.P.A. CONVENTION, 1985

THE DEVELOPMENT OF PROPHYLACTIC CHEMICALS FOR THE TREATMENT OF GREEN TIMBER

by D. A. Lewis; G. R. Williams and R. A. Eaton*
*Hicksons Timber Products Ltd; *Portsmouth Polytechnic.*

1. Introduction

An important sector of the wood preservation industry is the prophylactic treatment of logs and sawn timber in order to prevent post-harvest deterioration prior to and during seasoning. This deterioration, which can take the form of sapstaining and mould growth (Anon 1971); insect attack as well as decay, results in a significant reduction in value and yield of the logs or sawn timber. One of the accepted means to prevent these losses is by the application of fungicides or insecticides to the timber. Usage figures for anti-sapstain chemicals of 800 tonnes in Western Canada (Jones 1981), 800 tonnes in Portugal (Coggins 1982) and 500–600 tonnes in Finland demonstrate the significance of such treatments. Sodium pentachlorophenoxide (Na.P.C.P.), sodium tetrachlorophenoxide (Na.T.C.P.) and lindane have been the staple chemicals for prophylactic treatments but their future is doubtful due to environmentalist pressures being applied both to the end user of the products and, more importantly in terms of continued supply, to the manufacturers. These pressures have stimulated a considerable interest in the prophylactic treatments market with a number of active ingredients and products being promoted as potential replacements to the chlorinated phenols and lindane.

However, the development and introduction of new products for this field of application requires a significant research effort incorporating not only formulation work and studies on effectiveness but also an examination of the more fundamental aspects of the sapstaining problem. This paper details the results of an integrated programme of work carried out at Hickson's Timber Products Ltd. and Portsmouth Polytechnic. Formulation development and extensive field trial testing was conducted by Hickson's Timber Products Ltd. over a four year period. Under an S.E.R.C. (C.A.S.E.) award, with Hickson's Timber Products Ltd. as the Co-operating Industrial Concern, a research project was undertaken at Portsmouth Polytechnic to examine the ecological aspects of sapstain and mould defacement, the toxicity of selected chemicals towards target organisms and the interaction between the wood substrate and active ingredients which have been applied to the surface of the timber (Williams 1985).

2. Effectiveness of Prophylactic Chemicals

When examining the effectiveness of anti-sapstain chemicals, three phases can generally be established (Vihavainen 1976). (i) rapid screening tests; (ii) laboratory tests using a wood substrate; (iii) field tests under practical conditions.

Laboratory screening tests are recognised as the first step in an evaluation programme as they provide an efficacy ranking of the selected chemicals without resorting to expensive, long term field trials. Once the basic effectiveness of new products or active ingredients has been established, cost-effectiveness and efficacy, coupled with safety considerations, can then be reviewed. A number of initial screening tests using agar are available. This type of test is satisfactory as a primary screen where a large number of compounds of unknown effectiveness are being examined, but yields little information of the potential performance on a wood substrate. In order to derive information of a more specific nature it is important that the toxicity of candidate chemicals is evaluated, in the laboratory, on a natural wood substrate using fungal species known to be problematical in the field.

The third phase of Vihavainen's testing protocol is the field evaluation of potential chemicals and formulations. In the development of prophylactic products, field trials take account of climatic factors, flora and fauna, species diversity, local timber species and the different timber handling procedures. These factors are of considerable significance in establishing products in what is a worldwide market. Various techniques have been suggested as methods for the field evaluation of prophylactic chemicals but, as in the case of laboratory tests, there is not an accepted international test method. One of the most satisfactory techniques is to include both close stacked and open stacked material in the same test, thereby simulating the two extremes of hazard likely to be encountered in practice.

The following section describes the laboratory and field work conducted by Hickson's Timber Products Ltd. to evaluate candidate anti-sapstain and insecticidal formulations.

2.1 **Wood Substrate Screening Tests**

2.1.1 *Experimental procedure*

Matched sapwood slats (100 × 40 × 10 mm) of fresh, unseasoned Corsican pine (*Pinus nigra*) were immersed for 10 seconds in various concentrations of active ingredients or formulated products (Table 1). Chemicals were selected on the basis of primary screening tests, published information, or toxicological profiles. After treatment the slats were stored for 24 hours in polythene sheeting and then dip inoculated in a mixed spore-hyphal suspension comprising several mould and stain species including *Ceratocystis pilifera, C. picea, Phialophora fastigiata, Leptographium lundbergii, Trichoderma viride* and *Apsergillus niger.*

The slats were then individually placed into glass jars containing moist filter paper and incubated for five weeks at +25°C: the slats were assessed for the percentage surface area infected by stain and mould fungi and the results, from a representative series of tests, are shown in Table 1.

2.1.2 *Test Results*

Untreated sapwood slats were severely stained with the degree and intensity of stain being similar to that which developed on untreated close stacked boards during subsequent field trials. The alkyl ammonium compounds Gloquat C, Bardac 20 and Benzylkonium chloride could not be considered effective, in an unmodified form, at the concentrations tested. The carbamate fungicide 3-iodopropynyl butyl carbamate approached control of staining at levels not considered cost-effective against alternatives: subsequently the suppliers suggested that these results may have been due to inadequacies in the formulation supplied. Hager Blue, a product based on caprylic acid and borates (Hager 1979), was ineffective at a product concentration of 9.6 per cent whilst Kathon 886 MW allowed significant mould growth at all concentrations examined. Cunilate 2419 (based on copper-8-hydroxyquinolinolate) gave good control of surface stain but did not prevent severe internal stain, a feature found in subsequent tests.

Of the remaining formulations, those based on methylene-bis-thiocyanate (M.B.T.) and 2-thiocyanomethylthio benzothiazole (T.C.M.T.B.) emerged as candidates for further development work.

2.2 **Field Evaluation Programme**

In order to examine the full potential of the prophylactic formulations subsequently developed after laboratory tests and preliminary field tests, an extended field trial programme was conducted in both Europe and South East Asia. During

TABLE 1
Defacement of laboratory test samples treated with candidate anti-sapstain chemicals

Product	*Concentration %*	*Mean % Surface Area Affected By*		
		Stain	*Mould*	*Total*
Untreated	—	80–100	0	80–100
Gloquat C	1.75 ai	62	0	62
Bardac 20	1.75 ai	32	0	32
Benzylkonium chloride	1.75 ai	35	<1	35
3-iodopropynyl butyl carbamate	0.25 ai	69	0	69
3-iodopropynyl butyl carbamate	1.00 ai	11	0	11
Hager Blue	9.60	98	0	98
Triorganotin compound	0.50 ai	99	0	99
Sodium tribromophenate	2.50	3	0	3
Kathon 886W	1.15	0	40	40
Cunilate 2419	2.22	0	9	9
Fluoride/Bifluoride	5.00	0	0	0
Methylene-bis-thiocyanate	0.10 ai	0	0	0
Methylene-bis-thiocyanate	0.10 ai	10	0	10
+ 2-thiocyanomethylthiobenzothiazole	0.30 ai	0	0	0

the initiation of these tests particular attention was paid to local sawmill handling techniques although where possible both close stacked and open stacked conditions were simulated in Europe, whereas only the degree of protection afforded during air-seasoning required examination in Malaysia, Singapore and Indonesia.

The products selected for these trials are shown in Table 2 and contain active ingredients considered as potential replacements for Na.P.C.P. and lindane. It should be noted that the products were specifically formulated for prophylactic treatments and that formulation details can significantly influence the final performance of active ingredients (Section 6). All the products are emulsifiable concentrates which readily disperse on addition to water, forming stable treatment solutions. The ANTIBORER products are also fully miscible with the organic solvents commonly used in log sprays such as light diesel oil.

TABLE 2
Prophylactic products used in field evaluation programme

Product	*Type*	*Active Ingredient*
ANTIBLU 3737	Fungicide	Methylene-bis-thiocyanate
ANTIBLU 3738	Fungicide	Methylene-bis-thiocyanate
ANTIBLU 3739	Fungicide	Methylene-bis-thiocyanate + 2-thiocyanomethylthiobenzothiazole
ANTIBORER 3767	Insecticide	Cypermethrin
ANTIBORER 3768	Insecticide	Permethrin

2.2.1 *European Field Trials*

2.2.1.1 *Experimental Procedure*

Test boards were selected from freshly converted logs with the individual boards having a high proportion of sapwood whilst being free from obvious stain and insect attack. Where possible, timber was selected from production material. Pallet boards were used for tests in the United Kingdom and Portugal with larger dimensioned material, up to two metres in length, being included for trials in Finland and Spain. Treatment was by a 10 second immersion in the test solution followed by draining and stacking: 30 to 50 boards per concentration were block stacked and 25 to 30 boards were separated by stickers as for normal air seasoning practice. The test boards were not artificially inoculated with staining or mould organisms prior to storage.

After the requisite storage period, the boards were assessed for the percentage of surface area affected by stain, mould or decay fungi as well as insect damage if present. The results of various trials initiated within Europe are shown in Section 2.2.1.2.

2.2.1.2 *Field Trial Results: Europe*

UNITED KINGDOM (Table 3)

In the United Kingdom tests, four home-grown softwood species were used, Corsican pine, Scots pine (*Pinus sylvestris*), spruce (*Picea abies*) and larch (*Larix decidua*). The susceptibility of the pine species to staining and the severe hazard presented by close stacking is demonstrated by the high infection levels of stain, approaching 100 per cent, on the untreated boards.This staining was very intense and was also found to occur in the interior of the boards. Treatment with the ANTIBLU products at concentrations between 0.2 per cent and 0.25 per cent active ingredient gave very effective control of stain, mould and basidiomycete fungi on close stacked timber after eight weeks storage.

TABLE 3
Field trials conducted in the United Kingdom on selected softwood species (eight weeks storage)

Product	*Concentration % w/v*	*Timber Species*	*Close Stacked*			*Open Stacked*		
			Mean % Area Infected By:					
			Stain	*Mould*	*Total*	*Stain*	*Mould*	*Total*
Untreated	—	Corsican Pine	99	0	99	21	<1	22
ANTIBLU 3738	1.70	"	<1	0	<1	0	0	0
ANTIBLU 3738	2.40	"	<1	0	<1	0	0	0
ANTIBLU 3738	3.00	"	<1	0	<1	0	0	0
ANTIBLU 3739	0.85	"	3	1	4	0	0	0
ANTIBLU 3739	1.20	"	<1	<1	<1	0	0	0
ANTIBLU 3739	1.50	"	0	<1	<1	<1	0	<1
Untreated	—	Scots Pine	99	32	100	92	25	98
ANTIBLU 3737	2.00	"	2	4	6	<1	0	<1
ANTIBLU 3737	2.50	"	<1	7	7	<1	0	<1
ANTIBLU 3737	3.00	"	0	8	8	0	<1	0
ANTIBLU 3739	1.00	"	0	2	2	0	0	0
ANTIBLU 3739	1.25	"	0	2	2	<1	<1	<1
ANTIBLU 3739	1.50	"	0	7	7	<1	<1	<1
Untreated	—	Spruce	34	2	36	1	0	1
ANTIBLU 3738	1.50	"	0	0	0	0	0	0
ANTIBLU 3739	0.75	"	0	0	0	0	0	0
Untreated	—	Larch	74	2	76	1	<1	1
ANTIBLU 3738	1.50	"	0	<1	<1	0	0	0
ANTIBLU 3739	0.75	"	<1	<1	<1	0	0	0

Mould growth (*Trichoderma sp.*) was noted at all treatments on Scots pine in one particular test. However, in this test the control boards were also heavily infected by mould, a feature not often seen in the field trial programme. Discussions with sawmill managers suggested that the levels of mould recorded on the treated boards was not regarded as significant as it was easily brushed off and did not cause permanent disfigurement. Such mould growth was not found in the subsequent United Kingdom trials.

Although it is generally accepted that spruce is not particularly susceptible to staining, in trials conducted near Southampton, block stacked untreated boards showed an average degree of staining of 34 per cent with more than half the boards having staining levels in excess of 25 per cent. Untreated larch boards also showed a high level of staining although the intensity of colour was lower than that on pine sapwood boards. Treatment with 0.75 per cent ANTIBLU 3739 or 1.5 per cent ANTIBLU 3738 prevented defacement on close stacked spruce or larch boards for at least eight weeks.

As anticipated, the open stacking of timber considerably reduced the associated staining hazard. In the test with Scots pine, however, surface infection was rated at 92 per cent but the stain was not particularly intense and was only superficial. Of interest in this particular test was the development of mould on the open stacked untreated boards particularly in the vicinity of the stickers which are presumed to be areas where the drying rate is retarded.

FINLAND (Table 4)

Although a significant proportion of the timber in Finland is kiln dried after treatment the time period between treatment and placing in the kiln can be up to several weeks. The results of a test on Scots pine boards after eight weeks are presented in Table 4. The untreated block stacked samples were severely stained whereas those treated with ANTIBLU 3738 were free from both stain and mould growth except for a minimal level of mould found at 2 per cent ANTIBLU 3738 which appeared to originate from the under bark edges of boards. A significant degree of stain was also found on the untreated open stacked boards which were separated by softwood stickers. After

TABLE 4
Defacement of field trial boards (Finland) treated with ANTIBLU 3738

Product	*Concentration % w/v*	*Timber Species*	*Close Stacked*			*Open Stacked*		
			Mean % Area Infected By:					
			Stain	*Mould*	*Total*	*Stain*	*Mould*	*Total*
Untreated	—	Scots Pine	94	5	97	24	0	24
ANTIBLU 3738	1.5	"	0	0	0	0	0	0
ANTIBLU 3738	2.0	"	0	2	2	0	0	0
ANTIBLU 3738	2.5	"	0	0	0	0	0	0

TABLE 5
Defacement of field trial boards in Northern Spain (eight weeks storage)

Product	*Concentration % w/v*	*Timber Species*	*Close Stacked*			*Open Stacked*		
			Mean % Area Infected By:					
			Stain	*Mould*	*Total*	*Stain*	*Mould*	*Total*
Untreated	—	Insignis Pine	87	17	94	3	0	3
ANTIBLU 3738	1.5	"	0	<1	<1	0	0	0
ANTIBLU 3738	2.0	"	0	4	4	0	0	0
ANTIBLU 3738	2.5	"	0	2	2	0	0	0

TABLE 6
Defacement of close stacked Maritime pine pallet boards in Portugal (nine weeks storage)

Product	*Concentration % w/v*	*Timber Species*	*Mean % Surface Area Infected by:*		
			Stain	*Mould*	*Total*
ANTIBLU 3738	2.0	Maritime Pine	23	0	23
ANTIBLU 3738	2.5	"	12	0	12
ANTIBLU 3738	3.0	"	3	1	4
ANTIBLU 3739	1.0	"	4	<1	4
ANTIBLU 3739	1.25	"	<1	<1	<1
ANTIBLU 3739	1.50	"	<1	0	<1

TABLE 7
Defacement of pallet boards treated in Portugal and shipped to the United Kingdom for storage

Treatment	*Concentration % w/v*	*Eight weeks storage*			*Sixteen weeks storage*		
		Mean % Surface Area Infected By:					
		Stain	*Mould*	*Total*	*Stain*	*Mould*	*Total*
Na.P.C.P.	ca 3.0	47 (19)	0	47 (19)	25 (9)	<1	25 (9)
ANTIBLU 3738	2.5	<1	<1	<1	2	<1	2
ANTIBLU 3738	3.0	<1	0	<1	<1	0	<1
ANTIBLU 3739	1.5	0	<1	<1	0	0	0
ANTIBLU 3739	1.75	0	0	0	<1	<1	<1

assessment the treated open stacked boards were block stacked, banded and left in a warehouse for a further eight weeks during which time no further defacement had taken place.

A second test was conducted in Finland whereby freshly sawn ANTIBLU treated boards were kiln dried under commercial conditions, block stacked and then stored in the sawmill's warehouse for 10 weeks. During storage the untreated, kiln dried boards became re-wetted and showed severe mould and stain growth (58.5 per cent surface area coverage): the boards treated with ANTIBLU 3738 at 1.5 per cent w/v were free from infection.

SPAIN AND PORTUGAL (Tables 5–7)

At the sawmill in Northern Spain where the test reported in Table 5 was conducted, all boards of a thickness greater than 2 cm were air dried after treatment, prior to packaging and shipping. However, we took the opportunity to examine the performance of ANTIBLU 3738 under both block stacked and open stacked conditions of 3–4 cm thick boards cut from *Pinus insignis* logs. Air seasoned boards were free from stain at all treatment levels although it should be noted that the untreated boards showed only 3% surface staining, an indication of favourable drying conditions. Untreated, close stacked boards were heavily infected by both stain and mould fungi with control of stain being attained at ANTIBLU 3738 concentrations of 1.5 per cent w/v upwards. Slight mould infection was noted at the higher concentrations but was generally confined to the edges of boards and around the knot areas.

A second series of tests was conducted at the same sawmill and after eight weeks air drying, sapstain was prevented at 0.16 per cent active ingredient levels (i.e. 0.8 per cent ANTIBLU 3739 and 1.6 per cent ANTIBLU 3738).

In Portugal, trials were confined to Maritime pine (*Pinus pinaster*) pallet boards and the data for block stacked timber after nine weeks storage is shown in Table 6. Full protection was afforded by 1.25 per cent ANTIBLU 3739 although at an equivalent active ingredient level, 2.5 per cent ANTIBLU 3738 treated boards showed an average surface staining of 12 per cent.

In order to examine the longer term performance of timber under transit conditions, packs of pallet boards were treated in Portugal and then shipped to the United Kingdom to be placed in storage for an indefinite period (Table 7). After 16 weeks, boards treated with ANTIBLU 3738 or 3739 were virtually free from stain whereas boards treated with sodium pentachlorophenoxide, taken from the sawmill's treatment tank, showed significant levels of staining after eight weeks storage. Infection of the Na.P.C.P. treated boards was mainly caused by *Graphium aureum* although this fungus did not yield pronounced surface staining. Na.P.C.P. treated boards also showed internal staining. The bracketed figures in Table 7, for Na.P.C.P., relate to the type of defacement normally identified as 'stain' and was caused by *Ceratocystis pilifera.*

2.2.2 Field Trials in South East Asia

The trials in South East Asia were divided into two projects one of which examined the performance, in Indonesia and Malaysia, of prophylactic chemicals on current primary species such as ramin (*Gonystylus spp*) and jelutong (*Dyera costulata*). The second project was concerned with the treatment of logs and sawn timber produced from the rubber tree *Hevea brasiliensis.* Rubberwood is a medium density, light coloured hardwood (similar in appearance to ramin) and has attracted a significant amount of attention because of its favourable physical characteristics and working properties, particularly for use in furniture. Rubberwood, however, is very susceptible to fungal and insect attack at all stages of its utilisation and consequently tests were conducted in order to determine the effectiveness of the ANTIBLU and ANTIBORER products when applied to fresh, green boards and logs.

2.2.2.1 *Experimental Procedure*

SAWN TIMBER TREATMENTS

Due to the severity of hazard imposed by the climatic conditions of high humidity and high temperatures, it is accepted practice in South-East Asia to open stack all sawn timber for seasoning prior to packing for shipment. The period of air drying is dependent upon board thickness, the season and timber species but is subject to variations in normal mill procedures. For the field trials conducted in Malaysia and Kalimantan an open stacked storage method was used. Treatments were based on a 10 to 20 second immersion in solutions of the required concentration and after seasoning, assessments were made of the surface area infected by mould or stain fungi and the presence of any insect attack.

LOG TREATMENTS (Rubberwood)

Fresh rubberwood logs were received within two days of felling, carefully selected on the basis of bark cover and absence of fungal or insect attack. After preparation the logs were treated with selected concentrations of either ANTIBLU or ANTIBORER products applied by a coarse deluge, in order to prevent atomisation, at a rate of 250 ml m^2 of log surface. The ANTIBLU products were applied with water as the diluent whereas the ANTIBORER formulations were diluted in water or light diesel oil. After treatment the logs were exposed out of doors on wooden bearers for the duration of the test. Lewis and Spence (1985) describe the test procedure in greater detail.

TABLE 8

Defacement on open stacked boards in South-East Asia field trials

Treatment	*Ramin (Indonesia: 10 weeks) % Surface Area Infected*			*Ramin (Malaysia: 6 weeks) % Surface Area Infected*			*Jelutong (Malaysia: 12 weeks) % Surface Area Infected*		
	Stain	*Mould*	*Total*	*Stain*	*Mould*	*Total*	*Stain*	*Mould*	*Total*
Untreated	19	9	28	7	5	6	NA	NA	NA
2% Na.P.C.P.	1	0	1	0	0	0	0	<1	<1
2% ANTIBLU 3737	0	0	0	0	0	0	0	0	0
3% ANTIBLU 3737	0	0	0	0	0	0	0	0	0
1% ANTIBLU 3739	0	0	0	0	0	0	<1	<1	<1
1.5% ANTIBLU 3739	<1	0	<1	0	0	0	0	0	0

TABLE 9
Prophylactic dip treatments on sawn rubberwood (8 weeks)

	% Area Infected by Fungi During Seasoning		
	Stain	*Mould*	*Total*
Untreated	33	38	52
2% Na.P.C.P. + 0.75% Lindane	<1	0	<1
3% ANTIBLU 3737 + 0.1% ANTIBORER 3767	3	2	4
3% ANTIBLU 3737 + 0.25% ANTIBORER 3768	2	<1	2
1.5% ANTIBLU 3739 + 0.1% ANTIBORER 3767	<1	<1	<1
1.5% ANTIBLU 3739 + 0.25% ANTIBORER 3768	<1	<1	<1

2.2.2.2 *Field Trial Results: sawn ramin and jelutong* (Table 8)
The results presented in Table 8 record the infection levels on air seasoned timber using either stickers or cross stacking arrangements. As in the European trials, open stacking considerably reduced the expected degree of staining and mould growth on untreated material although infection was still present. The jelutong boards were air dried for 20 days prior to block stacking and banding for a further nine weeks; all treatments prevented defacement after drying and storage. The ramin boards were air dried for 6 to 10 weeks before assessment and 2 per cent ANTIBLU 3737 and 1 per cent ANTIBLU 3739 both gave clean timber, although slight staining was noted on boards treated with 2 per cent Na.P.C.P. in the test conducted in Kalimantan. In both tests on ramin, the untreated boards were affected by internal staining. Several boards treated with Na.P.C.P. demonstrated internal staining whereas those treated with the ANTIBLU products were clear, even those prepared from 'sinker' logs.

2.2.2.3 *Field Trial Results: Sawn rubberwood* (Table 9)
The susceptibility of green, sawn rubberwood was demonstrated by the high level of stain and mould growth found on open stacked untreated boards with an average total defacement of 52 per cent after eight weeks. On the treated boards, stain and mould growth when present, was usually confined to the sticker areas. In this test green rubberwood stickers were used and consequently, at the sticker-board interface, block stacked conditions of a higher hazard were being simulated. Very effective control was obtained with 1.5 per cent ANTIBLU 3739 and 2 per cent Na.P.C.P. while the performance of ANTIBLU 3737, although being marginally lower, showed a considerable improvement over untreated boards. In this particular test insect attack, despite being limited, was confined to the untreated boards with the insecticide treatment giving protection against pin hole borers. A second test on sawn rubberwood was also conducted in which the boards were seasoned and then block stacked for eight weeks. There was slight mould development at most treatment levels including 2 per cent and 3 per cent Na.P.C.P. This mould was easily brushed off and did not disfigure the timber. After storage the boards were rip sawn and it was noted that most of the treatments showed internal stain although the colour was not particularly intense.

2.2.2.4 *Field Trial Results: Rubberwood log treatments* (Tables 10 and 11)
The results of the fungicide spray tests (Table 10) are presented in terms of the percentage of stain free timber which it was calculated could be recovered by square sawing from the logs after a specified storage period. Whilst they do not indicate the total recovery factor, the results provide a simple quantitative means of comparing the effectiveness of various treatments. The susceptibility of untreated logs is evident from the recovery rates of only one per cent to four per cent after more than two weeks storage. Treatment of the logs with solutions containing fungicides significantly reduces the rate of lateral stain penetration although it is not fully prevented. ANTIBLU 3739 at a solution strength of 1.5 per cent yielded the highest recovery rate throughout the test with 63 per cent of unstained timber obtainable after five weeks storage.

In the log trials, insect attack was confined to damage caused by Ambrosia beetles and the results of the insecticide tests are presented (Table 11) according to a performance classification system described by Abdurahim (1978). Logs treated with water or diesel only were attacked within two weeks (the first sampling period) and were given an ineffective to poor rating. Treatment with waterbased emulsions of permethrin and cypermethrin, as presented in the ANTIBORER products, gave excellent protection at all the concentrations examined with gradings ranging from good to very effective. There was however, a significant reduction in the protection afforded by treatments using diesel as the diluent: 0.5 per cent ANTIBORER 3767 and 3768 gave only two weeks protection as opposed to four weeks when applied as emulsions.

3. Ecological Studies
In order to define the fungal ecology and colonisation patterns within packs of unseasoned timber, a series of field tests was established at a home grown hardwood-softwood sawmill in Hampshire, where the United Kingdom field trials described in Section 2 were conducted: eight overlapping trials, each of three months duration, were carried out during a 12 month period from April 1982 to May 1983.

TABLE 10
Calculated recovery rates of unstained timber from rubberwood logs

Treatment	*% Recovery of Clear Timber from Logs*		
	2 weeks	*3 weeks*	*5 weeks*
Untreated	70	1	4
2% Na.P.C.P.	81	55	19
2% ANTIBLU 3737	83	76	19
3% ANTIBLU 3737	80	64	43
1% ANTIBLU 3739	73	79	36
1.5% ANTIBLU 3739	83	80	63

TABLE 11
Protective period given by the application of synthetic pyrethroids to rubberwood logs

Treatment	*Performance Classification*	*Protection Period (weeks)*
Water	Ineffective — Poor	<2
0.1% ANTIBORER 3767	Good — Very Effective	3–4
0.2% ANTIBORER 3767	Good	3
0.5% ANTIBORER 3767	Good	3
0.5% ANTIBORER 3768	Very Effective	4
Diesel	Ineffective — Poor	<2
0.1% ANTIBORER 3767	Ineffective — Poor	<2
0.2% ANTIBORER 3767	Ineffective — Poor	<2
0.5% ANTIBORER 3767	Moderate	2
0.5% ANTIBORER 3768	Moderate	2

3.1 **Experimental Procedure**
In each individual ecological field test sapwood boards of either Scots pine or Corsican pine were close stacked for the duration of the exposure period. In order to examine the influence of prophylactic treatments on fungal growth patterns, both M.B.T. (as presented in a commercial formulation ANTIBLU 3737) and Na.P.C.P. were used: treatment consisted of a 10 second immersion in a concentration of 0.09 per cent, 0.15 per cent or 0.24 per cent of M.B.T. or 1 per cent Na.P.C.P. (control boards were dipped in water only). After immersion, the boards were close stacked on wooden bearers with the sides of the packs wrapped around with polythene. It should be noted that this storage system was not devised to test the normal field effectiveness of the treatments but to promote conditions for accelerated fungal growth beyond that normally attained in practice.

3.2 **Results**
At monthly intervals over the three months storage period, five boards were randomly selected for laboratory assessment and isolation of fungi, both at the surface of the boards and internally. Figure 1 presents the results of an eight week assessment of one trial and the data are presented in terms of proportions of the total defacement caused by moulds, staining fungi or Basidiomycetes. The untreated boards showed an overall defacement of 74 per cent, the M.B.T. treated boards (0.15 per cent) showed 59 per cent defacement and the Na.P.C.P. (1 per cent) treated boards 19 per cent infection. Over 30 fungal genera were isolated during the study but of significance is the relationship between the various fungal types found on treated and untreated boards and this table demonstrates the interactions generally noted throughout the ecological trials.

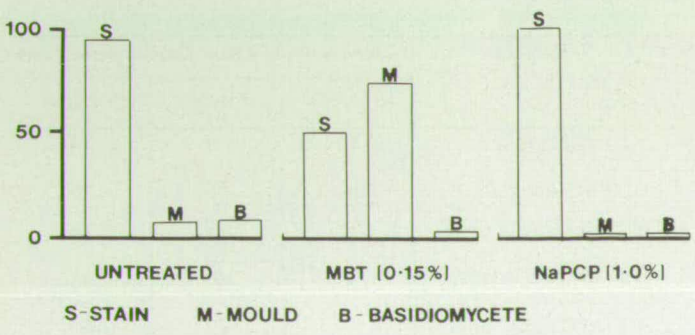

Fig. 1. Relationship between stain, mould and basidiomycete fungi on pine boards after 8 weeks close stacked storage.

The greatest diversity of fungal species was observed on (and isolated from) the untreated boards on which 93 per cent of the defacement was caused by staining fungi. The more important staining organisms were *Ceratocystis pilifera, C. piceae, Graphium aureum, G. penicillioides, Leptographium lundbergii, Phialophora spp.* and *Phoma spp.* Only 7 per cent of the total defacement was caused by mould fungi with *Trichoderma viride* and *Gliocladium roseum* being the most commonly recorded. Basidiomycete fungi were responsible for 8.6 per cent of the total defacement although their occurrence was variable and seasonally dependent.

The composition of the fungal population differed markedly between untreated boards and those boards treated with 0.15 per cent M.B.T. with the greater proportion of defacement, 74 per cent, being caused by mould fungi. Staining fungi were responsible for 49 per cent of the defacement and Basidiomycetes for 3.3 per cent. A close examination of the timber revealed that *T. viride* was the dominant mould organism whilst only a small level of *G. roseum* was recorded. Staining on the M.B.T. treated boards was caused by the uncommon ascomycete *Ceratocystiopsis falcata.* This particular fungus was also observed frequently on untreated timber but caused a lower degree of staining. It was not observed in other field trials conducted in the United Kingdom nor at those in other countries, suggesting a very localised distribution.

The lowest overall level of defacement in this particular test was recorded on timber treated with 1 per cent Na.P.C.P. As with an M.B.T. treatment, the composition of the fungal flora was significantly reduced in comparison with that found on untreated boards. Defacement was primarily caused by the stain fungi *G. aureum, L. lundbergii* and *Phialophora spp* although a small amount of *C. pilifera* was also recorded. Of interest was the very low visual incidence of mould growth on NaP.C.P. treated boards although *T. viride* was commonly isolated even from boards which did not overtly demonstrate mould colonisation.

4. The Fungal Toxicity of Prophylactic Fungicides
An alternative method for defining preservative efficacy besides that described in Section 2.1, is the measurement of the inherent toxicity of a compound towards specific target organisms. Such tests are useful since they can provide an indication

TABLE 12
Percentage spore viability after treatment with M.B.T. or Na.P.C.P.

Fungi	*0.15% M.B.T.*			*1.0% Na.P.C.P.*		
	Treatment Time				*Treatment Time*	
	10 secs	*1 min*	*2 mins*	*10 secs*	*60 mins*	*24 hrs*
C. falcata	ng	ng	ng	100%	<1%	ng
C. pilifera	ng	ng	ng	100%	5%	<1%
G. aureum	ng	ng	ng	100%	10%	<1%
P. fastigiata	ng	ng	ng	100%	95%	<1%
T. viride	95%	5%	<1%	100%	100%	<1%

ng = no germination

of the actual preservative loading needed to kill the fungi or that concentration which prevents fungal spore germination and subsequent growth. This approach was used to assess the toxicity of Na.P.C.P. and M.B.T. solutions towards selected fungi frequently isolated from the ecological trials.

The toxicity evaluation was divided into two distinct parts by virtue of test methodology:–

i. The first test was intended to assess preservative toxicity towards test fungi during the dipping phase when spores may either be present in the solution or on the surfaces of boards.

ii. The second test was devised to determine the equilibrium concentration of toxicant required on the timber in order to prevent germination and growth of fungi which may have survived the initial treatment procedure or which had subsequently been re-introduced by the various external vectors. This toxic level is commonly referred to as the Minimum Inhibition Concentration (M.I.C.)

4.1 **Toxicity During Treatment**

In order to assess the effect of the treatment solution during board dipping, spores of *T. viride* and of the staining fungi *C. falcata, C. pilifera, P. fastigiata* and *G. aureum* were exposed to solutions of M.B.T. and Na.P.C.P., at concentrations of 0.15 per cent and 1.0 per cent respectively, in the upper reservoir of a millipore filter apparatus. A 0.45 μm filter was used to retain spores. Following treatment the preservative was removed by drawing a vacuum in the lower reservoir with the spores then being thoroughly washed in sterile water to remove excess toxicant. The washed spores were plated on to a nutrient agar medium and incubated for 48 hours after which time, the percentage germination was estimated by direct microscopical evaluation.

The results of treatment solution toxicity are shown in Table 12 and demonstrate the relationship between treatment time and spore survival during the simulated dipping procedure. *Trichoderma viride* was the only organism capable of surviving a 10 second exposure to 0.15 per cent M.B.T. whereas the staining fungi showed no propensity to germinate after treatment. For the same 10 second treatment time, 1 per cent Na.P.C.P. did not prove toxic to either the staining organisms or *T. viride*: even after 24 hours in Na.P.C.P. solution spores of *C. pilifera, G. aureum, P. fastigiata* and *T. viride* were still capable of germination. These results would suggest that M.B.T. is considerably more toxic than Na.P.C.P. towards fungal inocula during the dipping procedure. The controls, treated with water showed a 100 per cent incidence of germination.

4.2 **Minimum Inhibition Concentration Determinations.**

Measurement of the M.I.C. for each of the selected fungi was carried out using a liquid culture system. In this test, spore suspensions of the fungi were prepared separately in a nutrient medium (modified Eggins and Pugh 1962 medium containing 1 per cent glucose as the sole carbon source) and then 20 ml aliquots were placed in universal bottles to which amounts of preservative solution were introduced in order to obtain predetermined active ingredient concentrations ranging from 0.1 ppm to 10 ppm of M.B.T. or Na.P.C.P. All the cultures were then incubated at +25°C for 10 days after which time each was inspected and a visual assessment of growth was made by comparison to the untreated controls.

The results are presented in Table 13 which gives the M.I.C. of M.B.T. and Na.P.C.P. towards the test organisms in parts per million (ppm). The M.I.C. values reiterate the relatively high level of tolerance of *T. viride* to both Na.P.C.P. and M.B.T. by showing an M.I.C. of 10 ppm for the two compounds. Against the staining fungi M.B.T. proved to be between two and at least five times more effective than Na.P.C.P. in preventing fungal development. It is interesting to note that *C. falcata* was susceptible to 0.1 ppm of M.B.T. and yet was isolated during the ecological trials; *P. fastigiata* was the most tolerant of the staining fungi to both M.B.T. and Na.P.C.P. and this may account for its presence on Na.P.C.P. treated boards.

In summary, the results of these two tests would suggest that M.B.T. is more toxic than Na.P.C.P. towards most of the test fungi both during the dipping procedure and also at equilibrium concentrations as determined by the M.I.C. test. The ability of the fungi to recover after immersion in Na.P.C.P. solutions and subsequent washing would indicate that Na.P.C.P. may provide a fungistatic effect compared with the direct fungitoxic effect of M.B.T.

TABLE 13
Minimum Inhibition Concentration values of M.B.T. and Na.P.C.P. against selected fungi

Fungi	*Minimum Inhibition Concentration (ppm)*	
	M.B.T.	*Na.P.C.P.*
C. falcata	<0.1	0.5
C. pilifera	0.5	5.0
G. aureum	1.0	5.0
P. fastigiata	5.0	10.0
T. viride	10.0	10.0

5. Preservative/Wood Substrate Interactions

The treatment of green, freshly converted timber is, in many instances, followed by close stacking prior to shipment and use. Within these packs of timber, high moisture contents are maintained (sometimes in excess of 120 per cent) and conditions would appear to be suitable for promoting diffusion of active ingredients which are deposited on the surfaces of the boards. Any preservative re-distribution clearly has an important bearing on the performance of treatments and a programme of work was therefore initiated to study, in detail, the potential for re-distribution of Na.P.C.P. and M.B.T. within pine sapwood boards following a momentary immersion treatment.

5.1 Experimental Procedure

In order to examine the mobility of the selected fungicides, a bioassay system was devised as this proved to be more sensitive than conventional analytical techniques in determining the amount of toxicant present in a wood sample. The bioassay system is described, in more detail, by Williams, Eaton and Lewis (1985) and basically relies upon the inhibition of spore germination and cell growth of the bacterium *Bacillus subtilis* in the presence of selected toxicants. Growth inhibition of the bacterium in agar can be measured by clearance zones around preservative treated wood discs. The zones of inhibition from discs containing unknown quantities of preservative can be related to those obtained from calibration discs in order to determine toxicant levels in the wood. The premise of the test is that a certain amount of toxicant in a wood disc will always give a similar zone of inhibition provided that the chemical is mobile and stable. This method was specifically devised in order to detect M.B.T. whilst *B. subtilis* was the most sensitive bacterium readily available.

The test method can conveniently be divided into two parts: (i) preparation of calibration curves, (ii) determining preservative content in sampled discs.

5.1.2 *Preparation of Calibration Curves*

The bioassay requires the preparation of a calibration curve in order to determine the reaction of *B. subtilis* to known concentrations of the preservatives which are present in wood samples. This was accomplished by using small dried wood discs, cut tangentially from fresh sapwood and measuring 13 mm diameter and 0.5 mm thickness. These 'calibration' discs were soaked for 24 hours in known concentrations of the test preservative then placed on the surface of a nutrient agar which had previously been seeded with the indicator bacterium prior to pouring. The plates containing the discs were then incubated for 18 hours at +30°C and measurement of the resultant inhibition zones around the treated discs permitted the construction of a calibration curve from which could be read estimates of the preservative content of treated discs. Calibration curves for both Na.P.C.P. and M.B.T. were prepared in this manner.

5.1.3 *Estimation of Toxicant Penetration*

The estimation of toxicant penetration into small test boards (300 × 100 × 25 mm), following a 10 second immersion treatment, was performed by removing 13 mm diameter core samples from the boards after specified periods from treatment. The boards were wrapped in polythene after treatment to prevent surface drying and were stored at +25°C. Twelve 0.5 mm discs were cut sequentially from each core using a sledge microtome and each disc was then placed on to the nutrient agar plate seeded with *B. subtilis*. After 18 hours incubation the resultant inhibition zones around the discs were measured and the quantity of preservative in each disc estimated from the previously constructed calibration curves in order to prepare a toxicant distribution profile of the treated boards.

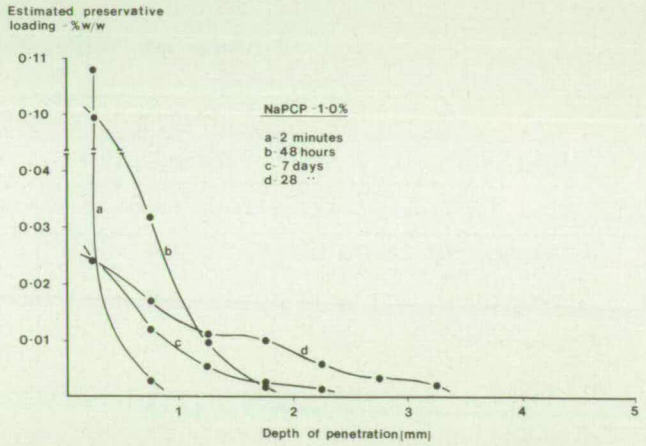

Fig. 2. Preservative Distribution Profiles (1.0% Na.P.C.P.)

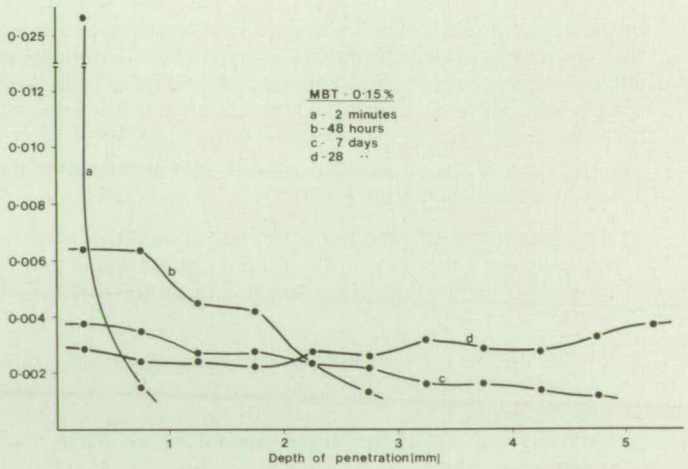

Fig. 3. Preservative Distribution Profiles (0.15% M.B.T.)

5.2 Results of Active Ingredient Penetration Tests

The results describing the movement and distribution of Na.P.C.P. and M.B.T., over a 28 day period following treatment, are shown in Figures 2 and 3 respectively. These graphs plot the percentage weight/weight active ingredient present in the wood discs (as calculated from the calibration curves) in relation to sampling depth at specific time intervals.

There are significant differences between the two preservatives in terms of the rate of penetration and the equilibrium distribution profile. The penetration of Na.P.C.P. is characterised by a gradual and limited movement into the sampled boards over the 28 day period with very little preservative being detectable at a depth greater than 3.0 mm. At equilibrium (28 days) the surface loading of Na.P.C.P. was judged to be at 0.025 per cent w/w or 13 per cent of the initial surface concentration two minutes after treatment. M.B.T. showed a more rapid change in surface loading from approximately 0.026 per cent w/w to 0.006 per cent within 48 hours, as well as a significant degree of penetration into the sampled board. At the end of the 28 day storage period, the M.B.T. had appeared to reach a state of equilibrium with an even distribution of chemical, within the first 5 mm from the surface of the board, of approximately 0.003 per cent w/w to 0.004 per cent w/w. At equilibrium the surface loading of M.B.T. was approximately 11 per cent of the initial concentration, a figure similar to Na.P.C.P.

The movement and re-distribution of the active ingredients in this manner has important implications for the performance of prophylactic chemicals and is discussed in Section 7.

6. Formulation of Prophylactic Chemicals

An examination of active ingredients currently being used or investigated as alternatives to Na.P.C.P. and lindane, will reveal many that are not readily soluble in water. A great deal of emphasis must therefore be placed upon formulation development in order to obtain a product which is easily handled at a sawmill and which gives stable solutions in use. The generally accepted formulating technique with water insoluble products is to dissolve the biocides into a compatible solvent along with emulsifiers or dispersing agents. Because of their convenience, formulations of this type can be regarded as the most popular form in which non-water soluble biocides are presented. It is beyond the scope of this paper to discuss in detail the due procedures for formulation development. Suffice to say that the products must be readily dispersible in water without excessive preparation, remain stable in use and be compatible with the other chemicals which are likely to be used in conjunction with them.

6.1 **Dispersibility of Emulsified Concentrates**

As part of the formulation programme on M.B.T. and M.B.T./T.C.M.T.B. based products, attention was paid to the initial dispersibility particularly as earlier formulations based on M.B.T., which had been marketed, showed a propensity towards active ingredient precipitation during mixing; the problem was exacerbated at low temperatures.

6.1.1. *Experimental Procedure*

To assess the dispersibility characteristics of M.B.T. containing formulations an *ad hoc* test was devised whereby test solutions were prepared by adding concentrates to water (at different temperatures) at a pre-determined rate; the solutions were left to stand for five minutes after addition and then gently stirred. This procedure was intended to simulate poor mixing at a sawmill where a large volume of concentrate could be added very quickly into a treatment tank with minimal mixing until use. After preparation the test solutions were stored at various temperatures ranging from +1°C to +20°C for 24 hours and then analysed, by H.P.L.C., for the M.B.T. content remaining in the dispersed phase.

6.1.2. *Analytical Results*

The results of dispersibility tests on two formulations containing 10 per cent M.B.T. are presented in Table 14 where the percentage of M.B.T. in the dispersed phase is shown against the nominal active ingredient concentrations with associated preparation and storage temperatures. Dilutions prepared from Formulation 1 were not stable under conditions of the mixing procedure. Only 68.5 per cent of the active ingredient from Formulation 1 remained in solution after preparation of a nominal M.B.T. concentration of 0.24 per cent at +10°C: this reduction in M.B.T. level was due to precipitation during mixing and not active ingredient breakdown. Formulation 2, containing different emulsifying agents, remained fully stable at the same temperature after a similar mixing procedure and this was noted throughout the concentration/temperature combinations examined.

TABLE 14
Analytical data from dispersion tests on M.B.T. based formulations

Water Temperature °C	*% Nominal M.B.T.*	*% M.B.T. Remaining in Dispersed Phase*	
		Formulation 1	*Formulation 2*
+1	0.24	43	100
	0.28	43	99
	0.32	39	98
+10	0.24	68	100
	0.28	66	98
	0.32	62	99
+20	0.24	80	100
	0.28	72	100
	0.32	67	100

6.2 **Active Ingredient Compatibility**

In certain market areas there is a requirement for insecticides to be used in conjunction with anti-sapstain chemicals. However, it is important to ensure that both the formulations and the active ingredients are compatible. Storage tests were therefore conducted on dilute-solution mixtures of the ANTIBLU and ANTIBORER products. Solutions were prepared from the various concentrates using water as the diluent with the ANTIBORER products being added to the dilute fungicide solutions. The prepared solutions were stored at +40°C for 28 days after which they were ananlysed for total synthetic pyrethoid content and for the cis : trans isomer ratio. The results are presented in Table 15 and it can be seen that neither the active ingredient levels nor the cis : trans ratios have changed significantly, from which it can be concluded that synthetic pyrethroids, M.B.T. and T.C.M.T.B. are mutually compatible as presented in the test formulations.

7. Discussion

7.1 *Formulation Development*

The performance of prophylactic products is related not only to the effectiveness of the active ingredients but also the formulations in which they are presented. Earlier formulations based on MBT exhibited a tendency for the active ingredients to precipitate during dilution and for the treatment solutions to have a limited stability, particularly at low temperatures. The effect is demonstrated in Table 14 where significant differences in the dispersion characteristics of two formulations containing 10 per cent M.B.T. are compared. One formulation is particularly susceptible to precipitation of the active ingredient during mixing whereas the second formulation, using a different emulsifier system, was able to tolerate a combination of poor mixing technique and low water temperatures. This is of importance when one considers the application of products of this type where, because of dilute solution instability, a sawmill may be treating with a solution of reduced strength.

As well as influencing product stability, formulation modifications can significantly alter the health and safety characteristics of a product: certain formulations containing M.B.T. or T.C.M.T.B. have been regarded as strong irritants. Tests conducted on the range of ANTIBLU products show them to have a low primary skin irritation rating and they are classified as non-sensitising, an important feature in sawmill usage and on this basis ANTIBLU 3738 has been granted registration in Finland.

The synthetic pyrethroid insecticides, cypermethrin and permethrin, offer considerable benefits in terms of effectiveness, permanence and environmental considerations (Carter 1984). Given the increased number of fungicides being promoted in market areas where dual purpose prophylactic treatments are performed, it is essential to confirm that the active ingredients are compatible as shown with the ANTIBLU and ANTIBORER products when mixed dilutions are prepared.

TABLE 15
Storage tests on dilute solutions containing synthetic pyrethroids and M.B.T./T.C.M.T.B. fungicides

Fungicide	*Storage Period (Days)*	*Permethrin (Antiborer 3768)*		*Cypermethrin (Antiborer 3767)*	
		Concentration % ai	*Cis : Trans*	*Concentration % ai*	*Cis : Trans*
NA	0	0.20	42.1 : 57.9	0.11	43.9 : 56.1
NA	28	0.20	41.3 : 58.7	0.11	42.7 : 57.3
0.3% ai ANTIBLU 3737	0	0.21	40.9 : 59.1	0.11	43.1 : 56.9
0.3% ai ANTIBLU 3737	28	0.21	42.0 : 58.0	0.10	42.2 : 57.8
0.3% ai ANTIBLU 3738	0	0.20	41.2 : 58.8	0.11	43.3 : 56.7
0.3% ai ANTIBLU 3738	28	0.20	43.2 : 56.8	0.11	41.9 : 58.1
0.3% ai ANTIBLU 3739	0	0.21	41.0 : 59.0	0.11	43.0 : 57.0
0.3% ai ANTIBLU 3739	28	0.21	42.1 : 57.9	0.11	42.0 : 58.0

7.2 **Ecological Studies on Mould and Staining Fungi**

An indication of the extensive problem facing anti-sapstain chemicals is the large number of possible target organisms. Kaarik (1980) lists 312 staining fungi, with an additional 29 mould organisms, as being found in temperate conditions. During the ecological trials (Section 3) at least 37 fungal species were isolated from two different timber species at one site, indicating the potential defacement problem.

Treatment with Na.P.C.P. (1 per cent) and M.B.T. (0.15 per cent) significantly reduced the fungal flora by eliminating the least tolerant species. However, significant inter-treatment differences in the species composition was also observed. Defacement on Na.P.C.P. treated boards was almost entirely caused by staining, particularly *G. aureum, Phialophora spp* and *L. lundbergii.*

Very little mould growth was observed on the Na.P.C.P. boards but when isolations were made from their surfaces, *T. viride* was present, suggesting that the fungicide was acting in a fungistatic manner by inhibiting spore germination rather than in a fungitoxic manner. *T. viride* was also observed on the M.B.T. treated boards and was responsible for most of the defacement. Staining on M.B.T. treated boards was caused by one particular species — *C. falcata.* This fungus has rarely been isolated previously and was not found at other trial sites suggesting a sparse distribution. Previous United Kingdom isolations have been from *Betula pendula, Fagus sylvatica* and *Quercus robur* (Rayner and Hudson 1977) and it should be noted that the ecological trials were conducted at a sawmill cutting hardwoods as well as softwoods and the appearance of *C. falcata* may therefore have been due to localised site factors. It was felt that the lower incidence of *C. falcata* on Na.P.C.P. treated and untreated boards was due to its lack of competitiveness with other staining fungi in the absence of *T. viride.* In the laboratory *C. falcata* did not grow on timber under monoculture conditions although in the presence of *T. viride* growth and sporulation was prolific and this interaction obviously requires further study. The predominant Basidiomycete fungus isolated during the trials was shown to have decay potential but has not been identified.

One aspect of the ecological study not reported here, but which has important practical implications, was the isolation of staining fungi from freshly felled logs indicating the rapid colonisation potential of these organisms. At certain times of the year during the main field trial programme the selection of stain-free timber was, in several instances, difficult because of the significant level of stain present in the logs. An examination of logs and freshly converted timber in Spanish, Portuguese and United Kingdom softwood sawmills revealed that pre-conversion staining would appear to be a far greater problem than had been appreciated, with obvious implications for treatment quality. Keirle (1978) notes that in New South Wales the storage of logs for periods longer than one month without pronounced deterioration was possible only in winter.

7.3 **Field Performance of Prophylactic Treatments**

The large number of species isolated in the ecological study and the interactions between fungi, validates the decision not to artificially inoculate test boards, prior to storage, in the main field trial programme. Besides challenging the chemicals to a far greater extent than would be the case in practice, artificial inoculation does not make allowances for specific on-site organisms and could induce competition between the indigenous and introduced fungi which would distort the resultant infection pattern.

The trials conducted on the ANTIBLU and ANTIBORER products in this development and assessment programme covered a wide range of timber species, handling procedures and climatic conditions. The susceptibility to staining of the timber species examined is shown by the very high levels of defacement recorded on untreated boards, particularly when held under close stacked conditions and demonstrates the requirement for active control measures. In general, the field trial results with the ANTIBLU products confirmed the efficacy of M.B.T. and M.B.T./T.C.M.T.B. mixtures as shown by previous work. Dickinson (1977) reported that M.B.T. gave effective control on pine at working concentrations between 0.1 per cent and 0.3 per cent and this was supported by Edlund and Henningsson (1982) after a series of laboratory tests and field trials. Cserjesi, Byrne and Johnson (1984) concluded that for both long term and short term protection on block stacked hem-fir, Douglas-fir and spruce-pine-fir, M.B.T. based treatments showed acceptable performance. On open stacked material stored for 10 months, 0.15 per cent M.B.T. gave similar protection to 1.5 per cent sodium pentachlorophenoxide (Dickinson and Henningsson 1984). Vidovic (1981) found a significant improvement in stain reduction on beech veneers using an M.B.T./T.C.M.T.B. mixture rather than T.C.M.T.B. alone whilst Plackett (1982) reports very good protection, after five months block stacking of timber in British Columbia, with an M.B.T. + T.C.M.B.T. product.

Mould growth was found on M.B.T. treated timber in the ecological trials and in one particular test conducted in the United Kingdom mould levels of between four per cent and eight per cent were recorded. In this test the untreated boards

were heavily contaminated with *T. viride*. Infection by this mould was not common upon untreated timber throughout this test programme, indicating the presence of a high mould inoculum and suitable environmental conditions for its establishment when the test was initiated or possibly the absence of another organism which had previously led to the inhibition of mould growth. Discussions with sawmill managers suggest that mould growth at the levels found is generally not regarded as significant because it is easily removed and does not create a permanent disfigurement. Mould infection of treated timber has been widely reported in the literature. Butcher (1980) mentions that a mouldicide should be added to Captafol in order to increase the spectrum of activity whilst Hulme and Thomas (1979) report mould growth on boards treated with sodium tetrachlorophenoxide and quaternary ammonium compounds. Timber treated with 3-iodopropynyl butyl carbamate also exhibited mould contamination (Cserjesi *et al* 1984). It would, therefore, appear that mould organisms, particularly *Trichoderma spp*, exhibit a tolerance to many types of fungicides used in prophylactic treatments.

A surprising feature of the United Kingdom tests was the degree of bluestaining found on close stacked untreated spruce sapwood boards. Such staining on spruce has also been recorded by Coggins (1982) and underlines a requirement for treatment if spruce is to be held for any length of time without drying. Although the stain found on both spruce and larch was not as intense as that on pine, the level of defacement was thought to be sufficient to reduce the commercial value for certain end uses.

In the Portuguese trials, Maritime pine pallet boards were afforded protection for at least 16 weeks after treatment with 2.5 per cent ANTIBLU 3738 and 1.5 per cent ANTIBLU 3739. However, the boards treated with solution from the sawmill's own dip tank (nominally 3 per cent Na.P.C.P.) showed bluestaining, possibly demonstrating one of the practical aspects of anti-sapstain treatment. Sodium pentachlorophenoxide is accepted as giving excellent protection and yet in the yards of many pallet manufacturers it is not unusual to find a number of stained packs. This, in part, may be due to the presence of preconversion stain, inadequate treatment methods or lack of treatment solution quality control. With the introduction of new products, the importance of quality control will need to be re-emphasised if treatments are to meet expectations.

Secondary and tertiary timber processing industries, as opposed to log exports, are becoming increasingly important contributors to the economies of South-East Asia. In these markets it is accepted practice to open stack timber for seasoning prior to shipment and the results presented in Table 8 are therefore indicative of the good practical performance of the ANTIBLU products. Stain on untreated ramin and jelutong, although present, was not particularly intense: however, according to the sawmill managers even this low level of defacement is considered as unacceptable and could lead to a reduction in the commercial value of the timber or subsequent customer claims for damages. With the tests using ramin conducted in Kalimantan, the untreated and Na.P.C.P. treated boards exhibited internal staining whereas those treated with ANTIBLU 3739 and ANTIBLU 3738 were clear even in those boards prepared from 'sinker' logs. The latter are claimed to be particularly susceptible to internal staining (Abdurahim 1981). In Tests conducted by Abdurahim (1981) on Basiment 235 it was found that 95.6 per cent of the untreated ramin boards showed internal stain, of which 73 per cent were badly infected. Treatment with Na.P.C.P. in the same test reduced the incidence of stain but 43 per cent of the boards were still internally stained: dipping in Basiment 235 (1.5 per cent concentration) also failed to totally eliminate internal staining.

On freshly sawn rubberwood boards, which are particularly susceptible to both fungal and insect attack, very effective protection was given by combinations of the ANTIBLU and ANTIBORER products. The performance of ANTIBLU 3737 was marginally lower than ANTIBLU 3739 but infection was confined to the areas under the green rubberwood stickers which were used to separate the boards for air drying. In these areas, localised conditions of close stacking were therefore being simulated. Rubberwood is also very susceptible to internal staining and in one test conducted the untreated samples showed severe staining which was significantly reduced in both incidence and intensity after treatment. Although the development of internal stain does not occur in all sawn rubberwood, for certain end uses such as furniture and decorative joinery its exposure during machining may be detrimental to the article's finished appearance and value. In order to minimise the development of internal stain the ANTIBLU and ANTIBORER products have been successfully applied by pressure treatment systems (Lewis and Spence 1985).

The differential in performance of the pyrethroids, when applied in water as compared to diesel for log treatments, is difficult to elucidate without further work but may suggest differences in penetration or retention characteristics of the two systems and warrants further investigation. The effect may also be species independent as tests carried out in Kalimantan on ramin logs showed the ANTIBORER products to give at least four weeks protection when applied in water (Abdurahim 1985).

Log treatments, both fungicidal and insecticidal are instrumental in reducing the level of wastage from sawn logs after storage. However, emphasis must still be placed on rapid extraction and conversion of the logs with prophylactic chemicals being used to minimise degradation and to provide a 'buffer' against unexpected delays in conversion or extended storage periods.

7.4 **Active Ingredient Toxicity**

The field effectiveness of the ANTIBLU products under a wide variety of conditions can be related to the toxicity of M.B.T. towards staining fungi, as demonstrated in the laboratory toxicity tests. M.B.T. was very toxic to spores of the staining fungi isolated from the ecological trials with a 10 second immersion in 0.15 per cent M.B.T. producing 100 per cent mortality whereas there was complete spore viability after treatment for a similar time with 1.0 per cent Na.P.C.P. *C. falcata* was observed on M.B.T. treated boards in the colonisation tests but it was very susceptible to M.B.T., which suggests that it may have been introduced after treatment possibly by insect vectors or local sawmill and test site conditions. In the toxicity tests, the most tolerant organism to M.B.T. and Na.P.C.P. was the mould *T. viride*: the M.I.C. concentrations were similar although *T. viride* was found to grow on M.B.T. treated boards, suggesting that other factors besides basic toxicity must be influencing active ingredient performance.

7.5 **Interactions between Fungi, Preservative and Wood Substrate**

From the toxicity tests *T. viride* exhibited a similar tolerance to M.B.T. and Na. P.C.P. although, in the ecological trials, it was only incidental on the Na.P.C.P. treated boards in terms of defacement caused. It was, however, dominant on 0.15 per cent. M.B.T. treated boards. This discrepancy between basic toxicity and performance can be related to the differing interactions of M.B.T. and Na.P.C.P. with the wood substrate. For maximum stability, sodium pentachlorophenoxide is generally applied in buffered systems; if the pH falls below a critical level there is a tendency for the water insoluble P.C.P. to precipitate from the water soluble Na.P.C.P. This is probably the situation on the surface of green timber where the acidic nature of the sap causes precipitation to non-mobile P.C.P. in the outer 2-3 mm as suggested by the distribution profile in

Figure 2. A high residual level of P.C.P./Na.P.C.P. is retained at the surface which may act in a fungistatic manner preventing germination or further growth of the fungal spores and hyphae which survived the initial treatment. The viability of *T. viride* spores when removed from the surface of treated boards suggests that Na.P.C.P. was not acting in a fungitoxic manner. Forty-eight hours after treatment, the bioassay technique showed that a significant depletion of M.B.T. from the board surfaces had taken place, with a concomitant increase in concentration at the sub-surface zones. The mobility of the M.B.T. may, in part, be due to its finite solubility in water associated with the dispersing action of the emulsifier system and because the molecule is stable under acidic conditions. Irrespective of the mode of movement, the practical consequence is of significance if the residual surface loading falls below the protective level. Under these conditions any spores of *T. viride*, the most tolerant organism tested, which may survive the initial fungitoxic effect of high M.B.T. levels are potentially capable of germinating on the wood surface. This is only applicable to close stacking as during air seasoning the surface drying of the timber will have the effect of reducing the rate of depletion thereby making the surface less amenable to germinating spores.

This fungal tolerance and preservative-substrate interaction demonstrates the requirement in any development programme for rigorous field testing pertinent to practical conditions. The field trial data in Section 3 show that effective treatment can be arrived at by the selection of concentrations which empirically compensate for the re-distribution potential of M.B.T. With these treatments, the initial active ingredient concentrations are such that at equilibrium the residual levels of M.B.T. on the timber surface are sufficient to prevent the development of both mould and staining fungi.

It is, therefore, proposed that the field effectiveness of M.B.T. containing products noted in this and other studies is due to:–

i. The immediate toxicity of M.B.T. being sufficient to kill a significant proportion of the fungal inoculum either during dipping or immediately after treatment whilst the surface concentration of M.B.T. is still sufficiently high.
ii. Treatment recommendations taking account of the re-distribution potential of M.B.T. in order to provide sufficient residual toxicity.

Important technical benefits can accrue from the re-distribution of M.B.T. as has been seen on the tests with remain where internal stain was prevented after treatment with the ANTIBLU products. The rapid movement of M.B.T. had precluded the subsequent penetration of stain or, if the interior of a board was already colonised, the concentration of M.B.T. proved toxic to the fungi before pigmentation developed.

A dual fungicide system, such as ANTIBLU 3739, may benefit from the high initial toxicity and mobility of MBT whilst an immobile active ingredient would remain on the surface to improve the residual surface toxicity. This may provide an explanation for the results in Table 6; at equivalent active ingredient concentrations, ANTIBLU 3739 performed better than ANTIBLU 3738 a feature also noted in the rubberwood dip treatments.

8. Concluding Remarks

This programme of work has demonstrated the potential effectiveness of the ANTIBLU and ANTIBORER products over a wide variety of conditions. However, the results have also shown that the development of effective prophylactic chemicals is a complex task, requiring a multi-disciplinary approach. Correct formulation is a pre-requisite for practical use and emphasis needs to be placed on field trial programmes. Due regard must also be given to investigating the fundamental inter-relationships between the target organisms, the wood substrate and the active ingredients. This integrated approach to product development promotes a greater awareness of the problems which may be encountered and provides the background for further product development and refinement.

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DISCUSSION ON PAPER 2

Chairman: C. R. Coggins

DR. C. R. COGGINS: Before throwing the paper open for discussion could I remind you please when you ask a question to give your name and organisation and speak loudly and clearly particularly if you are sitting behind the row of pillars so that the people upstairs can hear your question. Can I have the first question.

DR. D. J. DICKINSON (Imperial College): I think one of the most interesting parts of your work is this point about redistribution. It clears up a lot of questions in my mind and helps provide some of the answers for the previously unexplained field performance of M.B.T. based formulations, particularly the difference that one sees time and time again between a closed and open performance. On the point of redistribution, in the open stack situation where M.B.T. performs particularly well do you think you are getting a reverse effect with the chemical coming to the surface and being held at the surface by the fact that you are losing water and producing a sort of blooming effect, thereby explaining the excellent performance of M.B.T. formulations in the open stack situation and not such good performance in the closed stack situation.

MR. G. WILLIAMS: I think there are two points we have to consider in the open stack configuration. Obviously, first of all, the timber tends to be less susceptible to attack anyway by the various fungi, but I think it is not so much a blooming effect, but a reduction in the rate of diffusion of the chemical in the first place by removal of water from the surface.

DR. D. J. DICKINSON: Are you also absolutely sure that the redistribrution material is, in fact, M.B.T. and not a breakdown product?

MR. G. WILLIAMS: No, we have only determined the penetraon of the active ingredient by its toxicity and not chemically.

MR. D. P. BLOW (Fosroc Limited): I see that T.C.M.T.B. was used in combination with M.B.T. Did you use T.C.M.T.B. by itself and, if so, how did it perform?

DR. D. A. LEWIS: Yes, we looked at it in the early screening programme when we carried out field trials. We did find it particularly susceptible to mould and hence we examined M.B.T. and then M.B.T./T.C.M.T.B. formulations.

MR. J. DAVID (Catomance Limited and Deputy President, B.W.P.A.): You refer to one per cent sodium pentachlorophenate. Are you talking about sodium pentaclorophenate or technical sodium pentachlorophenate, the number of water molecules in association, technical pentachlorophenate having 85 per cent of sodium pentachlorophenate in it, and realising that you are at the edge of effectiveness what sort of water did you use to dilute the solution? Was it hard or soft water? Do you think that would have any effect and what was the P.H. of the timber, to give some idea of whether you are likely to be looking at sodium pentachlorophenate or pentachlorophenol. Could you tell me a little bit more about that?

MR. G. WILLIAMS: For the tests we used technical grade sodium pentacachlorophenoxide. The water we used was always the water that we found on site. For the toxicity tests the solutions are always buffered, so that we are testing against sodium pentacachlorophenoxide, but obviously in the field where there may be precipitation then the protection on the surface of the timber is going to be provided by pentachlorophenol and not sodium pentachlorophenoxide.

MR. E. BORSHOLT (Technological Institute, Denmark): Could you give us some idea about health and safety in connection with your product. I am thinking of soil contamination and destruction of wood waste.

DR. D. A. LEWIS: In terms of soil contact, T.C.M.T.B. is claimed by the manufacturers to be biodegradable; the representatives from Buckman Laboratories may be able to comment in more detail on that. In Finland, incineration is recommended for the disposal of wood waste. At the temperatures encountered, we are talking about the generation of generally harmless breakdown products.

MR. A. C. OLIVER (Bucks. College of Higher Education): Could I ask why you did not continue testing the fluoride/bi-fluoride combination. From the first table it looked very promising.

DR. D. A. LEWIS: We said in the paper that we looked at the products initially from a review of previous information, from the tests that we carried out and also from the point of view of health and safety considerations. Taking those three points together, we felt that we would prefer to move with M.B.T. and T.C.M.T.B. as active ingredients where we could perhaps control, by formulation aspects, the health and safety characteristics rather than a straight fluoride/bi-fluoride salt mixture. So we were mainly concerned with health and safety aspects of the fluoride formulations.

DR. MORGAN (Princes Risborough Laboratory): You spoke very briefly about unexpected staining on spruce. I wondered whether you could say a little bit more about this and whether it was associated with any particular type of spruce and/or any characteristics of the wood.

DR. D. A. LEWIS: We looked at two species of spruce, but generally we used *Picea abies* as an alternative to pine and we did find staining. I have to point out that although the percentage in the paper would seem high it was a rather faint stain, whereas that which we were getting on pine was particularly intense. So there does appear to be a species difference in the staining organism responsible or perhaps it is just a reduced colouration effect. I think Dr. Coggins's B.W.P.A. paper three years ago also mentions staining on untreated spruce.

THE CHAIRMAN (DR. C. R. COGGINS): Yes, that is right.

MR. B. JENSEN (G.O.R.I. Research Limited, Denmark): One of the disadvantageous features of M.B.T. is its gunpowder-like smell or odour. I wonder if you could tell me how long this odour would stick to the wood after treatment.

DR. D. A. LEWIS: I think at higher concentrations, may be about .3 or .4 per cent, there is a noticeable odour but at general working concentrations and also in combination with T.C.M.T.B. where you are working at lower M.B.T. concentrations we have not, nor have the people we have approached working in sawmills where it has been used, noticed any unpleasent smell. With the treated timber we have not noticed, nor again have sawmill users reported any unpleasant odours associated with it whilst the timber is wet or when the timber has dried.

PROF. E. B. GARETH JONES (Portsmouth Polytechnic): It is very nice to see that you are using pyethroids to replace organochlorines. For a variety of reasons one would like to see these phased out. The question I have to ask is, do you have any information about the persistence of cypermethrin or permethrin in the timber?

DR. D. A. LEWIS: In terms of persistence I think we would look towards the P.R.L. work. We have only examined persistence, for this particular application, in terms of the effective period against insect attack. I think with regard to the work at P.R.L., we are looking at a similar persistence to that of permethrin. I do not know whether Tony Bravery would like to comment on current thoughts about the persistence of pyrethroids in general compared with the organo-chlorines, but I know that they rate favourably.

DR. A. F. BRAVERY (Princes Risborough Laboratory); I can only really comment, Alan, in relation to the wood boring insect tests that Roger Berry has done and, although we have looked at toxicity before and after the standardised evaporative ageing procedure, we have not looked quantitatively at

residual levels of cypermethrin. However, in general terms you have summarised the conclusions we have reached on the basis at least of the bio-assay work which has been carried out.

DR. D. J. DICKINSON (Imperial College): Could I ask you about failures with *Trichoderma viride* when they do occur at low levels. Do you find it is an overall failure or do you get development in one part of the package and then infection through the package by the spores produced from one colony?

MR. G. WILLIAMS: It depends obviously on the treatment, but where there is defacement you do tend to get the growth in one particular part of the timber and it seems to spread from there.

DR. D. J. DICKINSON: That is exactly the same as I have noticed.

MR. G. WILLIAMS: In the actual toxicity tests we did notice that it is very difficult to kill *Trichoderma viride* at lower concentrations. Of course you only need one or two viable spores to produce a colony of growth and subsequent defacement. Having said that, I think what is often missed is the fact that there are many viable spores around on the surface of the timber but they can be prevented from germination by maintenance of a sufficiently high surface concentration of toxicant. You can especially see this in timber treated with Na.P.C.P. where one can actually isolate viable *Trichoderma* from the surface of the board. Quite commonly you can isolate the organism but it rarely causes defacement.

DR. D. J. DICKINSON (Imperial College): If I could continue to follow the question. You have experienced then the same sort of thing that I have seen so often with M.B.T., you probably pick out one spore which I consider may well be tolerant because there are so many spores around, you then get a build-up of the tolerant material in the package. Do you envisage a situation where this type of problem could build up in a yard, where you start to get one infected package, particularly when you are stretching out batch treatment at low levels, that resistance to one particular organism will build up and give a limited life to a compound? I am thinking particularly of the way it does in water treatments and M.B.T. has been used an awful lot in water treatments. You do get this need to flush through with another system cropping up because these tolerance organism do build up. Do you envisage this could happen with the type of products used for sapstain treatments?

MR. G. WILLIAMS: It is difficult to answer that, David. During the toxicity tests we actually utilised the particular strain that was isolated from a treated sample, so hopefully we were testing the preservatives against a tolerant organism.

DR. R. A. EATON (Portsmouth Polytechnic): I think that *Trichoderma* is something we really need to look at in a lot more detail. I think it is an organism which we have tended not to worry about too much because it does not cause decay as such but it is a very important problem organism. It does show terrific variability. We really need to look at as many strains as we possibly can and see what variations there might be. I think the point about whether you could get a problem arising which can get worse and worse within a yard so feasible, I suppose.

DR. D. A. LEWIS: I think it could be feasible if one is looking at systems which may be one active ingredient used at sub-effective levels. There is a trend to move perhaps towards cocktails, that is two or three active ingredients, as a result fo which the *Trichoderma* may be under stress from the M.B.T. and you then just need another active ingredient to prevent further growth. So I think that your question may perhaps be answered or overcome possibly by the use of dual or triple fungicide systems.

DR. D. J. DICKINSON (Imperial College): Or encouraged. It could happen the other way round. Sub toxic levels of materials, even admixtures can lead to the development of tolerance.

DR. D. A. LEWIS: That is where rigorous field testing must be implemented to account for that possibility.

THE CHAIRMAN: Ladies and Gentlemen, we have come to the end of the time available for discussion. Sapstain control is a matter of increasing importance to the timber preservation industry and I think you will agree with me that this paper represents a new level of the state of the art in looking at the problem and developing answers to it. So please will you join me in thanking the authors for preparing the paper and particularly Gareth Williams for making such a professional and interesting presentation. *(Applause).*

B.W.P.A. ANNUAL CONVENTION, 1985

INTERACTIONS BETWEEN COPPER AND WOOD DEGRADING FUNGI

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Introduction

Copper compounds are highly effective fungicides and their use in wood preservatives has a long tradition.The fungicidal action of copper is, generally speaking, brought about by precipitation of proteins and interference with vital enzymatic reactions (Lukens, 1971). Because of the high reactivity of the copper ion and a large number of possible reactive sites in the cell, copper toxicity is not a strictly specific action on fungal cell metabolism as known for many organic fungicides.

Of particular interest is the study of toxic effects of copper on wood degrading fungi that are copper tolerant. Brown rot fungi of the genus *Poria* and soft rot causing *Phialophora* species have repeatedly been isolated from copper treated wood in service, and have therefore been chosen for the investigation presented here.

1.1 General mechanisms of copper tolerance

The diagram in Fig. 1 illustrates the main mechanisms of copper immobilization that may operate in a fungal cell. Copper ions may be immobilized by extracellular mechanisms such as: reaction with metabolites that leads to insoluble or non-toxic copper complexes, it may be sequestered in the mucilage envelope (M) or in the cell wall (CW). The most selective barrier that has to be passed by the copper ions is the plasmalemma (P1). Once the ions have entered the cytoplasm, two effects are possible. Firstly, metabolic responses may be triggered off, that leads to changes in the metabolism to overcome the toxic effects — these mechanisms will not be further discussed. Secondly, copper that has been taken up can be immobilized by deposition. This implies that the toxic copper is converted into a non-toxic copper compound. Such compounds may be: copper-protein complexes, copper sulphide or copper polyphosphate.

The studies carried out investigate the mechanisms of copper tolerance in *Poria* and *Phialophora* species with an emphasis on extracellular mechanisms and intracellular deposition.

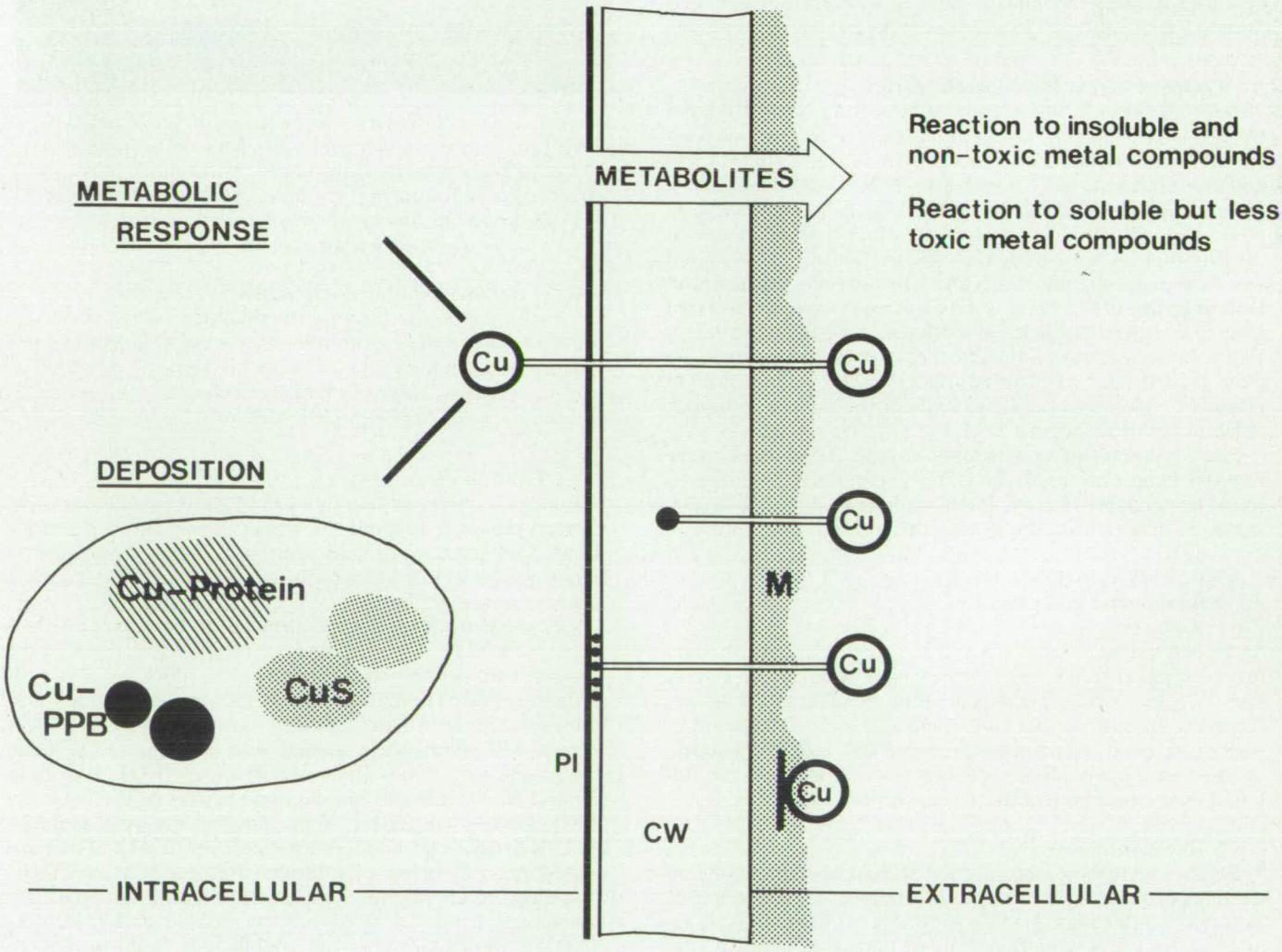


Fig. 1. Possible sites of copper immobilisation on the fungal cell. CW = cell wall, Pl = plasmalemma, M = mucilage.

1.2 Copper tolerant Poria species

Brown rot fungi are generally more copper tolerant than white rot causing fungi (Da Costa and Kerruish, 1964). Among the brown rot fungi, *Poria* species tolerate higher concentrations of copper than other basidiomycetes. Bavendamm (1949) found toxic values in pine sapwood, impregnated with copper sulphate of 3.24–4.1 kgm^{-3} for *Coniophora puteana* (Schum.) Karst and 0.38–0.8 kgm^{-3} for *Gloeophyllum abietinum* (Bull.) Karst., but of 25-30 kgm^{-3} for *Fibroporia (Poria) vaillantii* (D.C.) Cke., which is the most copper tolerant *Poria* species isolated from copper treated wood.

Investigations on *Poria* species have been carried out in the past by Rabanus (1939), Levi (1969) and Chou (1971). Rabanus (1939) suggested that copper tolerance in *Poria incrassata* (Berk. & Curtis) Burt. and *P. vaporaria* was brought about by conversion of soluble copper sulphate into insoluble and hence non-toxic copper oxalate. Levi (1969) and Chou (1971) showed a similar mechanism taking place in *P. monticola* Murr. (synon. *P. placenta*) but not in *F. vaillantii*. Instead, Levi (1969) detected microcrystalline deposits around the hyphae of *F. vaillantii*, which he assumed to be of copper sulphide. Chou (1971) obtained similar results, but additionally found granules consisting of sulphur, phosphorus and copper, in the vacuoles and also distributed in the cytoplasm of *F. vaillantii*. However, when the fungus was grown on wood, instead of agar or liquid culture, neither copper oxalate nor copper sulphide crystals or granules could be detected. Chou (1971) therefore concluded that the metabolism in wood may be different from that in an artificial medium, or that copper may be present in a form that prevents precipitation as copper oxalate or sulphide.

1.3 Copper tolerant Phialophora species

Among the soft rot fungi that have been isolated from copper treated wood, *Phialophora* species appear to be more successful than others (Gersonde and Kerner-Gang, 1976; Nilsson and Henningsson, 1977; Leightley, 1978, 1980).*Phialophora malorum* (Kidd & Beaumont) McColloch and *Phialophora mutabilis* (v. Beyma) Schol-Schwarz, which have been used in the experiments presented, were isolated from C.C.A.-treated wood in ground contact by Dr. Th. Nilsson (Nilsson and Henningsson, 1977). *Ph. mutabilis* was also frequently isolated from C.C.A.-treated poles in service in Australia (Leightley, 1980). Investigations on the effect of copper on *Ph. mutabilis* were carried out by Leightley (1980, 1981), but have not yet provided conclusive results to explain the copper tolerance exhibited by this fungus.

The copper sensitive *Phialophora* type A, B and C were isolated from untreated, Tn.B.T.O. and P.C.P. treated L-joints respectively (Carey, 1980), and made available by Dr. Janice K. Carey from the Princes Risborough Laboratory.

2. Observations on Poria Species

2.1 Experimental procedures

2.1.1 *Cultures*

Stock cultures of *P. placenta* and *F. vaillantii* were grown on malt agar plates containing 1.75 per cent powdered malt extract and 1.75 per cent agar in one litre demineralized water. Experiments with copper containing agar were carried out in malt agar, as described above. Copper was added as a sterile solution of copper sulphate pentahydrate in water to the still liquid agar, the temperature not exceeding 50°C.

2.1.2 *Wood specimens*

Transverse sections of pine sapwood of 2mm × 40mm × 40mm were impregnated with aqueous solutions of copper sulphate or copper naphthenate in white spirit. The sections were placed onto 14 day old mycelial mats of the fungus on oatmeal agar plates and incubated at 26°C for 3 to 8 weeks, depending on fungus and treatment (Fig.2). Alternatively, a series of sections were placed in a row on two glass rods, fixed to the bottom of a square petri dish (Fig.3). The untreated section was then inoculated with a small piece of mycelium and the fungus allowed to grow towards the sections treated with 7, 14 and 27 kgm^{-3} copper sulphate pentahydrate (Sutter *et al.*, 1983).

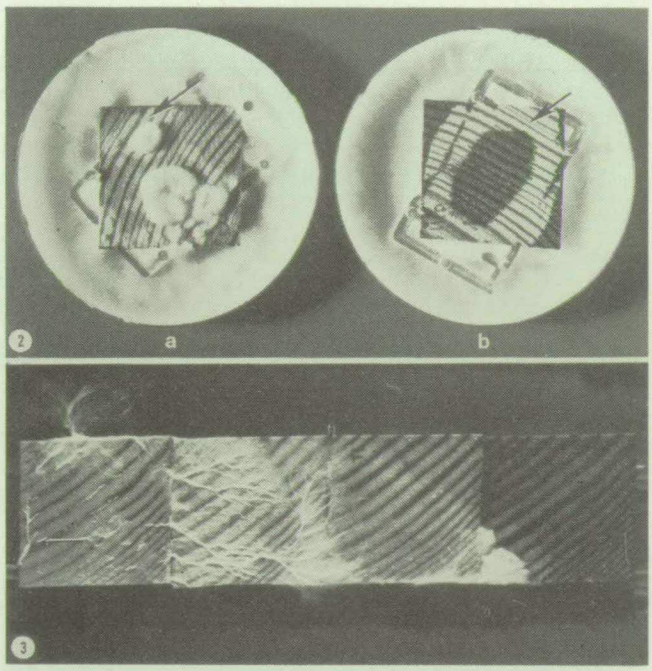


Fig. 2. Pine sapwood section treated with (a) 11 and (b) 42 kgm^{-3} copper naphthenate after 4 days incubation with Poria placenta *(a) and* Fibroporia vaillantii *(b). Note the decolouration around the mycelium (arrowed in a) and where the mycelium touches the wood without penetration (arrowed in b).*

Fig. 3. Series of pine sapwood sections of increasing copper content exposed to Fibroporia vaillantii. *The inoculum (arrowed) was placed on the untreated wood sections and was allowed to grow towards the sections containing 7, 14 and 27 kgm^{-3} copper sulphate pentahydrate. Note the decoloured areas.*

2.1.3 *Electron microscopy*

Scanning electron microscopy (S.E.M.) was carried out using osmium tetroxide (vapour) as a fixative and the material air dried. Specimens were gold sputtered (300 A) immediately before examination in a Philips S.E.M. 505 operated at 25–50kV and a spot size of 50nm.

Specimens for transmission electron microscopy (T.E.M.) were fixed in an aldehyde fixative (Karnovsky, 1965), post fixed in osmium tetroxide solution and block stained with uranyl acetate. Thereafter specimens were dehydrated and embedded in Spurr's low viscosity resin (Spurr, 1969). Thin sections (60–90nm) were stained with lead citrate (Venable and Coggeshall, 1965) and examined in a JEOL 100S or a Philips EM 300 transmission electron microscope (Sutter *et al.*, 1984). Energy dispersive X-ray analysis of bulk material (E.D.X.) was carried out on non-fixed, air dried and carbon-coated material, using a Cambridge Stereoscan Mark 2 scanning electron microscope with an EDAX-International Ltd. attachment. Energy dispersive X-ray analysis of thin sections (E.D.X.) was employed on material fixed in aldehyde fixative and block stained with uranyl acetate (Sutter *et al.*, 1984). After dehydration specimens were embedded in Spurr's low

viscosity resin. Sections of 200-250nm were cut and analysed in a JEOL Stereoscan 100CS electron microscope fitted with a Si(Li) detector (Link System 860), operated at 100kV and an estimated spot size of $10nm^2$.

2.2 Results and Discussion

2.2.1 *Agar plate experiments*

Preliminary experiments were carried out using malt agar plates containing copper sulphate. Plates were inoculated by placing a mycelial disk of 8 mm in its centre and incubated at 26°C for 14 (7) days.

P. placenta grew well on agar plates containing up to 2000ppm copper sulphate pentahydrate, but not at higher copper concentrations, even after one month incubation. Almost immediately after inoculation of the copper containing plates, a halo of precipitated small crystals appeared in the agar around the inoculum disk. Its diameter increased with time, indicating a steady diffusion of reactive metabolites into the agar. Inoculum disks removed from plates containing 4000ppm copper sulphate did not grow after this time on transfer to copper free agar.

F. vaillantii grew well on agar containing 2000ppm copper sulphate and also in the presence of 8000ppm, although growth was greatly reduced. Precipitation of crystals was only observed after the fungus had started to grow. However, after a longer incubation time (up to one month), *F. vaillantii* developed normal growth on all plates and precipitation of copper oxalate occurred.

In order to examine the influence of soluble metabolites (e.g. oxalic acid or water soluble oxalates) on the copper tolerance of *Poria* species, the experiment was repeated, but using inoculum disks, that had been washed in Ringer's solution prior to use. Some of the disks were additionaly soaked in solutions of organic acids and hydrochloric acid. The result of this experiment is summarised in Table 1. The experiment clearly demonstrated the protective effect of oxalic acid. Removal of the acidic shield resulted in a greater susceptibility of *P. placenta* to copper. *F. vaillantii*, however, was less affected by the removal of the acid. Growth of *P. placenta* was completely inhibited, even after transfer to copper free agar, *F. vaillantii* grew normally after a prolonged lag phase.

This greater copper tolerance in *F. vaillantii* may be the result of incomplete removal of oxalic acid (held back in hyphal strands), or of an intracellular detoxification mechanism for copper ions that have reached the cytoplasm.

2.2.2 *Experiments on wood sections*

Fungal material examined was taken from pine sapwood sections exposed to a fully grown mycelial mat (Fig.2) or inoculated with a small piece of mycelium (Fig.3). Both experiments yielded comparable results. This experiment proved that the mechanism of copper immobilisation by *Poria* species is independent of the size of the inoculum or the inoculum to wood ratio.

Observations on treated wood sections at various stages of fungal colonisation in both experiments suggest that decolouration and precipitation of copper oxalate crystals preceded colonisation of the wood. Decolouration of the green copper colour occurred as soon as the hyphae had reached the wood surface or penetrated it (*P. placenta*), or the wood surface was wetted by the mycelila exudate (*F. vaillantii*). This was particularly well demonstrated on wood treated with copper naphthenate, because of the intense green colour of this compound (Fig. 2).

P. placenta does not produce large amounts of liquid (exudate, droplets) as is typical for *F. vaillantii*. Therefore, closer contact between the fungus and the copper treated wood is necessary. This may, at higher copper concentration, be a limiting factor for successful colonization. It may, however, delay, but not prevent colonisation of wood treated with high loadings of the preservation.

Immobilisation of copper and colonisation of wood sections, treated with up to 30 kgm^{-3} copper sulphate, by *F. vaillantii* was straightforward (Fig.3). A hyphal strand grew towards the treated section, at its tip exudate accumulated (droplets) which diffused into the wood section. The droplets consisted of approximately 1.8 per cent potassium tetraoxalate solution (approx. 0.1 molar), as determined by infrared spectroscopy (Sutter *et al.*, 1983). Thus, by releasing an oxalate solution into the wood, detoxification of copper takes place and keeps the copper ions away from the growing hyphae. Dense crystals were interspersed with the mycelium of both *P. placenta* and *F. vaillantii* which had grown through the copper sulphate treated sections (and to a lesser extent the copper naphthenate treated wood). X-ray diffraction analysis confirmed that the crystals were of copper oxalate (Sutter *et al.*, 1983).

2.2.3 *Weight and copper loss*

The accumulation of copper oxalate crystals on the mycelium of both *Poria* species suggested that a considerable amount of copper must have been removed from the wood. Copper analysis by atomic absorption spectroscopy (A.A.S.) confirmed that up to 90 per cent of the copper sulphate originally present was removed, independent of the degree of wood decay (Table 2). Copper loss from copper naphthenate treated wood was between 31 and 45 per cent on colonised sections.

TABLE 1
The effect of Pre-treatment of Inoculum Cultures of *Poria* Species on their Copper Tolerance

Pre-treatment	*Poria placenta*			*Fibroporia vaillantii*		
	500ppma[a]	*1000ppm*	*2000ppm*	*500ppm*	*1000ppm*	*2000ppm*
Original (not treated)	98[b]	95	85	97	*	*
Ringer's solution	79	0	0	*	*	*
Hydrochloric acid 0.1M	79	67	0	89	56	0
Citric acid 0.1M	100	93	72	100	83	58
Oxalic acid 0.1M	100	99	87	100	100	95
Succinic acid 0.1M	86	62	0	85	0	0

a) Concentration of copper sulphate pentahydrate in malt agar plates.
b) Per cent growth of cultures on copper containing agar plates, calculated on the base of culture diameters, with the appropriate treated controls on copper-free agar as 100%.
* Growth after 7 days' incubation.

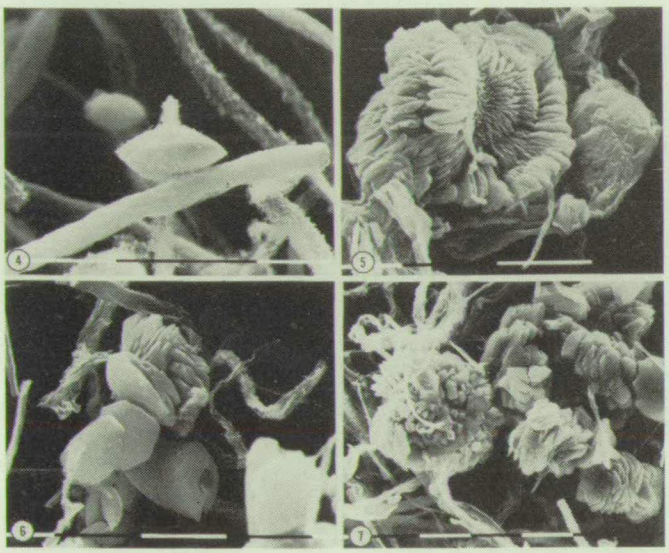
TABLE 2

Copper Content of Copper Sulphate Pentahydrate Treated Pine Sapwood Sections before and after Exposure to *Poria placenta* and *Fibroporia vaillantii*

Fungus	*copper content kgm^{-3}* retention	residual	*copper*[a] *loss %*	*weight*[b] *loss %*
Poria placenta	0.000	0.000	—	29.0
	0.665	0.543	18.3	16.8
	2.400	0.267	88.9	4.2
	4.835	1.018	78.9	5.5
Fibroporia vaillantii	0.000	0.000	—	12.0
	0.643	0.748	16.3	8.7
	3.298	1.286	60.0	3.7
	5.543	1.128	79.7	6.3
	7.475	1.972	73.6	6.7

a) mean ($\bar{x}$) of 3 sections

b) mean ($\bar{x}$) of 4 sections

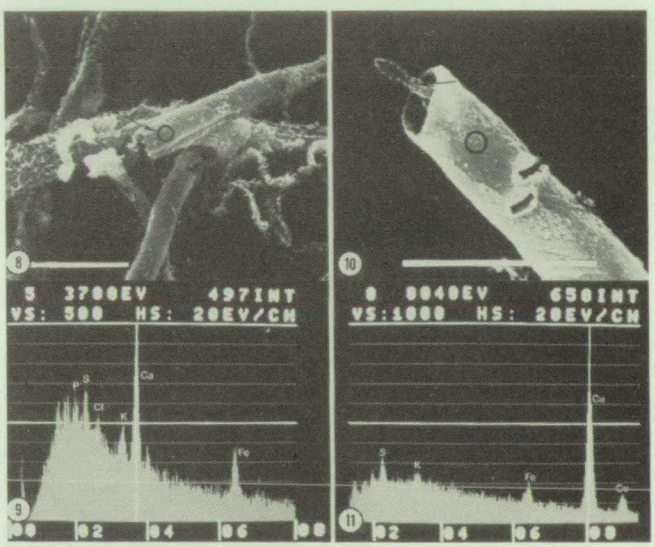


Figs. 4-7. S.E.M. micrographs of copper oxalate crystals found in the mycelium of Poria placenta *(4, 5) and* Fibroporia vaillantii *(6, 7).*
(4) A copper oxalate crystal around a mucilage covered growing hypha and (5) large druses from wood sections treated with 27 and 19 kgm^{-3} copper sulphate pentahydrate respectively. (6) A group of large, hexagonal, flake like crystals and a thick tube of copper oxalate, and (7) large aggregates of crystals in the mycelium of Fibroporia vaillantii *grown on wood sections treated with 25 kgm^{-3} copper sulphate pentahydrate. Scale bars = 10μm.*

2.2.4 *Crystals and crystalline hyphal sheaths*

Information on the fungal response to copper in wood was obtained from scanning electron microscopy combined with energy dispersive X-ray analysis. A large number of crystals, attached to the mucilage envelope on the hyphae of *P. placenta* and *F. vaillantii*, each showing a variety of crystal forms, were found on copper treated wood (Figs. 4–7). These crystals were mainly copper oxalate, but calcium and potassium oxalate were also present, the latter generally found on untreated wood.

Of particular interest are the *crystalline hyphal sheaths* fre-



Figs. 8–9. (8) S.E.M. micrography of a crystalline hyphal sheath (arrowed) on Poria placenta *grown on untreated wood. The area for E.D.X.-analysis is ringed. Scale bar = 10μm.*
(9) E.D.X.-analysis of the sheath showing calcium as the main constituent, but also signals for potassium, sulphur and phosphorus.

Figs. 10–11. (10) S.E.M. micrography of a crystalline hyphal sheath around a single hypha of Poria placenta *grown on a pine sapwood section treated with 2.7 kgm^{-3} copper sulphate pentahydrate. The hypha (arrowed) is surrounded by a tube formed by mucilage and microcrystals of copper oxalate. Scale bar = 10μm.*
(11) E.D.X.-analysis of the area ringed in Fig. 10, showing a main peak for copper at 8 KeV and weak signals for potassium, sulphur and phosphorus.

quently observed on untreated and copper treated wood. Figure 8 shows a S.E.M. micrograph of a hyphal tube (sheath) of *P. placenta* grown on untreated wood for three weeks. E.D.X.-analysis showed a high calcium content in the sheath (Fig.9). Figure 10 shows a S.E.M. micrograph of a hyphal sheath from *P. placenta* grown on a wood section treated with 2.7 kgm^{-3} copper sulphate pentahydrate for three weeks. The hypha (arrowed) shrunk during desiccation, leaving the rigid, crystalline sheath at its natural size. E.D.X.-analysis shows a higher copper content in the sheath material (Fig.11).

Crystalline hyphal sheaths are regularly found in the mycelium of *P. placenta* but only occasionally in *F. vaillantii*. The sheaths consist of mucilage in which microcrystalline inclusions of either calcium or copper oxalate are located, depending on whether the mycelium has grown on untreated or treated wood. Traces of other cations may also be present.

Transmission electron microscopy of crystalline hyphal sheaths from untreated material revealed their laminated structure. Figure 12 shows a T.E.M. micrograph of a section through a sheath of *Pl placenta*. The protoplast, showing the ground cytoplasm with a large vacuole and a golgi-like structure, is surrounded by a faintly stained cell wall (CW) and a strongly electron-dense crystalline sheath. The latter is composed of various layers of membraneous or crystalline material and has been observed in a number of preparations.

Although the role of these sheaths is not fully understood, it is assumed that they provide a barrier to prevent toxic copper ions from penetrating the cell wall. A similar role, however, is generally attributed to the mucilaginous, non-crystalline envelope of the hyphae. From the many examples studied, one can conclude that hyphal sheaths were frequently found on the first colonizing hyphae, and on wood without copper or with low copper contents, i.e. below 5 kgm^{-3}.

The amount of oxalic acid produced by the fungus is not necessarily a measure of copper tolerance, nor is the presence or absence of mucilage. From studies on copper naphthenate treated material (taken from routine DIN-tests) it was found that *Gloeophyllum trabeum* produces oxalic acid and mucilage, but is less copper tolerant than *Coniophora puteana,* which produces oxalic acid and no mucilage. Further, production of oxalic acid is highest in *P. placenta* and comparatively low in *F. vaillantii*, but the latter is by far the most copper tolerant of all the fungi examined. These observations suggest that other mechanisms may operate apart from copper precipitation and the mucilage barrier-effect (mucilage, crystalline hyphal sheaths, hyphal strands).

2.2.5 *Intracellular responses to copper toxicity*

Ultrastructural investigations on hyphal material grown on untreated and copper treated wood showed that the production of electron-dense deposits (bodies) in the vacuoles was the only detectable response of the fungal cell to the presence of copper in the wood (Fig.13).

Electron-dense bodies (E.D.B.) were analysed by E.D.X.-analysis of thin sections. No quantitative estimation fo absolute concentrations was made. Instead, mass fractions were calculated by subtracting the background counts from the peak count and dividing the net counts by the continuum counts per

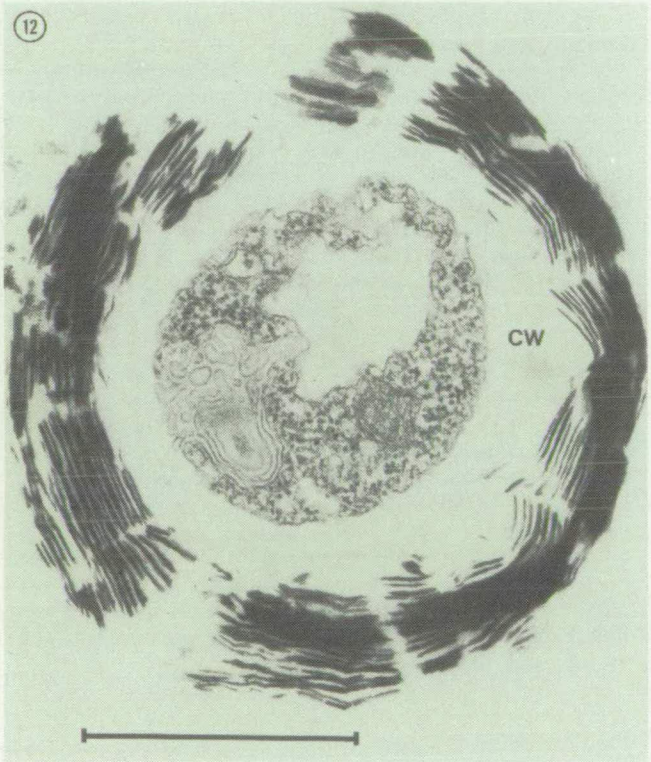


Fig. 12. T.E.M. micrograph of a hyphal tube of Poria placenta *grown on untreated wood. The protoplast shows a large vacuole, a golgi-like vesicle, a mitochondrion and is surrounded by a poorly stained cell wall (CW). Outside the cell wall is a laminated hyphal sheath composed of mucilage and micro-crystals. Scale bar = 1 μm.*

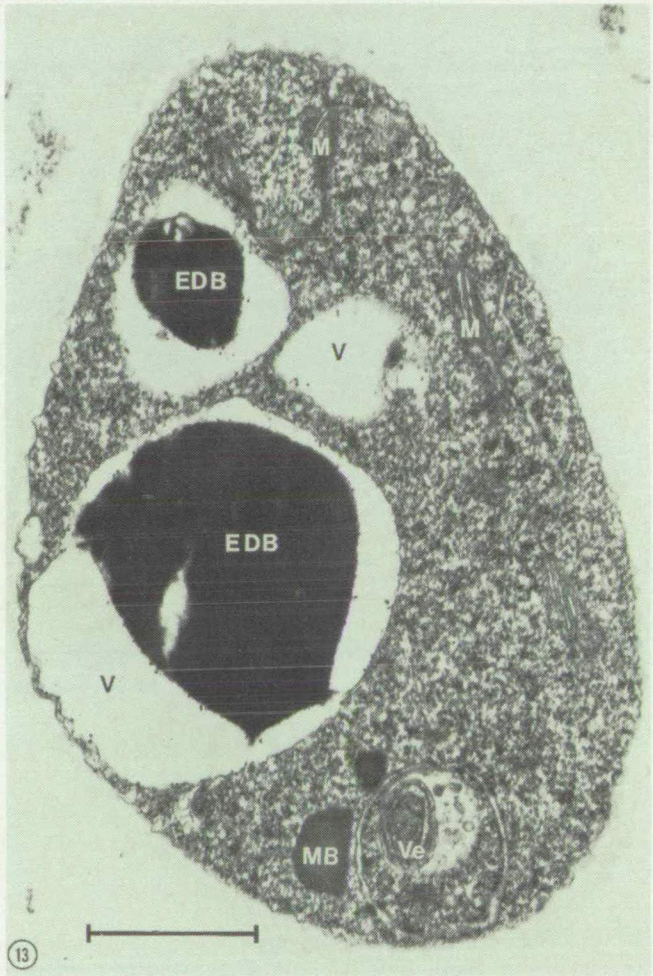


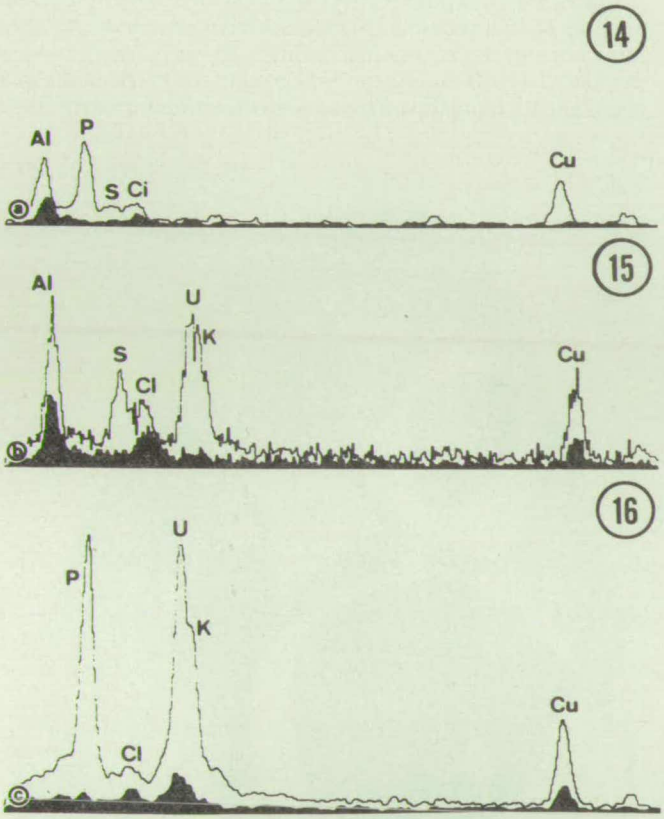
Fig. 13. T.E.M. micrograph of a section through a Poria placenta *cell grown on a wood section treated with 9.5 kgm^{-3} copper sulphate pentahydrate for three weeks. The cytoplasm around the vacuole in which large E.D.B. were located does not seem to be affected by the copper toxicity. Scale bar = 1 μm.*

channel. The mass fractions (M/F) give valuable information on the element ration present in the E.D.B.

2.2.6 *Analysis of electron-dense bodies*

P. placenta grown on copper treated wood produced two types of E.D.B.'s which could only be distinguished by E.D.X.-analysis. In copper naphthenate treated wood, mainly phosphorus-copper bodies were found (Fig.14) while in copper treated wood sulphur-copper bodies were detected (Fig.15). However, there was no correlation between the mass fractions of the elemental pairs.

F. vaillantii cells produced only E.D.B. of the phosphorus-copper type, irrespective of the origin of the material (Fig.16). There was a high correlation between phosphorus and copper M/F. The coefficient of correlation was r = 0.9126, corresponding to a significance at a 0.01 per cent level. These E.D.B. can be regarded as true polyphosphate bodies, widespread among many fungal groups under normal conditions of growth, but not in *Poria* sp. unless exposed to copper.



Figs. 14-15. E.D.X. spectra of electron-dense bodies in copper exposed Poria placenta *cells.*
(14) A phosphorus-copper, and (15) a sulphur-copper type of electron-dense body in Poria placenta.
The black spectra shown are background spectra.
Fig. 16. E.D.X. spectra of an electron-dense body of the phosphorus-copper type in Fibroporia vaillantii.

2.2.7 *Conclusions*

From the experiments presented one can suggest the following mechanism of copper immobilisation operating in *P. placenta* and *F. vaillantii*: both species produce oxalic acid or soluble oxalates, which react with any copper compound to precipitate copper oxalate, which is non-toxic under the conditions found in wood. If the copper concentration is higher than the neutralisation potential fo the oxalic acid, the hyphae may be protected by a layer of mucilage, a sheath or microcrystals and mucilage (*P. placenta*) or by a mucilage covered hyphal strand (*F. vaillantii*). Copper tolerance in *Poria* species is further characterised by the mobility fo the detoxifying agents. Tear drop formation enables *F. vaillantii* to detoxify treated wood prior to colonisation. Copper that has entered the cytoplasm of the fungal cell is immobilised by depositing it as copper-phosphate bodies in the vacuoles (*F. vaillantii*), or other sulphur and/or phosphorus containing electron-dense bodies (*P. placenta*).

3. Observations on Phialophora Species

3.1 Experimental procedures

3.1.1 *Cultures*

Stock cultures were grown on modified Abrams agar (Sutter, 1980), from which spore suspensions and inoculum disks were obtained. Agar plate experiments were carried out on malt agar plates as described for *Poria* experiments. The incubation temperature was 21°C.

3.1.2 *Liquid cultures*

Liquid cultures were prepared in 500 ml shake culture flasks, containing 200 ml of a glucose-peptone medium of the following composition: 20.0 g glucose, 0.5 g peptone (Merck), 1.0 g potassium dihydrogenphosphate, 1.0 g magnesium sulphate heptahydrate, 0.5 g glutamic acid and 1.0 ml of a trace element solution in one litre demineralised water. The pH of the medium was adjusted to 4.5 prior to sterilisation at 121°C for 15 minutes.

3.1.3 *Cell free filtrate — medium*

Cell free filtrates were prepared from 14 day old liquid cultures of *Ph. malorum* and *Ph. mutabilis*. The medium was separated from the mycelium by filtration through a glass fibre filter and then sterilised by membrane filtration. To 50 ml of each filtrate, 25 ml of a sterile four times strength glucose-peptone medium, and 10 ml of an appropriate spore suspension (from Abrams agar plates) were added. The spore concentration was 106/ml after dilution. Similarly, control cultures were prepared, using demineralised water instead of the cell free filtrates. Copper standard solutions were prepared containing 0, 1000, 2000, 4000 and 8000 ppm copper sulphate pentahydrate, of which one millilitre was added to metal capped 20 ml test tubes and sterilised by autoclaving. To each sterile tube, seven millilitres of the medium containing either water or cell free filtrate were added, giving final concentrations of 0, 125, 250, 500 or 1000 ppm copper sulphate pentahydrate.

3.1.4 *Mycelial homogenates*

Homogenates were prepared from 14 day old liquid cultures (3.1.2). The mycelium was washed with a 1.5 per cent glucose solution and re-suspended in a 0.1 molar phosphate buffer of pH 7.0, containing 0.1 per cent ascorbic acid and 0.003 per cent E.D.T.A. The buffer was made oxygen free by bubbling nitrogen through it for at least two hours. The suspensions were homogenised by passing them three times through a French press, operated at 120 $kpcm^{-2}$ (11 Nmm^{-2}) at 4°C. The supernatant was decanted into plastic bottles and quickly frozen in liquid nitrogen and stored at –15°C in a nitrogen atmosphere until further use.

3.1.5 *Determination of sulphydryl groups (SH)*

Determination of Sh-groups in mycelial homogenates was carried out using Elman's reagent (5,5 dithiobis-2-nitrobenzoic acid), following a procedure modified after Bürki (1977).

3.1.6 *Wood specimens*

Miniature wood blocks of 10mm × 10mm × 5mm of birch wood (*Betula* sp.) were machined so that the rays were orien-

tated perpendicular to the 10mm × 10mm in contact with the agar. The blocks were dried, weighed and impregnated with aqueous solutions of copper sulphate. After drying, the blocks were placed onto seven day old cultures on Abrams agar and incubated at 21°C for 10 weeks.

3.2 **Results and Discussion**

3.2.1 *Agar plate experiments*

When *Ph. malorum* and *Ph. mutabilis* were grown in the presence of copper, irrespective of whether solidified or liquid culture media were used, growth was considerably reduced, even at comparatively low copper levels.

On malt agar plates, *Ph. mutabilis* showed a greater copper tolerance than *Ph. malorum*, but both fungi tolerated 6000 ppm copper sulphate pentahydrate in the agar. When grown for ten weeks on malt agar containing 6000 ppm copper sulphate (subcultured every fortnight), no adaptive effect was observed, i.e. no increase in copper tolerance was recorded. No indication for the presence of a precipitation mechanism for copper was detected.

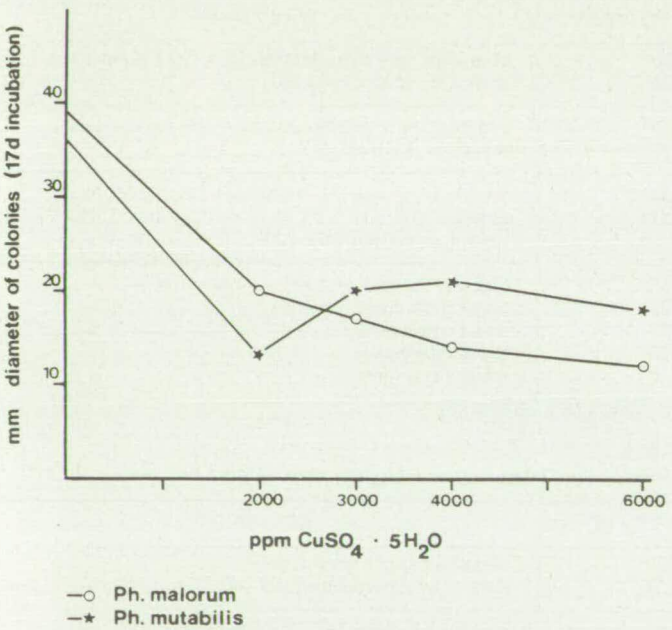


Fig. 18. The effect of copper on the growth of Phialophora *species on malt agar plates with added copper sulphate.*

Of particular interest is the growth pattern of *Ph. mutabilis* in the presence of concentrations below and around 2000 ppm copper sulphate (Fig.18). At these concentrations growth was more inhibited than at higher concentrations. A similar response to copper has been described in the literature for *Penicillum* species and has been explained by the influence of pH, since higher copper tolerance occurred at pH 2.8 (Singh, 1977) or even between 2.0 and 0.3 (Starkey, 1973) but not at higher pH values. The explanation given was that the uptake of copper by the fungal cell was inhibited because of the competitive reaction of the hydrogen ions with the reactive binding sites on the cell wall. Such an influence of the pH cannot entirely be excluded, but pH values in the agar used in our experiments were between 3.8 and 3.3 at 1000 and 6000 ppm copper sulphate respectively.

3.2.2 *Effect of low copper concentrations*

The effect of low copper concentrations (tolerated also by copper sensitive *Phialophora* sp.) on growth, copper uptake and pigmentation was studied in liquid cultures. Three copper sensitive *Phialophora* species (*Phialophora* type A, B and C) and two copper tolerant species (*Ph. malorum* and *Ph. mutabilis*) were grown in the presence of 50 ppm copper sulphate pentahydrate in liquid culture for seven days. Table 3 shows the mycelial dry weights as per cent of control growth (copper free), the copper content of dry mycelium and the percentage uptake from the total copper in the medium (2.54mg Cu = 100%). Changes in hyphal pigmentation were also recorded.

This experiment demonstrated that no significant differences in copper uptake was found between copper sensitive and copper tolerant *Phialophora* species at low copper levels. Growth was reduced in all *Phialophora* species with the exception of *Phialophora* type A, and was most pronounced in *Phialophora* type B and C. It is worthy of note that growth was also reduced in the two copper tolerant *Phialophora* species. Pigmentation was inhibited in *Phialophora* type B and *Ph. mutabilis*.

3.2.3 *Effect of high copper concentrations*

The effect of high copper concentrations on growth and copper uptake of *Ph. malorum* and *Ph. mutabilis* was studied on 14 day old liquid cultures to which 0, 125, 250, 500, 750 and 1000 ppm copper sulphate pentahydrate had been added.

Ph.malorum tolerated only 250ppm copper sulphate in the medium. At 125ppm, growth was almost 90 per cent of the control, spore production reached 50 per cent of control and pigmentation had changed from dark black (control) to grey in copper exposed cells. At 250ppm growth was only 30 per cent of the control and no spores were produced. The mycelium contained hyaline and some dark pigmented hyphae, the latter present as dense pellets. Copper analysis showed that the copper content in the dark pellets was significantly higher than in the hyaline mycelium (Table 4).

Ph. mutabilis tolerated up to 1000ppm copper sulphate pentahydrate under the same conditions (Table 5). Little variation was found between the mycelial yield and the copper content in the replicate samples. Compared with *Ph. malorum*, a higher copper uptake was recorded in *Ph. mutabilis*. Formation of dark pigmented globules were not observed.

Copper uptake by the fungal cells was detected by cytochemical staining with a 0.5 per cent solution of diphenyl carbazone (D.P.C.) in ethanol, which reacts with copper to form a red coloured complex. The material examined was taken from a five day old liquid culture containing 1000pm copper sulphate pentahydrate, inoculated with a spore suspension.

Staining with D.P.C. showed that the majority of the conidia and filamentous hyphae had taken up copper from the medium, chlamydospores and inflated cells seemed to be largely free of copper. In hyphal material exposed to copper, cells of both *Ph. malorum* and *Ph. mutabilis* were found which showed a positive copper reaction, but at the same time, copper free cells developed from them. This phenomenon cannot be explained by a different concentration of copper in the medium, since copper ions were evenly distributed in a liquid shake culture. A possible explanation may be the existence of 'sacrificing or sequestering cells' in which some of the copper is taken up from the environment. Such cells may not only lower the concentration of free copper ions in the medium, but also act a filter through which nutrient, in whatever form, is taken up but copper retained. In a liquid culture, such a mechanism may be less effective than in solid media or in wood.

3.2.4 Extracellular material and copper tolerance

Extracellular material other than oxalic acid or mucilage may also be involved in the immobilization of copper by the fungal cell. Reaction of amino acids with copper often leads to low-toxic complexes (Tröger, 1960; Martin *et al.*, 1942). Complex-

TABLE 3

Effect of Low Copper Concentrations (50ppm $CuSO4.5h_20$) on Growth, Copper Uptake and Hyphal Pigmentation of Copper-sensitive and Copper-tolerant *Phialophora* species in Liquid Culture after Seven Days Incubation

Philalophora sp.	*growth % of control*	*μg Cu/mg dry weight*	*% of total copper*	*change in pigmentation control : copper treated*
type A	115.4	1.8–2.6	55	creamy : dark yellow
type B	47.5	2.7–3.0	67	light olive : creamy
type C	30.4	2.3–2.4	45	no change
Ph. malorum	72.5	2.1–2.3	35	no change
Ph. mutabilis	81.7	1.7–1.8	45	black : grey

TABLE 4

Uptake of Copper by *Phialophora malorum* from a Liquid Culture Medium containing Copper Sulphate after 14 days Incubation at 21°C

ppm $CuSO4.5H_2O$	*mg mycelila dry weight*	*μg Cu/mg dry weight*	*observations*
0	1275 1257	0.16 0.21	abundant spore production (8×10^7) pigmented mycelium (black) pH 6.0
125	1110 1154	2.56 2.17	reduced spore production (4×10^7) grey-black mycelium (a)* pH 5.5
250	595 233	7.34 4.53	1.8×10^7 spores/ml, white mycelium with black globules (b), pH 5.1* no spores produced, fine, light, brown mycelium, pH 4.3
a) * a) a) b) b)		2.35 3.25 1.97 9.90 4.50	black globules black globules white mycelium black globules white mycelium

TABLE 5

Uptake of Copper by *Phialophora mutabilis* from a Liquid Culture Medium containing Copper Sulphate after 14 days Incubation at 21°C

ppm $CuSO4.5H_2O$	*mg mycelila dry weight*	*μg Cu/mg dry weight*	*observations*
0	1261 1112	0.39 0.24	abundant spore production dark brown mycelium, pH 4.0
125	618 570	6.74 9.83	no spore production, dark olive mycelium, pH 4.3
250 500	254 283 128 143	12.68 12.08 12.62 14.97	no spore production, light olive mycelium, pH 4.4 no spore production, light olive mycelium, pH 4.3
750	141 130	17.23 15.42	no spore production, light olive mycelium, pH 4.1
1000	10 18	17.20 12.30	no spore production, whitish-olive mycelium, pH 4.1

TABLE 6

Protein, Sulphydryl (Thiol) and Sulphur Content of *Phialophora* Homogenates

Phialophora species	*mg dry weight in homogenate*	*μg thiol (SH)/mg dry weight*	*μg thiol (SH)/mg protein*	*% sulphur in dry mycelium*
type A	540	0.09	3.3	0.49
type B	886	0.01	1.5	0.42
Ph. malorum	696	0.03	1.9	0.34
Ph. mutabilis	590	0.05	2.2	0.41

ation of copper with melanin was suggested to take place in *Aureobasidium pullulans* (de Bary) Arnaud (Gadd and Griffiths, 1980) and the pigmented hyphae could act as a sink for toxic copper ions. However, such an immobilization mechanism is unlikely to take place in *Phialophora* species because melanin synthesis was greatly inhibited.

An experiment using preincubated (cell free) medium was carried out in order to test for other extracellular metabolites that may contribute to the copper tolerance. From various experiments it was known that no acidic compounds were produced by both *Phialophora* species. Cell free filtrates of *Ph. malorum* and *Ph. mutabilis* contained large quantities of melanin compounds as indicated by the dark colour of the filtrates. However, comparison of cultures containing preincubated (cell free) medium and freshly prepared medium showed no increase in copper tolerance as the result of detoxification by extracellular metabolites.

3.2.5 *Intracellular detoxification mechanisms*

A possible mechanism of heavy metal tolerance is the reaction of the metal ion with sulphydryl compounds in the cytoplasm (Ashworth and Amin, 1964; Ross and Old, 1973; Ross, 1975). A higher sulphydryl compound content in copper tolerant fungi could be an indication for detoxification based on the reaction of copper with the SH-groups. However, when determination of total sulphur, sulphydryl groups and protein was carried out on the closely related copper sensitive *Phialophora* type A and the copper tolerant *Ph. mutabilis* (both belonging to the *Ph. hoffmannii* group), and the two *Ph. malorum* strains (the copper sensitive *Phialophora* type B and *Ph. malorum*), no conclusive results were obtained (Table 6). The highest sulphydryl level was found in the copper sensitive *Phialophora* type A and the copper tolerant *Ph. mutabilis*, with the lowest sulphydryl level in the copper sensitive *Phialophora* type B.

From these data one cannot deduce a direct relationship between sulphydryl content and copper tolerance. However, the determination of SH-groups was made with copper free mycelial homogenate, since the copper ions interfere with the analytical procedure and alternative methods were not available. Thus any metabolic response leading to an increased production of sulphydryl compounds could not be tested.

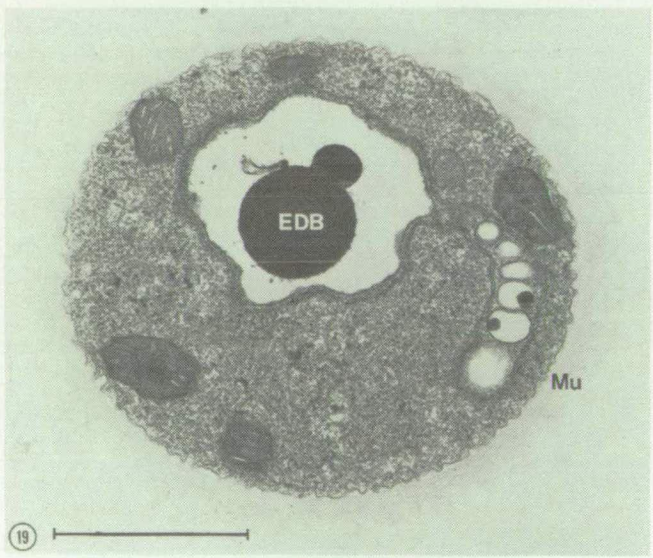


Fig. 19. (1) T.E.M. micrograph of Phialophora mutabilis *grown in a liquid culture containing 200ppm copper sulphate pentahydrate for 18 days. The vacuoles in which the electron-dense bodies are located are surrounded by the membrane system of the endoplasmic reticulum. Scale bar = 1μm.*

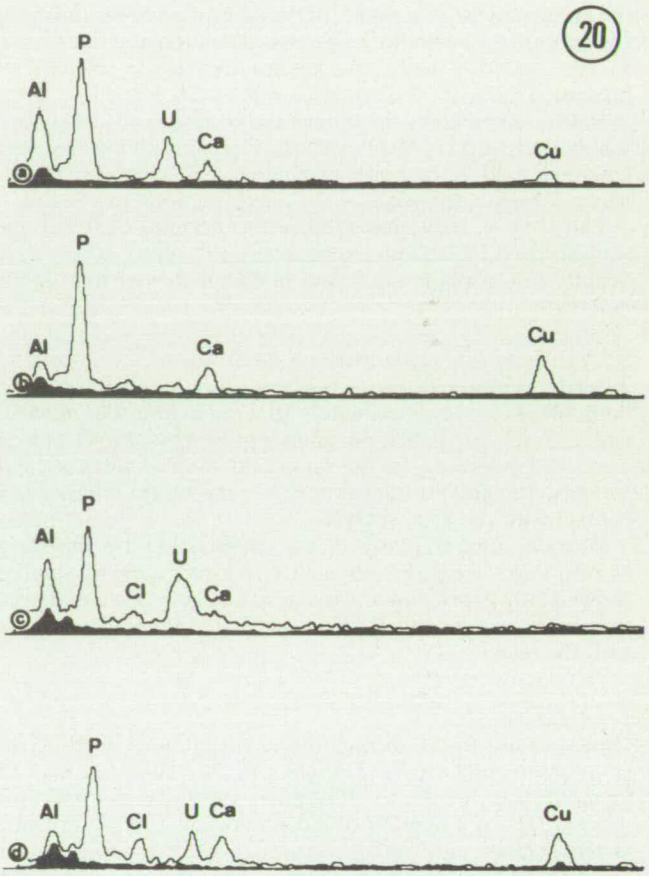


Fig. 20. E.D.X. spectra of electron-dense bodies (E.D.B.) in Phialophora malorum *and* Phialophora mutabilis *grown in copper free (a,c) medium, or in the presence of 200ppm copper sulphate pentahydrate for 18 days.*
(a) E.D.B. in an untreated cell of Ph. malorum, *showing a distinct emission from phosphorus and calcium. The copper peak was not significantly different from the background.*
(b) E.D.B. of a copper treated cell of Phialophora malorum *showing emissions from phosphorus, calcium and copper.*
(c) E.D.B. from an untreated cell of Phialophora mutabilis. *The main element present is phosphorus.*
(d) E.D.B. from a copper exposed cell of Phialophora mutabilis, *containing phosphorus, calcium and copper. The black spectra are background readings, emissions from chlorine derived from the embedding resin, those from uranium from the staining procedure.*

3.2.6 *Analysis of electron dense bodies*

Electron-dense bodies (E.D.B.) were found in *Ph malorum* and *Ph. mutabilis* in untreated and copper treated material (Fig. 19).

E.D.X.-analysis of thin sections from cells grown in liquid culture containing 200ppm copper sulphate pentahydrate showed that the E.D.B. contained phosphorus and calcium (controls) and copper (Fig. 20). E.D.B. produced by *Ph. malorum* exposed to copper showed a good correlation between mass fractions of calcium and phosphorus ($r = 0.9041$, significant at a five per cent level), but not between copper and phosphorus. E.D.B. produced by *Ph. mutabilis* exposed to copper showed a high correlation between mass fractions of copper and phosphorus ($r = 0.9712$, significant at a one per cent level) and of calcium and phosphorus ($r = 0.8210$, significant at a 10 per cent level).

What are the consequences of these analytical data? A significant correlation between the mass fractions of the cation and

the anion may be a measure for the saturation of the polyanion (polyphosphate) with the respective cation (copper or calcium). In *Ph. malorum* cells, this means that more calcium was present. Thus a good correlation was found, while less copper ions were taken up by the fungus and consequently less copper was bound to the polyphosphate. Copper and calcium were equally bound to the polyphosphate in *Ph. mutabilis* cells and hence a high correlation of the mass fractions was found.

The E.D.X. data also confirm the findings of the copper analysis by A.A.S. from copper exposed hyphae, where significantly less copper was found in *Ph. malorum* than in *Ph. mutabilis*.

3.2.7 *Weight loss experiment on birch wood*

After 10 weeks exposure to the fungi, weight loss in untreated birch blocks was approximately 18.4 per cent in *Ph. malorum* and 22.3 per cent in *Ph. mutabilis* exposed blocks. The blocks were well colonised by the fungi and showed soft rot cavity formation mainly in the lower half o the block, which was in contact with the agar surface.

Despite comparatively dense colonisation by the fungi, wood blocks treated with up to 13 kgm^{-3} copper sulphate showed only approximately five per cent weight loss and cavity formation was restricted to the surface in immediate contact with the agar.

3.2.8 *Conclusions*

Observations made during the investigations lead to the assumption that copper tolerance in *Ph. malorum* and *Ph. mutabilis* was not the result of an extracellular detoxification process, but of a number of morphological and physiological factors such as: reduced copper uptake in chlamydospores and 'inflated' yeast-like cells; production of mucilage, melanin and polyphosphate bodies. Unfortunately, most of these features which were associated with copper tolerance, are common to both copper sensitive and copper tolerant *Phialophora* species. There is some evidence for an exclusion mechanism for copper ions operating in *Ph. malorum*, but not in *Ph. mutabilis*, which is more tolerant to copper. Both fungi were able to deposit copper as copper-polyphosphate within the cell.

The ability of *Phialophora* species to survive and to develop (though greatly reduced) in the presence of copper may be primarily the reason for their occurrence in treated wood. Fungal growth, once established, may continue with the reduced growth of the fungus and sequestering of copper. In addition to these environmental factors may also operate in favour of the fungi, such as poor microdistribution of preservatives, simultaneous colonisation of soil and wood by other microorganisms, or chemical interference of soil constituents with the preservative.

4. General Conclusions

The study of copper tolerance in *Poria* and *Phialophora* species has clearly shown that different mechanisms are operating.

Copper tolerance in *Poria* species is primarily brought about by precipitation of copper oxalate. Individual differences in copper tolerance among the *Poria* species are the result of individual features such as : a) amount and chemical composition of mucilage produced, b) amount of free liquid exudated by the mycelium, c) presence of organic acids other than oxalic acid (which may dissolve copper oxalate and increase toxicity), d) the presence of crystalline hyphal sheaths, e) mycelial strand formation, f) permeability of cell wall and plasmalemma, and g) internal detoxification mechanisms (polyphosphates, sulphur compounds).

Unlike *Poria* species, the copper tolerant *Phialophora* species developed only poor growth in the presence of copper, but they were able to survive for a long time. There is no indication of extracellular copper immobilisation by fungal metabolites. Therefore it is assumed that copper tolerance in *Phialophora* species is a combination of morphological, physiological and environmental factors. There is, however, some evidence for the exclusion of copper from *Ph. malorum* cells and this aspect warrants further investigation. Internal deposition of copper-polyphosphate has been proved, but polyphosphate was not produced as a response to copper toxicity as observed in the *Poria* species.

Investigations on the permeability of the cell wall and plasmalemma, as well as metabolic changes in copper sensitive and copper tolerant strains could not be carried out. Such investigations would be very helpful in revealing the precise mechanisms of copper tolerance. They may involve an extended E.X.D.-analysis of selected organelles on a quantitative basis and the qualitative analysis of copper compounds within the cytoplasm using biochemical methods such as gel chromatography and autoradiography.

Although the majority of timber treated with copper-chrome-arsenic is adequately protected, problems with copper tolerant fungi are encountered. A full understanding of copper tolerance in wood decay fungi is essential before timber preservation formulation can be improved. In *Poria* species copper tolerance may be overcome by the incorporation of a divalent ion that reacts preferentially with the secreted oxalic acid, thus freeing copper to control fungal growth. A greater understanding for the reasons and the metabolic pathway of oxalic acid synthesis in *Poria* species might also be rewarding. Such studies will lead not only to a greater scientific understanding of copper tolerance but also to better product formulation.

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We are indebted to Mr. K. Jauch (University of Zürich) for assistance with the E.D.X. analysis, Dr. M. Müller (Federal Institute for Technology, Zürich) for T.E.M. facilities, Dr. S. T. Moss (Portsmouth) for valuable discussion, and to B. Zellweger and the late E. Hawton for photographic assistance.

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DISCUSSION ON PAPER 3

Chairman: Dr. D. S. Belford

THE CHAIRMAN: The paper is now open for discussion. Perhaps I could remind everybody to speak up and give your name and organisation clearly for the Conference record. Could I now have the first question, please.

DR. W. P. K. FINDLAY (Consultant): I noticed when I was testing low concentrations of copper naphthenate where the hyphae were coming over the colour disappeared. Into what was the copper being transformed to become colourless? Some reaction was taking place between the hyphae and the copper and the colour went. What happened to that colour?

DR. H. P. SUTTER: What compound was this?

DR. W. P. K. FINDLAY: Copper naphthenate.

DR. H. P. SUTTER: Copper oxalate crystals, particularly when you are using copper naphthenate are very small, they are minute and they are whitish. When you get larger crystals they turn blue, greenish blue, or light blue.

DR. W. P. K. FINDLAY: So it was copper oxalate.

DR. H. P. SUTTER: Copper oxalate, yes.

DR. A. F. BRAVERY (Princes Risborough Laboratory): It is a very interesting paper, Peter. It has some very interesting micro-graphs which are very thought provoking. There is just one assumption I think you have made. I ought to know better than to ask perhaps, but I think you are suggesting that the mucilage sheath is saturated with oxalic acid in the *Fibroporia vaillantii*. Did you test that or is that an assumption from the mechanism that you are proposing?

DR. H. P. SUTTER: We tested that, but not analysing oxalic acid; we did that with copper oxalate, The problem with that was that I tried it but the mucilage is dense and there is little free liquid in *Poria placenta*. It is awfully difficult to collect the droplets. It was easy in *Fibroporia vaillantii*. That is why I can say it was a 1.8 per cent solution of potassium tetraoxalate because I could collect it and analyse it, but we could not do that with *Poria placenta*. But it has to be because an analysis of the crystals shows that it is copper oxalate.

MR. E. BORSHOLT (Technological Institute Denmark): Can you tell us why these fungi and some others, brown rot fungi, produce oxalic acid.

DR. H. P. SUTTER: Oxalic acid is produced also in white rot fungi but the problem is that in brown rot fungi there is no somatic degradation of the system so it is part of the normal fungal metabolism. In almost all fungi it is like that, oxalic acid is produced but then re-used in the bio-chemical pathway.

PROF. E. B. GARETH JONES: One can, in fact, speculate that the oxalic acid is produced as some form of inhibitor. If you in fact examine soils in forests, then you can pick up oxalic acid or oxalates. It may very well be that the production of oxalates confer some sort of inhibitory mechanism allowing the fungus to grow through the litter and outcompete competitors.

MR. E. BORSHOLT (Technological Institute, Denmark): Could you comment on this, that one of my colleagues, J. Bech-Andersen, thinks that the oxalic acid is produced to break down lignin which is necessary for the fungi to come to the energy in the cellulose.

DR. H. P. SUTTER: Yes, that is true. It has been demonstrated in some fungi, particularly the break down of pectins, the synergistic action between some enzymes and oxalic acids.

DR. C. R. COGGINS (Rentokil Limited): Peter, when I was working on *Serpula lacrymans* one of the phenomena I noticed when looking at growth, particularly in a petri dish situation was that under conditions which restricted the growth of *Serpula lacrymans* often you would find a sprout of mycelium from the growing front which would seemingly produce a mycelium which overcame whatever it was that was slowing down the growth rate. That slide you showed of *Fibroporia* mycelium growing from an untreated, treated through to the highest level of copper sulphate I think it was, seemed to me to be exhibiting that very same phenomena. You had what looked to be a slowing down of growth rate on the first level producing a sprout of mycelium on to the next one, then that we slowed down, producing a sprout on to the next one. I wondered if you had considered that. I think we have not really identified the mechanism of that action but I wondered if you had considered it in this work.

DR. H. P. SUTTER: This is coming from the hyphal strain. There is some similarity between *Serpula lacrymans* and *Fibroporia vaillantii*. I observed that a couple of times. There is a sort of bridging, the growth tip with the exudate accumulated on the tip approaches the treated wood surface. Then the droplet difuses into the wood, detoxifies the copper in that area and then grows over it.

THE CHAIRMAN: You look unsure.

DR. C. R. COGGINS (Rentokil Limited): Only that clearly it is an observation that perhaps needs a bit more investigation.

DR. D. J. DICKINSON: Have you noticed any close response between the copper present and the amount of oxalic acid produced or is it just oxalic acid quite independent of the copper.

DR. H. P. SUTTER: Well, that is difficult to answer. Some work has been done by the Japanese. They quantified the amount of oxalic acid produced. If you have a cation which is capable of capturing the oxalic acid there is obviously a stimulation, but this can be calcium or it can be copper. I did not quantify that.

DR. R. J. MURPHY (Imperial College): As you probably know we also did some work on the production of copper oxalate by wood destroying fungi and wood colonising fungi a couple of years ago. This is in agar media and liquid culture.

We demonstrated the production of copper oxalate crystals by *Penicillium, Verticillium* and *Aspergillus* species, all isolated from preservative treated wood at the I.R.G. field site at Selwood Park and we also went on and used *Poria placenta* as a check and again demonstrated copper oxalate crystal production in liquid media and agar media and analysed the crystals by X-ray defraction. Have you any comments about this line of colonisation of preservative treated wood in the field, any ideas as to whether certain groups of fungi producing oxalate might lower toxicity in treated wood allowing decay to commence. It is very difficult. These mechanisms exist and they can be broken but their effects in terms of the performance of a piece of treated wood is quite difficult to assess.

PROF. E. B. GARETH JONES: I think there is undoubted evidence to show that in the case of *Poria* this detoxification does occur on the wood and as you have demonstrated there is oxalate production in *Penicillium* and so on. One has seen evidence for this in others species. So I would assume that this process does go on on the field and it is one of the processess by which the toxic levels in a piece of wood are reduced enabling perhaps other organisms then to colonise.

MR. D. P. BLOW (Fosroc Limited): Just a very general question really. There are many forms in which copper could be introduced into the timber. I was just wondering if for a given species of fungus which is resistant to copper the same sort of mechanisms would be working no matter what form the copper takes.

DR. H. P. SUTTER: Yes, that is right. It really does not matter in what form the copper is because the mechanism of copper precipitation is simply a matter of the solubility of copper oxalate. You get — I do not know what it is called — an equilibrium of solution.

MR. D. P. BLOW (Fosroc Limited): There is no real potential then for altering it in some way.

DR. H. P. SUTTER: No. The only thing you can do is use a different fungicide which stops these particular fungi from growing, but you cannot do anything about the production of oxalate.

MR. D. P. BLOW: Sort of coming back to the cocktail idea again.

DR. H. P. SUTTER: Right.

THE CHAIRMAN: Cocktails seem to be cropping up with regular monotony in this particular session!

DR. D. G. ANDERSON (Hicksons Timber Limited): Could I just make a general comment that C.C.A. is a cocktail.

THE CHAIRMAN: Yes indeed. I think we might even say it is a fairly powerful cocktail.

DR. D. J. DICKINSON (Imperial College): I think it is a very pertinent point here and it should not go unrecognised that the subject of the mechanisms of copper tolerance is probably one of the most fundamental things we have to solve, with the possibility, dare I say it, we may have to find an alternative for arsenic, and arsenic is there because of these fungi. The more we understand about copper tolerance and how to stop it the better.

THE CHAIRMAN: That really highlights the commercial significance of this work. There is one point I wonder if you would like to comment on. Given the provision of further time and resources what do you see as the next logical step in developing this programme that you have started. What would you like to look at next given the time and resources?

DR. H. P. SUTTER: I should like to look at the *Phialophora* species and the bio-chemical pathways because there seems to be some internal mechanism operating although they are not particularly copper tolerant. It is interesting to know how these fungi manage to survive such high concentrations of copper without falling victim to them and then wait in the wood until the environmental situation has changed and then start growing and causing problems.

PROF. E. B. GARETH JONES: I think it is very interesting data which Peter has generated on the sequestering of cells in *Phialophora*. It is similar to the sort of suggestions that Gadd has presented with quite different species e.g. *Aurebasidium pullulans*. The results are quite compatible with one another, although they have used different techniques to examine this particular problem.

DR. M. HALE (Portsmouth Polytechnic): How do you thik the decay machanisms of fungi relate to the type or mechanisms of tolerance they display, for example, with the brown rot fungi you will probably find a quite high release of copper from the wood to the decay hyphae within the timber. With soft rot fungi, *Phialophora*, they will probably be able to get around without releasing a great deal of toxicant into the wood, and we find that the decay mechanisms which they show on the wood are probably activated when the hyphae get within the S.2 layer of the cell wall. There is evidence to suggest that they do detoxify extracellularly when they are forming decay mechanisms in the cell wall. How do you think the decay mechanisms of the fungi relate to the type of tolerance that they show?

PROF. E. B. GARETH JONES (Portsmouth Polytechnic): I think this is a very complex question you have asked. I think that Peter was not able to demonstrate in the work that he has done extracellular immobilisation by mucilage. I think this is what we are finding in *Phialophora* once it actually gets inside the cell walls. I think that aspect needs further work.

MR. E. BORSHOLT (Technological Institute, Denmark): Have you observed if the *Poria* fungi are able to promote their own environment through oxalic acid. They need to grow, for instance, in potassium carbonate. We know if we have a C.C.A. treated fence post in concrete it will not survive as long as if it is in sand soil loam.

DR. H. P. SUTTER: This is rather an old question which was posed by Rabanus in 1939. This is a purely chemical problem I think; it is the solubility of copper carbonate, for instance. But in answer to your first question, I must state that the *Poria* species go on quite well with the oxalic acid they produce, and there are always quite a lot of cations in the environment to balance. There is a sort of regulation mechanism, because the fungus is not alone in the world; it is always in connection with the environment. So it is more fungal ecology you have to look at than isolated species.

THE CHAIRMAN: Are there any last points?

DR. R. A. EATON (Portsmouth Polytechnic): I was intrigued by the comments on extracellular mucilage in *Phialophora* when they are in wood. I wondered about the polymorphic characteristics you get when you have the organisms in culture. What are the details of the conditions of growth that make you get these different forms of fungus. For instance, I wondered about the cell wall charateristics, the yeast like conditions as against the hyphal conditions. The characteristics of the polymers of the cell wall might have some influence on the extracellular material produced on the culture as against when you find the fungus is growing in wood, when the hyphal conditions exist.

THE CHAIRMAN: Would you speak up, please.

DR. R. A. EATON (Portsmouth Polytechnic): I am just thinking around these ideas. I wondered whether physiological control of the organisms does influence this ability to maintain the copper in the extracellular mucilage layer in wood and it does not in the culture. Probably we do not know enough about the fungus, I suppose.

DR. H. P. SUTTER: I would say so.

PROF. E. B. GARETH JONES: I think the chlamydospores, for example may, in fact, have some mechanism which excludes the copper from getting into the cell because, as Peter has demonstrated, the copper is only sequestered in the hyphae or in the conidia. It does not seem to be taken up by the chlamydospores and yeast like cells and this therefore

suggests that perhaps there is something different in the cell wall. This is in agreement with the work of Dr. Gadd. I think I am right in saying all of these structures are surrounded by mucilage so there is no difference in that sense but there seems to be a distinct difference in their ability to take up copper and sequester it. It may very well be that the chlamydospores, in the sense that they do not sequester copper, may enable growth to take place from those chlamydospores when conditions are right, because chlamydospores are resting stages produced in response to adverse conditions. So I think you have to take a situation where you have a mass of polymorphic material in terms of yeast like cells, conidia, hyphae and so on. Some of them are sequestering copper and therefore detoxifying the areas around them. Other cells do not take up the copper, and it may very well be that those cells that do not take up the copper are the ones that then germinate to carry on growth once the level of copper overall has been decreased. I do not think you can consider the situation in isolation. The whole thing has to be taken together.

Dr. A. F. Bravery: Actually Rod has picked up a point in a slightly different way which interested me. I wondered whether you had tested again to be sure by a different technique that there was not copper there, and that it was the histo-chemical staining agent that was being excluded by perhaps different wall composition or structure. Have you checked with an alternative method to see whether there really is no copper there and therefore eliminated the possibility that it was an inter-action with the staining agent.

Dr. H. P. Sutter: I have looked at this particular point in using the Edax analysis but it was not very conclusive. This might be a point, yes. On the other hand when I checked the uptake of copper by a chemical method, but not looking at the location of the copper in the cell, I found that some of the other forms took up more copper. But again this needs to be further investigated really.

Prof. E. B. Gareth Jones: I think there are details which obviously need further work carried out on them but I think the main thing that has come out of this is that there is no single factor we can put forward to explain the toxicity of the *Phialophora* strain because similar structures, similar processess, are operating in strains which are not tolerant of copper. This is the dilemma which I think we are in.

The Chairman: Well, Ladies and Gentlemen, I have been asked to close this session in order to allow time for a short 10 minute break before the next paper. The next session will start promptly at 3.30. In both reading this paper and listening to the excellent presentation of it I must say that personally, having been involved in some of the first faltering steps of looking at copper in plant cells back in the 1950s, I am absolutely green with envy at the battery of techniques that are available to researchers today. I think what comes through very clearly from this paper is that one sees a very, very skilful use of a wide range of powerful research techniques which have been assembled to attack a very complicated problem in bio-degradation and the authors have come up with some very, very sound conclusions from that work. I certainly found it extremely interesting. I think the content of the paper was certainly matched by the quality of the presentation which has become a feature of this Convention. I should like you all to join with me in thanking both Prof. Gareth Jones and particularly Dr. Sutter for such an excellent presentation. *(Applause).*

WOOD PROTECTION RESEARCH AT IMPERIAL COLLEGE

by J. F. Levy, D. J. Dickinson and R. J. Murphy
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Teaching and research on timber at Imperial College goes back nearly a century to the early years of one of the three institutions which was later to become part of the Imperial College. The Central Institution of the City and Guilds of London Institute was founded in 1884 with four departments, one being the Department of Engineering under Professor W. C. Unwin F.R.S. which gave courses in mechanical and civil engineering. As early as 1894, Unwin is recorded as having undertaken tests on Empire timbers for the neighbouring Imperial Institute which had no test machines of its own (Brown 1984). The strength tests were carried out in Unwin's laboratory on timbers from, amongst others, Ceylon, South Africa, Australia and the West Indies, the results were reported in the Institute's journal and summarised in Unwin's standard text book *'The Testing of Materials of Construction'*. Unwin's original laboratory notebooks 1894–1900 are in the College library.

Unwin was succeeded in 1904 by Professor W. E. Dalby who continued testing materials. In 1907 the City and Guilds College merged with its neighbours, the Royal College of Science and the Royal School of Mines to form the Imperial College. In 1913 the Department of Engineering was divided into two new departments, Mechanical Engineering under Dalby and Civil Engineering to which Professor S. M. Dixon was appointed. Following the interruption of the First World War, Dixon began tests in 1919 which were carried out on timber specimens for a Committee of the Institution of Civil Engineers on the Deterioration of Structures exposed to Sea Action. Brown (1984) records that 'this involved treating them with various chemicals such as arsenic and creosote. The results of this work were presented to the Institution in 1930'. On Dixon's retirement in 1933, A. J. S. Pippard was appointed Professor of Civil Engineering.

Meanwhile research on timber had developed in the other precursors of Imperial College. The College of Chemistry was founded in 1845 and the Government School of Mines and Science applied to the Arts in 1851. Both moved to the South Kensington site in the 1870s' the former to become the Royal College of Science and the latter, the Royal School of Mines. Biology teaching began in the Government School of Mines in 1851 and in 1854 Thomas Henry Huxley was appointed to teach the subject. By 1895 the Biology Department had expanded and was divided into two to form the departments of Botany and Zoology. At that date J. B. Farmer (later Sir John Farmer) was appointed Professor of Botany, which had now become a separate department in the Royal College of Science, and remained head of the department for over thirty years.

Farmer saw Botany as the botanical sciences whose basic understanding would be of inestimable value to the development of agriculture and horticulture on the one hand and the exploitation of natural plant products on the other. It has been said of him that he took Botany out of the herbarium and established it in Britian as a basic science. As part of this development, Percy Groom was appointed lecturer in the Technology of Woods and Fibres in 1908.

Groom was over forty at that time and had already had a varied and interesting career. He had spent time as a postgraduate in the University of Bonn working under the great Professor Strasburgher with A. F. W. Schimper as a fellow student. For three years he had been Professor of Botany at the Imperial University at Whampoa in China. On his return to England he spent five years at Oxford before becoming Professor of Botany at the Royal Engineering College at Coppers Hill where he was charged with the instruction of students destined for the Indian Forestry Service. When that Institution was closed down he had a brief period at the Northern Polytechnic before joining Imperial College, where he was to remain until his retirement and death in 1931. During that period he became first Assistant Professor and finally Professor of the Technology of Woods and Fibres and a Fellow of the Royal Society.

Sir John Farmer in Obituary Notices of Fellows of the Royal Society wrote of Groom in 1932:–

> 'At South Kensington he was able to devote himself wholeheartedly to the work of his choice and soon became recognised as a leading authority on his subject. He published a considerable number of papers in technical journals but he did not neglect the more severely scientific aspect of the range of problems which arise in connection with the structure of timber and its various diseases . . . The breadth of his technological knowledge soon became recognised in commercial and other circles and led to the prosecution of interesting and important investigations, which as a side issue, had the merit of establishing and extending a connection between Botany and some of the important industries which deal with plant products. His work on pit props and the importance of attending to timber sanitation in coal pits may be cited as an example; while yet another, which was concerned with the utilisation of various American oaks in the manufacture of casks by the brewing industry during the Great War, was a model of careful technical work and suggestive of further botanical and biochemical investigation'.

Surprisingly Farmer does not refer to the intensive work Groom did during the First World War in relation to wood for aircraft construction.

The aeroplane was little more than a recent invention in 1914, with body, wings and tailplane consisting of a wooden frame covered by fabric. By the end of the war, thousands, if not hundreds of thousands, of wooden framed aircraft had been designed and built and the multitude of problems of structural design, high strength, low weight, high shock resistance in struts and wing booms, durability and stability had been researched and answers found.

Propeller development from solid wood to laminated structures was carried out at this time, as well as the analysis of wood from captured German aircraft which enabled assessments to be made of the way German aircraft designers were overcoming the increasing shortages of prime quality timber as a result of the naval blockade. All this came under Groom's aegis and he led the search for suitable timbers from all over the world and directed the research and tests carried out at Farnborough at the (now) Royal Aircraft Establishment. His analyses of the results and his reports went to the Ministry of Munitions where they were annotated and minuted by one A. J. S. Pippard, a structural engineer who was later to become Professor of Civil Engineering at Imperial College.

Groom worked on many things; his account of dry rot and means for its prevention and eradication was a standard work in its day. He built up an active research school which included S. E. Wilson, (who worked out the relationship between the

powder post beetle (*Lyctus* sp) and the starch reserves in the sapwood of hardwoods with vessels large enough for the eggs to be laid in their lumina); and W. P. K. Findlay, B. J. Rendle and E. W. J. Phillips.

The value of the work carried out by Groom and by R.A.E. Farnborough on the properties of wood in relation to a specific end use was clearly not restricted to wartime expediency, but likely to be of equal value to both government and industry in peacetime. It formed part of the thinking which led to the recommendation of the Empire Forestry Conference in 1920 that Centres of Research in both Forestry and Forest Products should be established in Britain. Groom was one of the chief architects of the Forest Products Research Laboratory set up at Princes Risborough over sixty years ago within the Department of Scientific and Industrial Research. He produced a number of interesting papers on the requirements, scope and staffing of such a laboratory and there was even a possibility at one time that it might have been formed at Imperial College under his direction. Certainly he had a role to play as an adviser on the botanical side whilst Professor J. W. Munro of the Department of Zoology at Imperial College acted as an adviser to the entomological studies. On its foundation it was staffed by a number of Groom's former research students including M. Oliphant and K. St. G. Cartwright as well as W. P. K. Findlay, B. J. Rendle and E. W. J. Phillips.

Following Groom's death in 1931, his successor Dr. Frank Y. Henderson had to re-establish timber as a subject for teaching and research, since, with the formation of the F.P.R.L. and the move of L. Chalk to Oxford and J. N. Branfoot to be a school master, Groom's research group at Imperial College had become greatly reduced and Groom's chair lapsed. Henderson thus became first Lecturer and later Reader in Timber Technology. Just when the course in timber technology for undergraduate students of Civil Engineering began is uncertain. Certainly Professor Pippard if he did not initiate it was a very strong advocate of its importance. His work with Groom in the First World War had convinced him that Civil Engineers should be made aware of the structure and properties of wood and also its diseases and methods for their prevention. Certainly the course flourished under Henderson and was given to all third year Civil Engineers as part of their engineering materials. In the mid-1940s, Henderson resigned to become Director of the Forest Products Research Laboratory and once again the study of timber in the College was at an interegnum.

On Professor Pippard's insistence that the Department of Botany should give a course on timber and its properties to third year undergraduate Civil Engineers, Professor W. Brown, head of the Botany Department, sought for a replacement for Henderson. J. F. Levy was a demonstrator in the department at that time, (1945), and since Brown, in his own words, 'could not find a person qualified to teach the subject', Levy was offered the chance to learn about the subject over a two-year period and then take over the course. In the meantime, Henderson supplied suitable lecturers from the staff at F.P.R.L. and Levy came under the guidance of Dr. W. P. K. Findlay, who has remained a good friend, teacher and enthusiastic encourager ever since.

Levy taught the Properties of Timber course single handed for nearly fifteen years with the emphasis on wood structure and the prevention of insect and fungal attack. In 1963, Dr. L. G. Booth, a former post-graduate student, re-joined the Civil Engineering Derpartment as a lecturer in Timber Structures and it became possible to include increasing amounts of timber engineering into the course. In 1977 the course title was altered to reflect this change and became Timber Structures and Technology and in 1979 was changed again to Timber Enginering, which still included Levy's course on wood preservation.

In the mid 1960's under the initial sponsorship of the then Ministry of Overseas Development, Booth started a new post-graduate one-year MSc course called Timber Structures and Technology in which Levy collaborated, whilst F. Potter joined the staff of the Civil Engineering Department as a Lecturer in 1965 to help teach this course. In 1974, Dr. D. J. Dickinson was appointed Lecturer in Timber Technology in the Botany Department, partly to help supervise Levy's rapidly increasing research group and partly to assist in teaching the MSc course. In the mid 1970's entry to this course was restricted to graduates in Civil Engineering and the numbers fell. By the early 1980's it was decided that the scope of the course needed broadening so that in 1984 it was revised with a core course in timber technology taught jointly from both civil engineering and botanical aspects (the Botany Department had by now become the Department of Pure and Applied Biology) followed by the options, either timber engineering or wood protection; the course being renamed Timber Technology: Timber Engineering and Wood Protection.

In 1981 Levy had the title of Professor of Wood Science conferred on him and in 1982 Booth was promoted to Reader in Timber Engineering. This year, thanks to the generous support of the Forestry Commission, the Timber Trade and the Wood Preservation Industry a new lectureship has been instituted and Dr. R. J. Murphy has been appointed Lecturer in Timber Technology and Forest Products.

In his inaugural lecture in 1983 Levy stressed the debt these members of staff at Imperial College owed the Directors and staff of the Princes Risborough Laboratory over the years. Their willing help, advice, discussion and ever open door had done so much to sustain and develop the teaching and study of timber at Imperial College. Mr. J. G. Savory of the P.R.L. was appointed a Visiting Lecturer to the College some eight years ago and has continued in this appointment following his retirement from P.R.L. Booth was Chairman of the former P.R.L. Timber Advisory Committee. Long may this happy liaison continue and develop between the two institutions in the years ahead.

In the twenty seven years that have elapsed since 1958, 53 postgraduate students have carried out research in the Timber Technology Group at Imperial College as their project for higher degree.

31 — have been awarded the PhD degree of the University of London.
4 — have been awarded the D.I.C., Diploma of Imperial College.
8 — have completed their research project, but have not yet written it up for submission for a PhD.
6 — are presently actively involved in research projects.
4 — withdrew before completing their research.

In addition, a number of post-doctoral research assistants, have worked with the group and many research workers from overseas universities and research institutions have spent periods varying from three weeks to a year as Academic Visitors. Many overseas students have taken the MSc course since 1965, 10 of whom have carried out six-month research projects on subjects which combine their local needs with the overall direction of the research being undertaken in the Timber Technology Group. Nine have been awarded the MSc degree of the University of London and one the D.I.C. Diploma of the Imperial College.

The development of new lines of research took time. It was not until the mid 1950's that a fortunate combination of circumstances took place to stimulate the initiation of a series of research projects which have expanded and flourished over the last thirty years. Three things happened — (a) Savory published his three classic papers which established his newly observed soft rot as an important economic factor in wood decay; (b) the B.W.P.A., looking for a suitable test site for long-term exposure trials of preservative treated wood, undertook to replace the wooden ladder sides in Tywarnhale Mine, a field

station of Imperial College, with preservative treated ones; (c) Levy undertook a survey of the existing timbers underground in Tywarnhale Mine and found soft rot well established and widespread, but could isolate none of the then known causal organisms.

Levy and Lloyd (1960) gave an account of the fungal survey in Tywarnhale Mine and of experiments involving the release of spores underground and an assessment of the distance travelled by them. An extension of the long-term field trials of wood preservatives was set up by the B.W.P.A. at the main college field station, Silwood Park, near Ascot between 1958 and 1961 when fence posts of a softwood, Scots pine and a hardwood, birch, treated by a variety of wood preservation processes was established on three sites. Levy reported work on both these trials to the B.W.P.A. Convention in 1962, (Levy 1962), since when, over a hundred and fifty articles and papers have been published on various aspects of the research work as it has developed.

The obvious starting point for research following the initial surveys at Tywarnhale and Silwood was to find out more about the fungi colonising wood, their effect on the wood cell walls — 'the micromorphology of decay' — and 'the pecking order', of the organisms involved — 'the microbial ecology of decay'. This began with the brilliant original observations of Nanette Corbett, who showed how soft rot decay was initiated in the cell wall by the penetration of a fine hypha which branched in the middle layer of the secondary wall in a characteristic fashion which she named the 'T-branch'. She was followed in this line of work by Greaves, Stevens, Banerjee, G. W. D. Findlay (who was the first person to use the scanning electron mocroscope — the S.E.M. — to given a three dimensional picture of the anatomical structure of wood and was also the first to cut ultra-thin sections of soft rot fungi and their cavities for examination in the transmission electron microscope — the T.E.M.), Bravery (the first to show the difference in the micromorphology of decay between brown rot and white rot decay as seen in the S.E.M.), Zainal, Sorkhoh, Crossley and Kennmar-Gledhill.

Corbett initiated the study to attempt to unravel the sequence of events involved in the colonisation of wood in ground contact up to the initiation and development of decay. This work was further developed by Greaves, Banerjee, Rossell (who made a special study of bacteria in relation to the increase in permeability in ponded wood and in wood in ground contact), Baines, Dwyer (who applied the concept of subjective and objective observation to fungal decay and enabled a degree of numeration to be introduced into the study of the ecology of the micro-organisms colonising wood), Murphy, Clubbe (who consolidated the concept of grouping the micro-organisms that colonise wood into physiological/ecological groups rather than taxonomic ones), and Morris (who has made observations on the way internal decay is initiated in electricity supply poles in service and the problems to be overcome before biological control can be effective). The microbial ecology of wood out of ground contact was investigated successively by Carey, Mendes and Le Poidevin.

The water relationships of wood and associated studies on wood permeability and treatment, including the important relationship of the effective microdistribution of wood preservatives between cells and within the cell wall layers to effect control of decay has been studied by Banerjee, Baines (who demonstrated the movement of water along the grain by wick action), Banks, Uju, Ofori, Vinden, Amofa, Drysdale, Newton, Caley Montgomery, Woodward, Kennmar-Gledhill and Gray.

Biochemical studies on the cell wall components and on the mechanisms of fungal decay have been undertaken by Fuller, George, Orsler, Lewis, Richard Montgomery and Green. The interaction of wood preservatives and the biochemistry of the wood cell wall on the one hand and the activity of the micro-organisms colonising wood on the other has been studied by G. W. D. Findlay, Bravery, Baines, Clubbe, Sorkhoh, Ofori, Murphy, Gray and Drysdale. Cutler, Carrington and Gasson have worked on anatomical problems, whilst Catling and Woodward have studied panel products.

The work of Levy and his students from the 1950's established a firm basis for the research activities of the group at Imperial College. Since Dickinson joined the group in 1974 he has initiated a substantial increase in the scope and diversity of the research work (which will ensure the safe transition of the group's research efforts on Levy's retirement). The recent appointment of Murphy to assist Dickinson promises to maintain the group's continued evolution in the future and it is hoped by his colleagues that Levy will continue to play an active role in the group's activities long after his official retirement next year.

Today the group stands at the threshold of novel opportunities, when changes in forestry practice which have been developing since the end of the Second World War are likely to impose revolutionary changes to well established concepts of timber resources and supply. These will demand reassessments of existing concepts of durability and the means to induce it satisfactorily by techniques of wood preservation. Natural durability of plantation grown timber, often at short rotation, is unlikely to resemble that of the mature forest trees of a century ago. Its utilisation in various forms of panel products is likely to test the ingenuity of the industry to find treatment methods that, on the one hand give adequate microdistribution of the preservative throughout the treated zone and, on the other, control decay in wood which is subject to wetting under high relative humidity as well as that wetted by liquid water. Clearly both basic and applied research needs to be done to tackle these and other problems.

Work in progress and planned for the near future in the group is concerned in part with these existing problems, but is also intended to take a more fundamental look at some areas where little accurate knowledge is recorded. Current studies in the group can conveniently be considered under the four headings below:–

1. Decay and preservation of wood in service.
2. Preservation techniques.
3. Action and assessment of wood preservatives.
4. Other areas.

1. Decay and Preservation of wood in Service

The main effort in this area is in the performance of joinery components and in the remedial treatment of poles and railway sleepers. The former work is being carried out as a contact with the Princes Risborough Laboratory and represents a continuing interest and collaboration in the performance of joinery. This is being fully reported by the Princes Risborough Laboratory at this meeting. The collaboration and progress in this area has led to the U.K. being increasingly recognised as the leader in this field. At the same time the work has highlighted other problems, particularly with regard to surface performance of treated and untreated wood and the biological and abiotic factors influencing that performance (Mendes 1982). It is intended that further work will be carried out in this area and linked with other studies on joinery preservatives.

Research on poles has been active for six years with Morris, and has been reported previously to this Association (Morris, Dickinson and Levy, 1984). The main objectives of the current work is to develop and test a modified inoculum for the establishment of biological control fungi as a prophylactic remedial treatment for the prevention of decay in inadequately creosoted electricity poles. The parameters affecting the longevity of such a treatment and the process of decay by basidiomycetes are also being investigated. At the same time alternative chem-

ical systems based on borates are being studied. In particular, an overall assessment of the problems facing the electricity boards with regard to wooden poles is being made and several areas for future work have been identified, including: the role of soft rot in pole decay, methods for early decay detection and alternative safer chemical treatments. It is hoped to continue effort in this area and to co-ordinate it with similar work being carried out in Scotland at the Dundee College of Technology.

Morris's research work has now been extended to include a study on the decay and prophylactic treatment of creosoted railway sleepers as part of a major project supported by the Department of Trade and Industry, British Rail and the Preservation Industry. Much of the background microbial ecology studied by Levy's former students and applied by Morris to creosoted poles, has also proved invaluable in understanding the infection and progress of decay in sleepers, as has our understanding of the water relationships of wood, when being rewetted in service.

2. **Preservation Techniques**

Probably the most significant recent development within the group has been the recognition that it is not possible to study biological problems in isolation from the chemistry and technology of preservation. This has necessitated us becoming more involved in these areas whilst still maintaining a primary interest in the biology of the system.

Whilst studying for his PhD at Imperial College, Vinden, from the F.R.I., Rotorua, New Zealand helped to develop further our interests in treatment problems. Vinden's studies were greatly assisted by the Preservation Section at the Princes Risborough Laboratory, the Preservation Industry and the Electricity Council. This work (Vinden 1983) laid the foundation for recent studies on the treatment and performance of European grown spruce by diffusion methods with the appointment of Murphy on an E.E.C. collaborative research award. It is intended that further work and collaboration with at least our European colleagues (T.N.O., Netherlands, Teknologisk Institut, Denmark and B.F.H., Germany) and hopefully more widely, can be undertaken to ensure the proper utilisation of this major British and European resource.

In addition to this work, Khan (supported by the German Pakistan Project) has extended the diffusion studies to the treatment of hardwoods with particular reference to plantation grown *Eucalyptus camaldulensis*. Further work is also in hand to study Burmese timbers and the physical and anatomical factors that affect diffusion in hardwoods.

As well as working on fixed systems, diffusion of borates has been recognised as having an increasing potential in the protected environment and investigations into accelerated diffusion techniques are in hand. The work on diffusion techniques has opened up the whole area of greenwood treatments, an interest strengthened by Murphy's recent studies in New Zealand. A co-operative programme to begin later this year is planned with the V.T.T. in Finland when Nurmi will spend two years at Imperial College working in the treatment of spruce.

As pointed out by Coggins (1982) the major activity in the area of sapstain control has been limited to searching for new chemicals to replace sodium pentachlorophenate. Although Dickinson has been closely involved in this work particularly in association with Professor Henningsson at Uppsala, Sweden, our efforts have been restricted to advisory work rather than basic research. However, we now recognise the need to develop technology alongside the new chemicals and to this end a collaborative programme with Sweden and the W.H.O. Pesticide Application Centre at Silwood Park, Imperial College, is due to start this autumn.

3. **Action of wood preseratives and their assessment**

The problem of C.C.A. performance in hardwoods has been studied at Imperial College for over a decade and has been taken up in many other laboratories. Current work in this area is funded by a co-operative award in which the Preservation Industry are supporting a major grant from the Science and Engineering Research Council. This funding supports Gray, Waite and Rennie. The principal aim of the work is to optimise the preservative action of copper wtihin the wood cell wall, with particular reference to the control of soft rot in hardwoods. The microdistribution of the wood preservative as determined by bioassay and electron probe micro-analytical techniques is being studied together with investigations to determine the relationship between individual cell wall components and the preservative chemicals.

The biological detoxification of organo-tin compounds by wood inhabiting fungi has been one of the most interesting aspects to come out of the co-operative work on joinery. Bravery (1972) was the first to point out the possible involvement of white rot culture filtrates in detoxification but it is only due to the recent developments in lignin degradation that Belford has been able to postulate probable pathways of breakdown. Belford is co-operating with the International Tin Research Institute and the prospects for developing biologically active, stable organo-tins seems very promising.

Work in the area of soft rot testing and assessment of modified preservative systems is dependent on understanding and establishing decay tests in unsterile soil. Mwangi is investigating the factors that effect soft rot testing and these studies are being extended into bacterial systems (Waite) and 'fungal cellar' assessment techniques (Gray).

4. **Other areas**

The major development in wood decay research in recent years has been the realisation that wood decaying organisms offer a unique range of enzymes with potential for biotechnological exploitation. During the last three years Professor Palmer's group in the department of Pure and Applied Biology at Imperial College has made significant advances in the field of lignin degradation and in understanding the role of white-rot fungi. Co-operation between Timber Technology and the Lignin group has been essential and several joint projects are planned, including one with Portsmouth Polytechnic to study the decay of timber by bacteria and possible exploitation of their lignin degrading abilities. The spin off into wood preservation research is already happening with our understanding of free radical degrade of organic preservatives being a direct result of the progress made in our understanding of the process of lignin degradation.

The Timber Technology group is also a member of the Centre for Environmental Technology at Imperial College. This offers scope for collaborative research work on environmental problems and last year a significant joint research project between industry, the Centre and Timber Technology was completed on the 'Effects of Acid Rain in the Leaching of C.C.A. preservatives' (Benazon 1984). It is planned to foster these links and carry out rsearch into other environmental problems facing the industry.

It can be seen that much of the present and future work at Imperial College is dependent on co-operation with other departments and bodies, both at home and abroad. With over 90 years of timber research behind us, Imperial College, with its breadth and depth of expertise, is in a unique position to pursue these links and go forward with the increasingly important fundamental and applied research into wood decay and protection.

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APPENDIX

Titles of theses of students awarded the PhD degree of London University

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PAPER 4

Chairman: The Deputy President (Mr. J. David).

THE CHAIRMAN: I said at the beginning that Prof. Levy had another fifteen months to go. I think, having regard to the work he has presented this afternoon, he had better condition himself to thinking in terms of perhaps another fifteen years. It has been a fascinating account of 40 years experience. He mentioned, I think, twelve counties and he ranged from elementary observations in the field to the innermost recesses of enzyme chemistry and radical chemistry. It has been a most interesting paper and wide ranging paper. It is obvious that Imperial College has not only a great past but a great future. I hope that John will continue to play a part in that. Having overrun his time he cannot answer any questions. My duty is to close the proceedings for this evening and to say that we are to meet again at 9.30 tomorrow. *(Applause).*

STABILITY AND PERFORMANCE OF SOME MODERN FUNGICIDES USED FOR WOOD PRESERVATION

by F. IMSGARD and B. JENSEN *(Gori Research Ltd.)* and H. PLUM and H. LANDSIEDEL *(Schering AG)*

1. INTRODUCTION

The wood preservation industry is today challenged by an increasing demand for more effective and environmentally acceptable preservatives.

These two demands are conflicting by nature, as 'more effective' very often means higher loadings of hazardous chemicals, whereas 'environmentally acceptable' means lower loadings and/or less hazardous chemicals.

Therefore it is by no means an easy task to fulfil both of these claims. Two alternatives for improvements exists:

1. Development of new preservatives with an acceptable efficacy and environmental impact.
2. Enhancement of an already used preservative with a known record of performance.

The first alternative is a very costly and time consuming one. A number of tasks and obstacles have to be overcome, including a costly toxicological documentation.

It is therefore logical to concentrate on the other alternative and seek ways of improving the preservatives using well established fungicides with a proven basic and satisfactory record of efficacy.

The possible improvements which we have investigated are:

1. Enhancing the inherent stability of fungicides.
2. Adding stabilisers to particular wood preservatives.
3. Increasing effectiveness by using mixtures of fungicides.

We have focused on the group of organotin fungicides, which in the form of tributyltin oxide or tributyltin esters has been used extensively during the past 20 years for wood preservation.

Prior to discussing these possibilities we will, however, summarise our knowledge concerning performance and stability for the organotin fungicides.

2. STABILITY AND PERFORMANCE OF TRIBUTYLTIN FUNGICIDES

Despite the fact that several investigations have shown tributyltin compounds to degrade and/or evaporate from treated wood (Henshaw *et al.* 1978, Jermer *et al.* 1983a, Jermer *et al.* 1983b, Barug 1981, Plum and Landsiedel 1980, Beiter and Arsenault 1981), records of failure of double vacuum treated joinery are remarkably scarce (Henshaw *et al.* 1978, Imsgard and Jensen 1981, Jensen and Imsgard 1982, Imsgard *et al.* 1984).

The excellent performance in practice is in our opinion based on the following two properties of treated wood:

Extra high preservative loadings around the joints will both enhance the resistance against water entry through the vulnerable endzone and effectively prevent decay in these parts.

This subject has been brought up at an earlier B.W.P.A. Convention (Jensen and Imsgard 1982) and shall not be discussed further here.

The distribution of the preservative in a treated piece of wood gives rise to a lateral as well as an axial concentration gradient. Results from previous investigations are shown in figure 1. (Jensen and Muller 1979, Imsgard *et al.* 1984).

The gradient is certainly depending on various factors such as treatability of wood, penetration properties of the preservative, and the treatment process used. In pine sapwood treated according to the Nordic Classification System, Class B, we typically find 3–4 times more fungicide in the outermost 2 mm of the lateral faces of wood, compared to the average loading. In the axial direction the first 20 mm from the end grain contains the same relative surplus of preservative.

This pattern of preservative distribution is important. Partly because it leaves an extra good initial barrier against fungal entry, and partly because organotin fungicides obviously are more stable at high loadings.

It is clear, however, that we face two possible routes of depletion of the fungicide. One is through evaporation and the second is through chemical or microbial degradation.

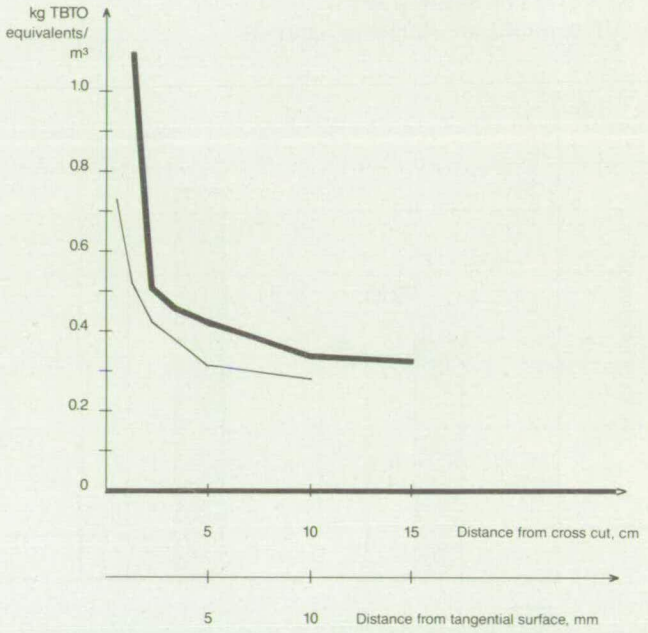

Fig. 1. Axial and lateral distribution of tributyltin naphthenate in double vacuum treated wood. Average retention 0·3–0·4 kg TBTO equivalents pr. m³ sapwood

TABLE 1:
Sn-concentrations in air over treated boards. Surface area: volume = 6:1, air exchange quotes 0.4 times/hour

Formulation	*µg Sn/m³ air*		
	initial value	*after 3 months*	*after 12 months*
3% T.B.T.O.	61.0	17.0	9.4
6% T.B.T.N.	14.0	5.3	3.2
6% T.B.T.L.	15.0	5.8	3.3
3% T.B.T.O. + 12% alkyd resin	28.0	11.3	6.7
6% T.B.T.N. + 12% alkyd resin	8.1	4.8	3.0
6% T.B.T.L. + 12% alkyd resin	9.8	3.8	2.4

2.1 Evaporation from wood

The rate of evaporation of tributyltin compounds from boards treated with different tributyltin formulations are shown in table 1. The figures show clearly that the tributyl tin esters, i.e. the naphthenate and linoleate are considerably less volatile than tributyltin oxide.

Additionally the effect of formulation is demonstrated. Thus the initial value of tin evaporation from a resin-containing preservative is especially depressed.

The rate of evaporation drops relatively fast, and after one year the rate is reduced to 15–35 per cent of the initial value. It is not clear whether this is due to depletion of tin in the surface layer or an increased degree of fixation.

The difference in evaporation rates between tributyltin oxide and tributyltin naphthenate is also found by residual analyses of 4 year old spruce poles.

The results are shown in figure 2.

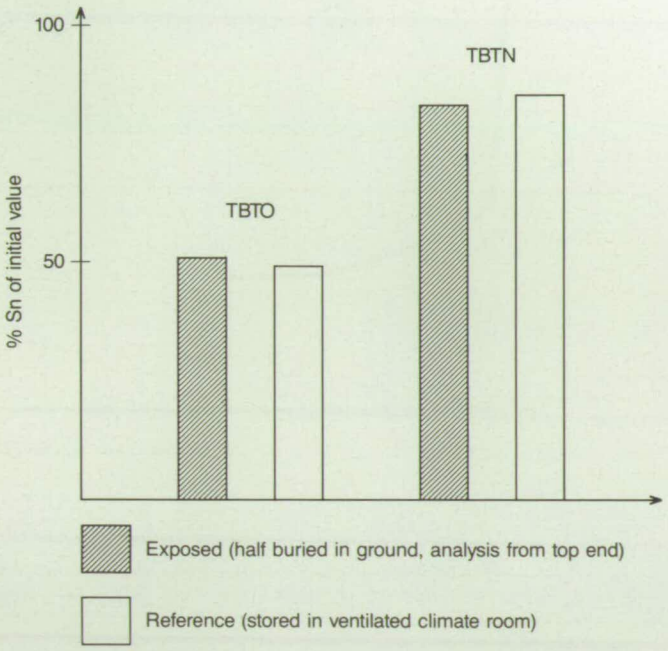

Fig. 2. Residual tin in four-year-old treated spruce poles

Both the reference sample and the exposed sample treated with T.B.T.O. showed considerable loss of tin, whereas the losses in T.B.T.N.-treated poles were less distinct.

The differences in evaporation rates shown in table 1 and figure 2 correspond fairly well. The results indicate that T.B.T.O. evaporates 2–3 times faster than T.B.T.N.

2.2 **Degradation**

As we have already mentioned, the depletion of tributyltin compounds is a combined effect of evaporation and degradation.

Degradation of the tributyltin moiety leads to the formation of di- and monobutyltin compounds. The mechanism of this degradation is not known, nor is the rate of degradation in relation to the rate of evaporation known. These two rates would certainly vary depending upon the prevailing conditions. From a practical point of view the relative rates of different tributyltin compounds are more useful information.

Residual tin-analyses of 4 year old spruce poles impregnated with T.B.T.N. and T.B.T.O. are shown in figure 3. The poles were exposed half buried in soil and reference samples were kept in a conditioned room. The poles were split into an outer and an inner section before the tin analyses were made.

The average retention of the poles was 1.7 kg T.B.T.O./m^3 and 2.7 kg T.B.T.O. equivalents /m^3 (T.B.T.N.). The core retention was approximately one tenth of the outer retention. At low total tin concentrations the degradation is relatively higher than is the case for the high total tin concentration.

In the outer section of the T.B.T.N. treated pole the relative amount of tributyltin is as high as 91 per cent.

The figures for T.B.T.O. are lower, but a higher loss of tributyltin due to evaporation can account for this difference.

At lower concentration, i.e. in the core of the pole, the loss due to evaporation — should be low. The relative tri-content here is however lower for both T.B.T.N. and T.B.T.O.

There are several ways of explaining these differences in stability. The dependence of preservative concentration seems to be a plausible one and is also supported by other investigators (Jermer *et al.* 1983).

The latter investigation has been conducted on 5 year old window joinery in service. The analytical results have been evaluated and are shown in figure 4.

The analytical values are shown as total tin versus the relative amount of tributyltin.

Again the figures indicate that the tributyltin is more stable at higher loadings.

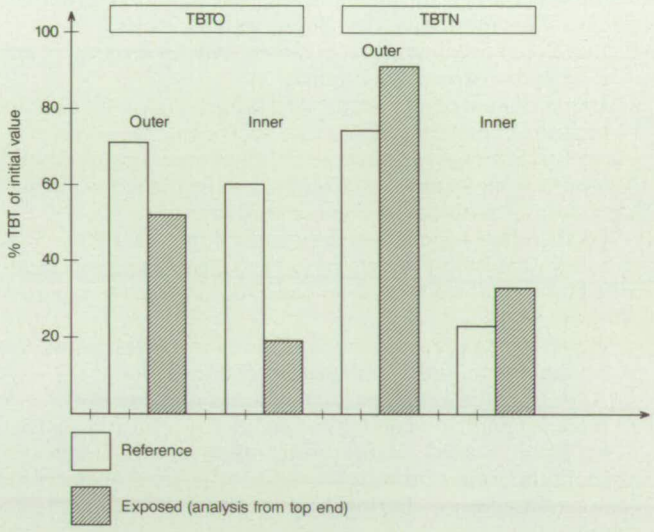

Fig. 3. Relative amount of tributyltin in four-year-old spruce poles

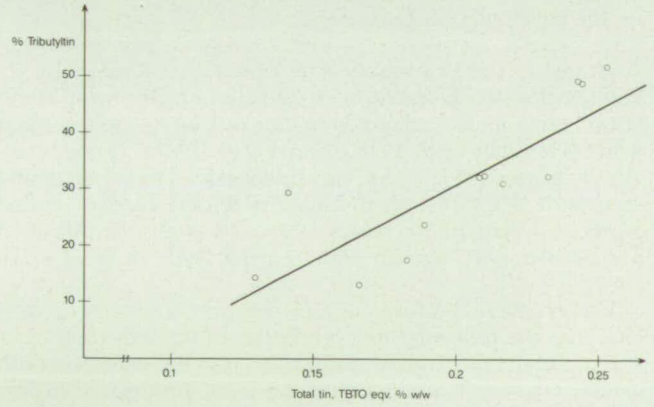

Fig. 4. Relative amount of tributylin versus total tin (calculations based on Jermer et al. 1983)

2.3 **Fungicide effectiveness**

As tributyltin compounds will degrade to di- and monobutyltin compounds it is interesting to investigate the toxicity of these degradation products.

Some data concerning the toxicity of butyltin derivatives have already been reported by Henshaw *et al.* (1978). The toxic values here were established for the butyltin chloride derivatives.

We choose butyltin linoleate derivates as more representative for wood preservation.

The compounds were dissolved in xylene and miniblocks (5 × 10 × 30 mm) of pine sapwood treated with these solutions. After drying of the blocks they were tested against Coniophora

puteana B.A.M. (Eb.) 15, using soil-block methodology. Toxic limit values are shown in table 2 and as can be seen the magnitude of toxicity correlates rather well with the values from Henshaw *et al.* The relative efficacy of the butyltin species is shown in the left column of the table.

TABLE 2:
Toxic limit values of butyltin compounds again Coniophora puteana BAM (Eb) 15.

Compound	*Toxic limit value, kg Sn/m³*	*Relative efficacy*
Tributyltin linoleate	<0.15	1
Dibutyltin linoleate	1.20–1.72	0.1
Monobutyltin linoleate	4.29–10.73	0.02

Henshaw *et al.* further presented decay tests on aged sapwood samples treated with T.B.T.O. These tests showed strong evidence to support the relationship between the tributyltin content and weight loss, but no evidence for a relationship between weight losses and content of either di- or monobutyltin.

Using soil-block methodology with miniblocks, we tested different mixtures of tri- and dibutyltin linoleate in white spirit against Coniophora puteana (figure 5). A synergistic effect of tributyltin and dibutyltin compounds could not be detected.

As a matter of fact our results support the findings by Henshaw *et al.*, as the tests demonstrated a strong relationship between weight loss and the content of tributyltin derivative.

In other tests it was stated that wood impregnated with both tributyltin naphthenate and tributyltin linoleate to some extent lost biological resistance after heat treatment.

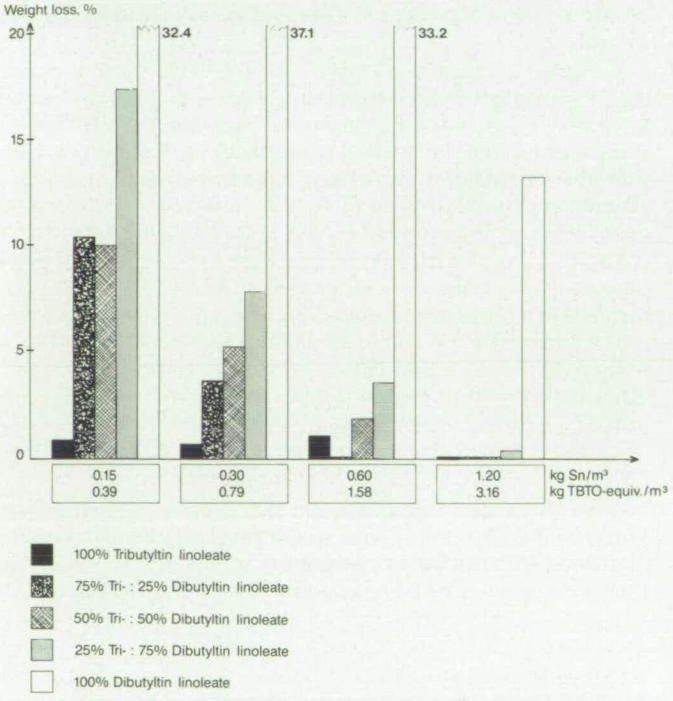

Fig. 5. Effect of tri-, dibutyltin linoleate and various mixtures thereof. Test fungus: Coniophora puteana BAM (Eb) 15.

Some few decay tests were performed with tributyltin linoleate and mixtures of tri- and dibutyltin linoleate. Before incubation half of the blocks were kept in a drying oven at 80°C for one week. Only a high retention was used for this test corresponding to 0.76 kg Sn/m³ (2 kg T.B.T.O./m³). Results are shown in figure 6.

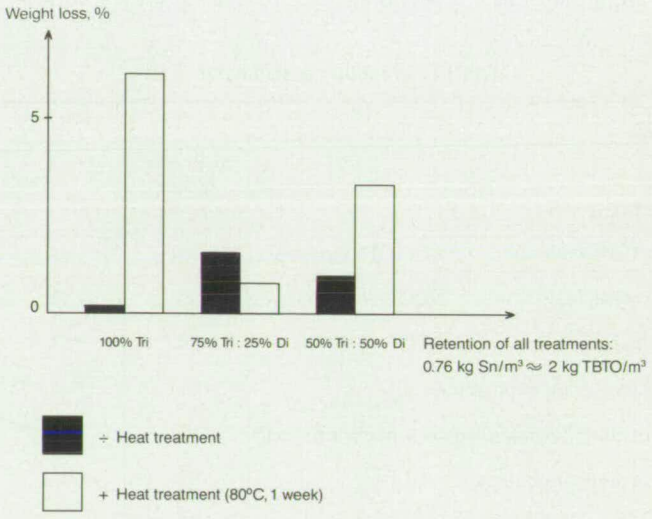

Fig. 6. Effect of various mixtures of tri- and dibutyltin linoleate with and without heat treatment. Test fungus: Coniophora puteana BAM (Eb) 15

As can be seen there is an indication that the content of di- stabilises the effect of tri- at a high retention. The retention corresponds to the retention achieved in the endzones of double vacuum treated Scandinavian joinery.

So far this observation corresponds with the findings from figure 3 and figure 4, indicating that at high loadings formation of dibutyltin may exert a certain stabilisation of the tributyltin compound.

3. Stability of New Tributyltin Compounds

Although the mechanism of degradation of tributyltin compounds from wood is still virtually unknown Orsler and Holland (1984) indicated that formation of free radicals within wood may play a role.

Cellulose as a wooden component does apparently not affect the degradation of tributyltin (Orsler and Holland 1984). The effect of wood extracts on tributyltin oxide in diluted solutions is small and the results ambiguous (Landsiedel and Plum 1985).

In this investigation we have found that carboxylic acids have a detrimental effect on the stability of organotin fungicides.

Wood blocks were treated with solutions of a trimeric fatty acid esterified with T.B.T.O. to different levels, T.B.T.-naphthenate and T.B.T.-linoleate with and without addition of the corresponding acid.

The wood blocks were kept 4 weeks at room temperature and half of the blocks were additionally stored two weeks at 80°C. After storage the blocks were analysed for total tin and tributyltin content. The results are shown in table 3.

The detrimental effect of carboxylic acids is dependent on a certain chain length since acetic acid does not affect stability (Orsler and Holland 1984).

These findings lead to the proposition that reaction products of T.B.T.O. with hydroxyl-containing compounds (i.e. phenols and alcohols) could possibly show an increased stability.

Stability tests of a number of such reaction products were performed in the same way as mentioned above. The results are shown in table 4.

The fully reacted bis-phenol is more stable than the partially reacted bis-phenol. A possible negative influence of acidic hydroxyl groups in phenols is therefore indicated.

However the results clearly show that reaction products of tributyltin and hydroxyl-containing components are more

stable against heat than the above tested tributyltin esters (Schering patent application 1985).

An improvement of the stability of organotin fungicides using these new compounds look promising for the future.

TABLE 3: **Stability of tributyltin esters**

Compound	*% Tributyltin*	
	Reference (room temperature)	*80°C/2 weeks*
Tributyltin-ester of trimeric fatty acid — 3-COOH esterified	99	32
Tributyltin-ester of trimeric fatty acid — 2-COOH esterified	80	17
Tributyltin-ester of trimeric fatty acid — 1-COOH esterified	56	1
Tributyltin naphthenate	91	47
Tributyltin naphthenate + naphthenic acid	81	5
Tributyltin linoleate	98	48
Tributyltin linoleate + linolic acid	85	6

TABLE 4:
Stability of tributyltin ethers

Reaction product between T.B.T.O. and		*% Tributyltin*	
		Reference (room temperature)	*80°C/2 weeks*
Bisphenol A	100% reacted	98	53
(2,2—bis—(4-hydroxyphenyl)-propan)	50% reacted	96	36
L(−)—Ascorbic acid	—	99	68
D(+)—Glucose	—	99	73*
Tricyclodecan—3,8 dihydroxymethyl	100% reacted	98	77
	50% reacted	99	74
Polyester containing OH-groups	100% reacted	89	75*
	50% reacted	98	74

4. Adding Stabilisers to the Wood Preservative

Normal autooxidation is likely to be one route of degradation of tributyltin fungicides. A great variety of stabilizers which act by inhibition of autooxidation is commercially available, and it should be possible to find a suitable compound for the stabilisation of tributyltin fungicides in wood.

Some stabilisers have already been tested, but the results were ambiguous (Orsler and Holland, 1984).

We have tested several stabilisers in a field exposure where treated pine sapwood panels were exposed for 1 year (45° inclination, south).

The panels were impregnated with a commercial formulation including a resin and the different tested organotins +/− stabilisers. Additionally the panels were surface treated with an exterior solvent based wood stain. Corresponding panels were kept in darkness in the laboratory at 20°C. After 1 year the panels were analysed for the amount of total tin and content of tributyltin. The ratio tributyltin: total tin could then be taken as an expression for the stabilising effect of the stabiliser.

A few results are presented in table 5.

At this stage it is not possible to disclose the exact nature of the stabilisers as a patent application has been filed recently.

As can be seen from table 5, the stabilisers gave a different degree of stabilisation, but the best type (stabiliser Z) rendered a true improvement of stability of the used T.B.T.N.

TABLE 5:
Stabilisation of T.B.T.-compounds in wood panels

Fungicide	*Stabiliser*	*Tributyltin/Total tin, %*	
		Exposed 1 year outdoor	*Reference 1 year stored indoor*
Tributyltin naphthenate	(−)	14	17
Tributyltin naphthenate	(x)	38	38
Tributyltin naphthenate	(y)	48	30
Tributyltin naphthenate	(z)	65	60
Tributyltin versatate	(−)	<6	<6
Tributyltin linoleate	(−)	27	29
Tributyltin naphthenate	(−)*)	18	25

Type of stabiliser:
(x) — amine
(y) — metal salt of organic acid
(z) — phenolic
*) Without resin in the preservative

There does not seem to be any difference between the results from the field and from the reference samples stored indoor. This again states that degradation is primarily a matter of interrelationship between the organotin derivative and the wood.

As stated in chapter 2.3 there is strong evidence to support the relationship between tributyltin content and weight loss in laboratory decay tests. Furthermore, exposure to high temperatures (e.g. 80°C) of treated wood blocks will lead to a considerable degradation of tributyltin compounds. Any stabilizing effect of a stabilizer could then be detected by performing decay tests on heat treated blocks before fungal exposure.

Soil-block tests with mini blocks (5 × 10 × 30 mm) of pine sapwood and Coniophora puteana B.A.M. (Eb) 15 were performed with both unstabilised T.B.T.N. and T.B.T.N. stabilised with stabiliser Z (table 5). Half of the blocks were heat-treated 80°C for 1 weeks before fungal exposure, whereas the other half was tested without heat-treatment.

The results are shown in figure 7.

As can be seen the non-stabilised T.B.T.N. is much less effective against decay after heat treatment.

Joinery treated according to the Nordic Classification System, Class B, contain comparable levels of fungicides in the endzones. A basis for increasing the service life of joinery is therefore at hand by using stabilisers in the preservative.

5. Mixture of Fungicides

It is well known that tributyltin compounds at higher concentrations may be skin-irritating. Seen from a hygienic point of view it is recommendable to decrease the concentration of these compounds as much as possible in the formulated wood preservative. Naturally, this is in conflict with the demands for increased efficacy. In order to solve this conflict it is of interest to evaluate the possible use of mixtures between tributyltin fungicides and other less irritating fungicides.

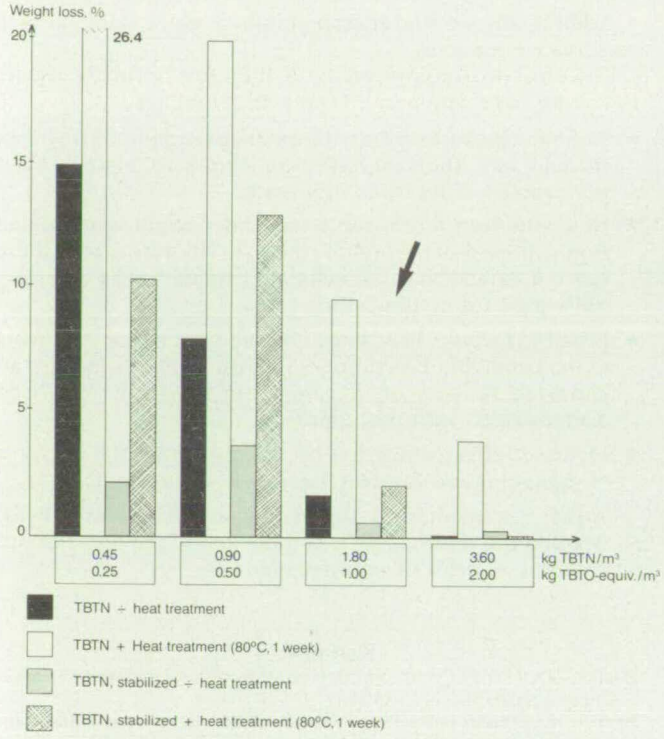

Fig. 7. Effect of heat treatment on stabilized and non-stabilized TBTN. Test fungus: Coniophora puteana BAM (Eb) 15

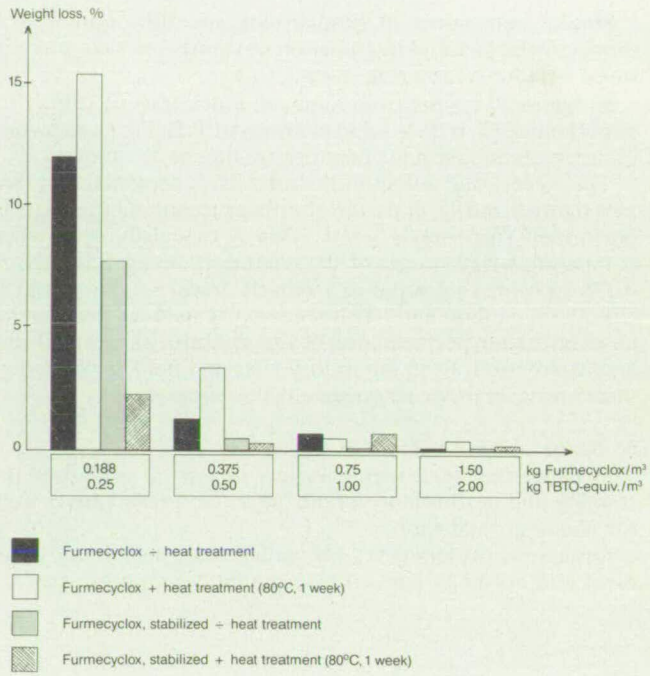

Fig. 8. Effect of heat treatment on stabilized and non-stabilized Furmecyclox. Test fungus: Coniophora puteana BAM (Eb) 15

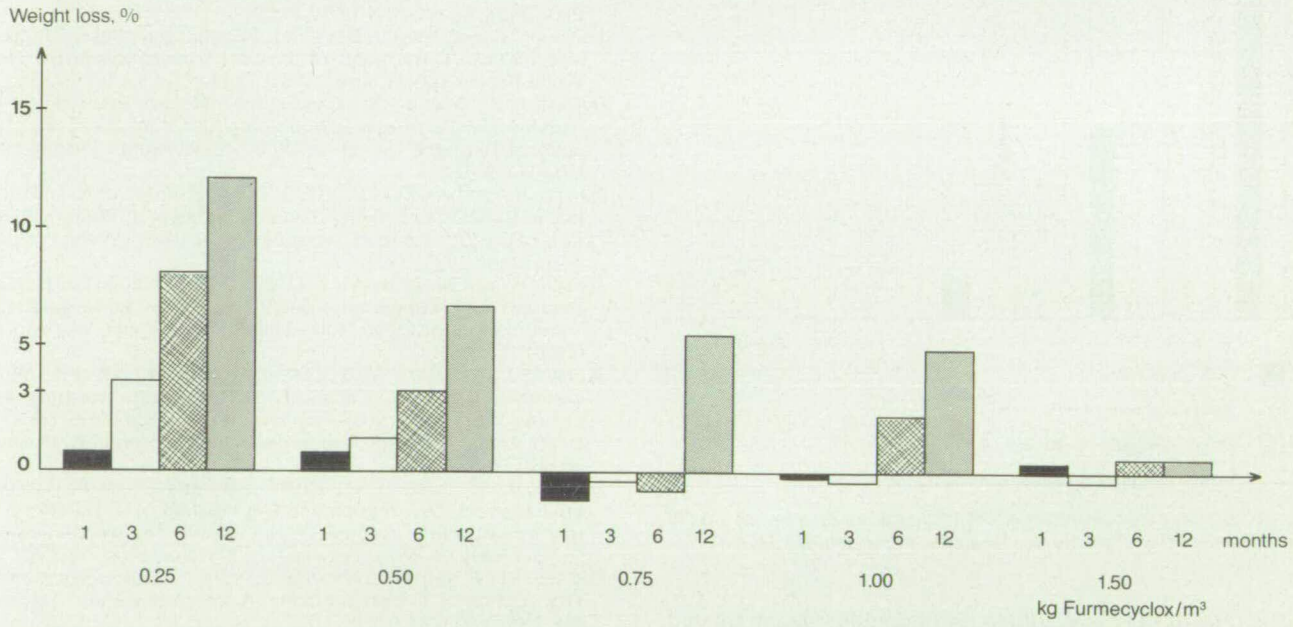

Fig. 9. Decay test of Furmecyclox with different storage periods of the treated blocks before fungal exposure. Test fungus: Coniophora puteana BAM (Eb) 15

An obvious possibility to evaluate this is the mixture of furmecyclox and tributyltin. A German patent application for such mixtures used for wood preservation already exists (Schering 1982). This application is further justified by the finding that the mixture of T.B.T.O. and furmecyclox seems to show a synergistic effect. It is difficult to tell if this is a case of true synergism, but mycological tests performed both by Princess Risborough Laboratory and GORI show similar results, indicating that 1.8 per cent T.B.T.N. could be substituted by a mixture of 0.9 per cent T.B.T.N. + 0.375 per cent furmecyclox showing even better results than the organotin compound (in a joint internal study).

The same type of mini-soil block test as earlier described was performed with furmecyclox. Here again stabiliser Z was added in order to evaluate if the same type of stabilisation could be found as was the case with tributyltin naphthenate.

As can be seen from figure 8, the stabiliser showed a much less pronounced effect than in the case of T.B.T.N. (see figure 7). Obviously furmecyclox is more heat-stable than the organotins, but other tests show that the effectiveness of furmecyclox decrease in dependence of the storage time of the treated blocks before mycological testing (figure 9).

Similar behaviours of furmecyclox and the organotins is shown by the fact that degradation obviously can take place in wood without weathering stress.

In figure 10 results from mini soil-block tests of tributyltin naphthenate (T.B.T.N.) and mixtures of T.B.T.N. and furmecyclox with and without heat-pre-treatment are shown.

The 'synergistic' effect of the mixture is demonstrated (see also figure 8 and 9), and even after heat-treatment the mixture performed surprisingly good. This is especially seen when comparing weight losses of the mixture (0.45 kg T.B.T.N. + 0.188 kg furmecyclox per m^3) with the lower retentions of the tributyltin naphthenate. This tendency is showing promise for an even better performance of the mixture when stabilising agents are used. Both laboratory tests and field tests are now under way, in order to document this suggestion.

6. Conclusions and Final Remarks

This paper has dealt with a variety of aspects regarding the stability and performance of the organotin preservatives used for above-ground timber.

Organotin preservatives are widely used in joinery treatment and normally applied by a double vacuum process.

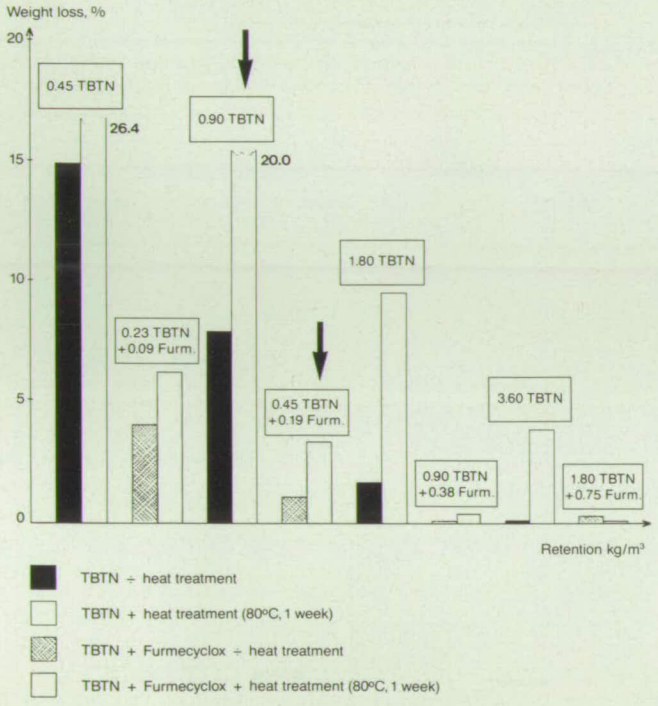

Fig. 10. Effect of heat treatment of TBTN and mixtures between TBTN and Furmecyclox. Test fungus: Coniophora puteana BAM (Eb) 15

The records of failure until today of double vacuum treated joinery in the United Kingdom and Scandinavia are still after 20 years service time extraordinary good.

We have related this to the extra high loadings of preservative around the joints, thus improving the water repellency and securing high loadings of fungicides in these vulnerable parts.

Additionally we find that organotin is more stable at high preservative loadings.

The basis for improvements is therefore virtually sound. Below we have summarised our actual findings.

- ★ In field exposures tributyltin esters exemplified by -naphthenate and -linoleate have been shown to possess better performance than tributyltin oxide.
- ★ New and even more stable fungicides could be expected from synthesis of tributyltin ethers. In laboratory tests these new compounds have shown better stability than commercially used tributyltin esters.
- ★ Promising results have been obtained by adding stabilizers to the tributyltin based preservatives. In field exposure an improved stability of the organotin fungicides has been demonstrated with this approach.
- ★ Increased effectiveness has been demonstrated by mixtures of organotin and furmecyclox in laboratory trials.

Further documentation from field trials and research work on degradation mechanism is still needed to explore the full potential of all possible improvements.

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DISCUSSION ON PAPER 5

Chairman: Dr. F. W. Brooks.

THE CHAIRMAN: Thank you very much for that presentation. I think it is a little unfortunate that the paper was not available to us before yesterday morning because there is a great deal of work presented here and I am sure that we would have all enjoyed an opportunity of studying it in advance. There were not many people, in fact, at the bridge by the Mill reading the paper last night I did notice. However, it was a very clear exposition and I am sure that there will be an interesting discussion arising from it. Could I please again remind everyone who is going to participate in the discussion to speak clearly so that everyone in the hall can hear us, and give your name and your affiliation.

DR. A. F. BRAVERY (Princes Risborough Laboratory): Since we know that the white rot fungi, especially *Coriolus versicolor* tends to be that much more aggressive against T.B.T.O., and I think there is some evidence for furmecyclox which suggests this compound have weaknesses against white rot, have you looked in any of the bioassay work at the performances of the mixtures and the stabilised mixtures with white rot? I think, unless I have missed it, all the evidence was with *Coniophora.*

MR. B. JENSEN: No. Until now the only test fungus which we have used has been *Coniophora puteana.* Naturally it is worthwhile to explore a wider range of different fungi. I agree with you that *Coriolus versicolor* would be a very interesting one to test. On the other hand, there has been extensive testing work going on in the European Wood Preservative Manufactures Group especially studying *Coriolus vericolor* and this has led to the proposition to C.E.N. that this fungus be left out as a test fungus because it is too unstable and gives too widespread results between the different laboratories.

DR. A. F. BRAVERY: (Princes Risborough Laboratory): Could I just come back on that. I know this is true but I think I should make it clear that the combination that is giving great concern is *Coriolus* in Beech and I should have said in my previous remarks to you that the U.K. interest, of course, is in *Coriolus* in Pine, which is relevant to joinery in the U.K. but seems to be less relevant, less important, in other parts of Europe.

MR. B. JENSEN: Yes, that is correct.

DR. D. J. DICKINSON (Imperial College): I should like to come back on that point as well. I think the importance of white rot fungi cannot be over-emphasised and we start to understand the possible mechanisms of the detoxification of tin through a free radical system. It is the white rot organisms which are producing this type of degradation system to a much higher level than the brown rot organisms and of course these organisms are decaying joinery as well.

MR. B. JENSEN: As a matter of fact I agree with you. A lot can be achieved by doing laboratory testing but in the end what counts really are service trials and that is why, for instance, the mixture Furmecyclox and tributyltin naphthenate for the time being is L-joint tested by P.R.L.

DR. R. J. MURPY (Imperial College): I should like to thank the authors for their very clear presentation and I should just like to ask a question of clarification. The 80 degrees centigrade heat treatment that you give, is that intended to simulate an accelerated aging of the chemical in your tests? Is it just a means of accelerating what you would expect a natural aging to do?

DR. F. IMSGARD: Yes, it is a way of accelerating the tests. We find on a qualitative basis the same results by one year exposure times as we can show by this short heat treatment test, but I must say one has to be careful when using this heat treatment and relate that directly to the long term stability.

MR. B. JENSEN: One could also add that with the lack of a very expensive wind tunnel a rather simple treatment of the test blocks is drying over one or two weeks. This will give exactly the same results as, for instance, achieved in a wind tunnel over twelve weeks.

DR. J. W. MORGAN (Princes Risborough Laboratory): I did not have the advantage of many others who went to the Mill of seeing the paper last night and I only piked it up this morning so I cannot really say that I have read it with the thoroughness that I should have done, but it is clear that there is a lot of work here which needs some careful study, with all the analytical background methods considered as well. But one point which I should like clarification on at the moment from the presentation today is the question of how concentration of T.B.T.O. affects the loss because it would seem to me that, in the first place, the loss has been expressed as a percentage and, in fact, the absolute amount loss could possibly be the same in both cases and therefore the more preservative you have the less it appears as a percentage. The second point relating to that is that this is all expressed in terms of tributyltin oxide. Did the authors in fact look at the lower alkylated compounds when examining the loss in relation to concentration?

DR. F. IMSGARD: No, more frequently we have only looked at the tributyltin compound content and related that to the total amount of tin that you can analyse in the sample. If you, for instance, remember the result from this tributyltin naphthenate the evaporative loss is relatively small. This means that the residual amount of tributyltin you find is mainly a result of degradation. The combined effect of evaporative loss and degradation might be more important when you are looking at tributyltin oxide because there the evaporation losses are somewhat higher.

DR. J. W. MORGAN (Princes Risborough Laboratory): Could you answer the first point about the absolute loss?

DR. F. IMSGARD: Yes. for example with the four year exposure of spruce poles, the absolute losses were 50 per cent of the total loading and the total loading was, on average, two kilos tributyltin oxide per cubic metre of wood. So it means you have lost one kilo of preservative per cubic metre of wood within four years. From the one year old exposure trials with pine sapwood the evaporative losses are around 20 per cent for the tributyltin naphthenate. However, I would not dare to make too much of a comparison between the different tests because the conditions are so different. In fact, it is difficult to compare one experiment to another if the conditions are not exactly the same.

MR. J. M. BAKER (Princes Risborough Laboratory): Could I follow up with a question on mechanism of loss. If the loss mechanism is physical and chemical then there are several explanations as to why the loss is less with the higher concentrations, but if it is largely biological components it seems fairly evident that when you have a lot of T.B.T.O. there it is inhibiting the biological activity. When there is little there you get a more rapid breakdown. I wonder if you have compared the effects of the breakdown in the poles which are exposed to biological action with sterile exposure. I wondered perhaps if Dr. Orsler has got any comments on the same subject.

DR. F. IMSGARD: We find approximately the same losses in reference samples. I cannot guarantee that both reference samples were sterile, but they were anyway not exposed in the same way as the samples which were exposed outside. I believe that the reason for this is that there is a chemical explanation for the effect more than an eventual biological one. I think this is because the reference samples do show exactly the same pattern of degradation as in the exposed samples.

MR. B. JENSEN: It seems to be exactly the same in every test that we have been doing. The reference samples were kept, for instance, in a dry room at 20°. They seem to show exactly the

same degradation or somewhat the same degradation as, for instance, the samples which have been exposed in the field.

DR. D. G. ANDERSON (Hicksons Timber Products Limited): You mentioned, I think, in the work you did, looking at the new organotin formulations that phenol was apparently a bad material to have in contact with organotins, yet you are saying that phenolic type stabilisers appear to be the preferred stabilisers. Would you just like to comment on that, please.

DR. F. IMSGARD: You might remember that Orsler also tested a variety of phenols and they gave both positive and negative results. I do not exactly know the nature of the phenols which would improve the stability of tin and the ones which would do the opposite. I would not like to guess what the nature of the phenols would be.

DR. D. G. ANDERSON (Hicksons Timber Products Limited): Is it possible you are looking at a chemical mechanism in the case of the high concentration of phenols. Perhaps you could comment. Is it more an electro-philic attack on the tin rather than a free radical reaction which you are trying to stop. You have a lot of competing possible reactions in which to examine the manifestations in different ways.

DR. F. IMSGARD: What we have really shown is that the long chain carboxylic acids do have a detrimental effect and apparently acetic acid — we have not tested it ourselves but this was also tested by Orsler — does not have any effect. With regard to the long chain carboxylic acids, I do not know whether they can function as initiators. That would be my guess, for the effect that we see.

DR. D. G. ANDERSON: You did not mention the concentration in the case of the carboxylic acid.

DR. F. IMSGARD: The amount of carboxylic acid was the same as the amount of tin weight/weight.

DR. D. G. ANDERSON: So it was a fairly high concentration?

DR. F. IMSGARD: Fairly high, yes.

DR. D. J. DICKINSON (Imperial College): If I could return to the previous point on the relative importance of biological and physio-chemical degradation, I think from our own work the ideas which are beginning to evolve are that obviously the initial stages of degradation are physio-chemical and that we envisage a situation where the T.B.T.O. tolerant organisms, which Janice Carey referred to yesterday, are coming in and having an ability to further degrade the T.B.T.O., and the wood decay organisms, which again have an ability to degrade the tin, are finally coming in. But the important thing is from our own work that we feel the actual chemical mechanism involved in the degradation may be common to all three.

MR. B. JENSEN: Do You want us to comment? (*Laughter*).

MR. J. DAVID (Catomance Limited and Deputy-President): The use of fatty acids in forming esters, particularly pentachlorophenol, has been very long established. I was surprised to see some of the errors which were made early in the formulation of pentachlorophenol esters being repeated. The use of unsaturated fatty acids with a large number of double bonds creates instability in the phenol molecule and I can see very good reason why it creates instability in T.B.T.O. Did you look at unsaturated straight chain simple fatty acids, using those round the C.8, C.10, C.12, C.14, which might be perhaps more stable.

DR. F. IMSGARD: No. We have one example here with an unsaturated fatty acids and in fact the stability of the tributyltin esters of that acid was not better. I would say rather the opposite. This could have been as a result of the extra acid in that ester. We did not check because we did not know that at the time when these exposure trials were started. But it seems to me that linolic acid compares with naphthenic acid and naphthenic acid does not contain a large amount of double bonds but you see the same results of degradation, whereas in linolic acid you have double bonds which could be thought to initiate degradation. Apparently the difference is not very big, but we have not looked specifically at that point.

MR. L. SHEARD (Hicksons Timber Products Limited): In your soil block test there is some evidence to suggest that the phenolic stabiliser may have some fungicidal properties itself which bring about some of the improvements that you observed of higher retention. Is this a possibility which you may have considered?

MR. B. JENSEN: It is a possibility. We have to admit that we have not tested the stabiliser alone and that we should have done this. But we are using this stabiliser in such a low concentration that we do not think that it will have any real influence on the effectiveness of the tributyltin or any effectiveness on its own. As a matter of fact, the mini-soil block test methodology which we use here is a rather sharp one which gives rather high weight losses within a very short time.

DR. J. W. W. MORGAN (Princes Risborough Laboratory): If I may be permitted a second question, it is a very interesting table at the end in which you have looked at alternative ethers as a means of stabilising T.B.T.O. One of the compounds was Glucose which seems a rather unlikely sort of chemical to stabilise T.B.T.O. Nonetheless, it raises the question of whether the Glucose units in the cellulose in wood could be used for stabilising, and in that regard can you say to which hydroxyls in the Glucose the T.B.T.O. is attached. Is it attached to C.1, which is not available in cellulose or is it attached to one of the other hydroxyls which may be.

MR. H. LANDSIEDEL: This reaction we found in T.B.T.O. compound and Glucose was totally. All OH-groups are reacted by T.B.T.O., and Glucose was only chosen for a model substance.

THE CHAIRMAN: I am going to exercise the Chairman's privilege and ask the last question, and change the subject slightly. As You know in the U.K. we only use T.B.T.O. and indeed that is the only organotin molecule which is approved by our Pesticides Safety Precautions Scheme. I understand that at the moment there are some problems in receiving approval for other T.B.T. compounds. Could you please tell us from your European experience what the position is about approval of alternatives to T.B.T. compounds in various countries.

MR. B. JENSEN: It is right that we started at Gori using Tributyltin naphthenate back in 1975 or 1976 and we have been registering these preservatives in European countries. I think that the U.K., might form the one exception from the rest of Europe, and T.B.T.N. is not registered yet. We have tried to register T.B.T.N. with your Health and Safety Executive but it has taken a great deal of time. People have been looking upon the material as a brand new compound which means that we have to supply the sort of toxicological documentation that is needed for a brand new compound. I think that is a little bit out of the question for us, when we are talking about millions of Danish crowns. You can divide that by 14 and you will have the amount in English pounds.

THE CHAIRMAN: With that comment I think that I will bring this discussion to a close with again thanks to the speakers. I thank all the people who have contributed to an interesting discussion. I am quite sure that the discussion of this paper will continue for many, many months to come. I would particularly like to comment that I find it encouraging for the future of wood preservation that research of this calibre is being carried out to improve the molecules which we believe are being successful now. I should like to thank you all for sharing this experience with us. (*Applause*).

CREOSOTE – NEW ASPECTS OF TECHNICAL DEVELOPMENTS AND ENVIRONMENTAL REQUIREMENTS

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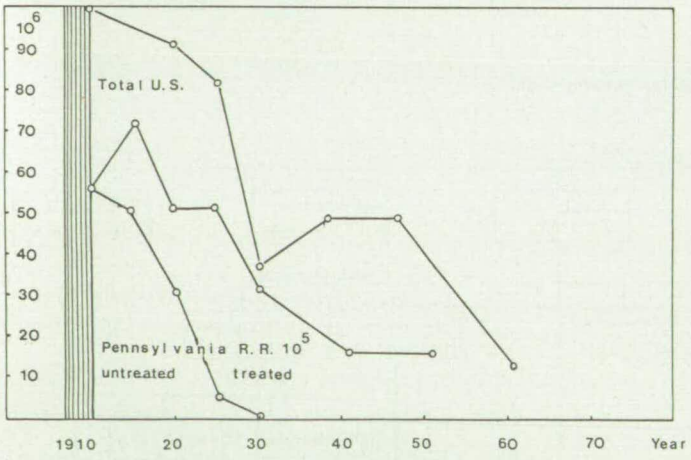
Verkaufsgesellschaft für Teererzeugnisse GmbH, Western Germany

Tar Products of both coal and wood origin have been used as wood preservatives since biblical times (Anon, 1980), but it was only the beginning of railroad services in the last century which established the industrial importance of creosote leading to its systematic scientific and technical development. The pioneering country was the UK where the situation which particularly promoted the development of creosote application was a scarce supply of wood suitable for railroad sleepers and an abundant availability of coal tar from the rapidly emerging coal and steel industry.

Many European countries quickly followed suit so that by the turn of the last century, wood creosoting was a firmly established industry in most of Europe. Among the first entrepreneurs is this field was Julius Rütgers, the founder of Rütgerswerke AG.

A somewhat different development took place in the U.S. regarding sleeper impregnation. Although the first creosoting plant, according to the Bethell process, was introduced in the U.S. in 1875, until well into the 20's untreated hand hewn wood was mainly used for sleepers on the U.S. Rail-lines as can be seen in Table 1.

TABLE 1
Annual sleeper production in the U.S.A.



The beginning of large scale creosoting in the U.S. started around 1910 and became an important industry only in the 20's as can be seen from the enormous number of 100 million raw wood sleepers used annually before the advent of creosoting plants and the dramatic fall of new sleeper installation, thereafter.

Science has played an important role in the still continuing success of creosote. It would far exceed the scope of this presentation to mention the many highlights of the multi-discipline scientific progress in creosote research. One highlight was certainly Mr. Bett's presentation at this convention in 1982, giving a live impression of the wealth of experience accumulated in creosote research by the example of an almost 100-year-old creosoted pole's analysis.

Research has confirmed that practically all major biocidal ingredients in creosote can substitute each other to a wide extent while still maintaining its fungicidal and insecticidal effectiveness, and that they remain chemically unchanged in wood.

This knowledge has led to the setting of physical parameters to formulate requirements of specifications for creosote qualities. As creosote's industrial success began with the development of the vacuum pressure process, its specifications were consequently influenced by further developments of its application processes.

Development of Application Processes

The full cell process invented by Bethell in 1838 laid the basis for its industrial use, but proved to be uneconomical due to excess retention of creosote in European Softwoods. Empty cell processes were consequently developed by Lowry and Rüping and progress of these techniques continues actively today. As an example, the next table (Table 2) shows a diagram of the special process of Rüping/Rütgerswerke, the improved 'Double Rüping' process for beech sleeper impregnation.

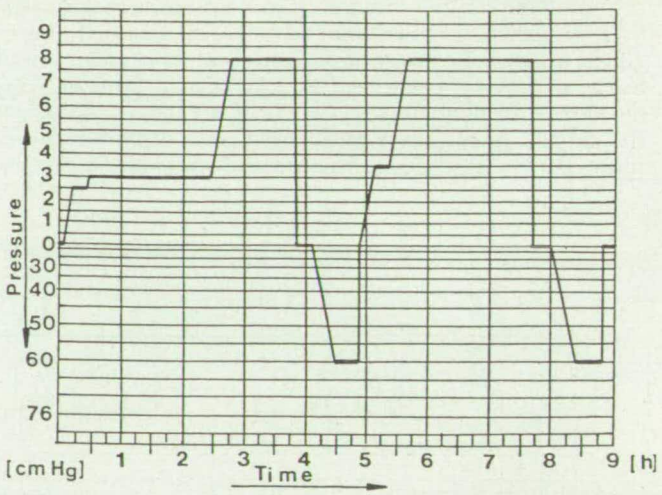


Diagram of improved double Ruping process for beech sleeper impregnation (Table 2)

In a preconditioning stage, hot creosote is pressed into the cylinder against initial air pressure, but the pressure is not immediately increased. Preconditioning of the wood in hot creosote takes place at ca. 100°C. for 1–2 hours. Only then is the pressure increased and the 'Double Rüping' process continued. The improved process provides more uniform distribution of creosote in wood compared to the normal 'Double Rüping'. In 1879, Boulton used a hot creosote 'Vacuum Preconditioning Bath' to reduce the moisture content in timber to prepare them for impregnation. The preconditioning step under pressure in the improved Double Rüping process prevents an uncontrolled penetration of larger quantities of creosote into the wood, which is a disadvantage of the earlier method.

To prevent excess bleeding, e.g. in pine poles, the final vacuum is kept for a longer period than indicated in the diagram, e.g. by keeping it overnight (Broese van Groenou, 1983).

From research of the structure of wood, improvement of vacuum-pressure processes was proposed, for example by a

method called 'Pulsation Process' (Hösli, 1979) with the aim of better impregnation of wood difficult to impregnate, such as heartwood.

Although vacuum-pressure processes are of the greatest significance in modern wood impregnation, other still important processes for creosoting timber are the immersion or 'Hot-Cold' trough impregnation, which is for example used for impregnation of vineyard stakes and fenceposts, furthermore a fair quantity of creosote is also applied by manual processes.

Current Sources for Creosote

Coal tar, more precisely high temperature coke oven tar, is the source for most of today's creosote supply in the world, whereas other sources such as low temperature tars are important in certain regions. Worldwide, there is a total of approximately 16 million metric tons of high temperature coke over tar produced, of which close to 3 million tons is produced in Western Europe.

Coke oven tar is a byproduct generated in approximately 4 per cent by weight based on coke in the coking of bimunious coal, which produces the coke needed for pig iron manufacture (Table 3).

Per ton of pig iron, 0·5 tons of coke are needed. Consequently, 155 million tons of pig iron production in Europe in 1984 require 80 million tons of coke with the generation of the mentioned 3 million tons of coke oven tar.

During the last two decades, crude tar production decreased by approximately 50 per cent in Europe, due to the closing of all gas works and conversion to natural gas for heating, as well as the decline of specific use of coke in blast furnaces. This development has now ended and the situation has stabilized on the current level. There might even be a slight increase in future partly due to coal conversion processes which may come on stream, so that tar production in the world could increase to 20 million tons from the present 16 million tons. Low temperature tars are currently generated in the U.K. as by-products of the production of smokeless fuels at a quantity of roughly

TABLE 3
Coking of bituminous coal

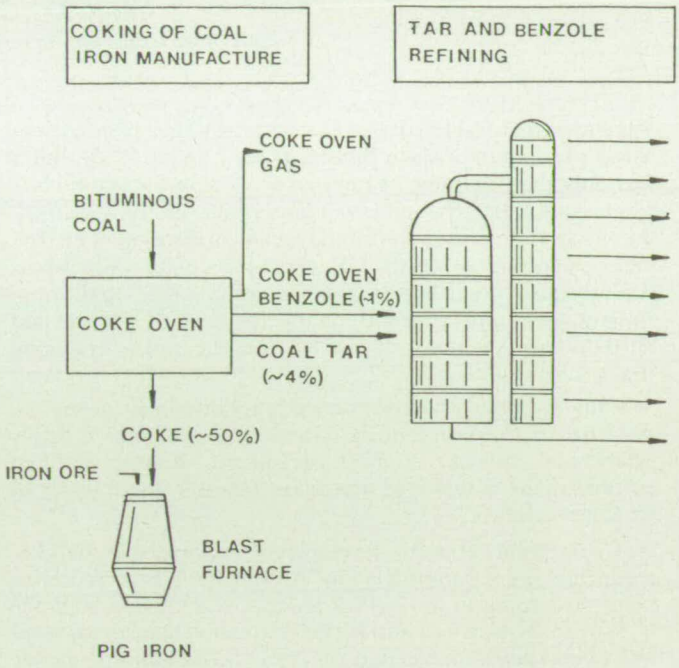
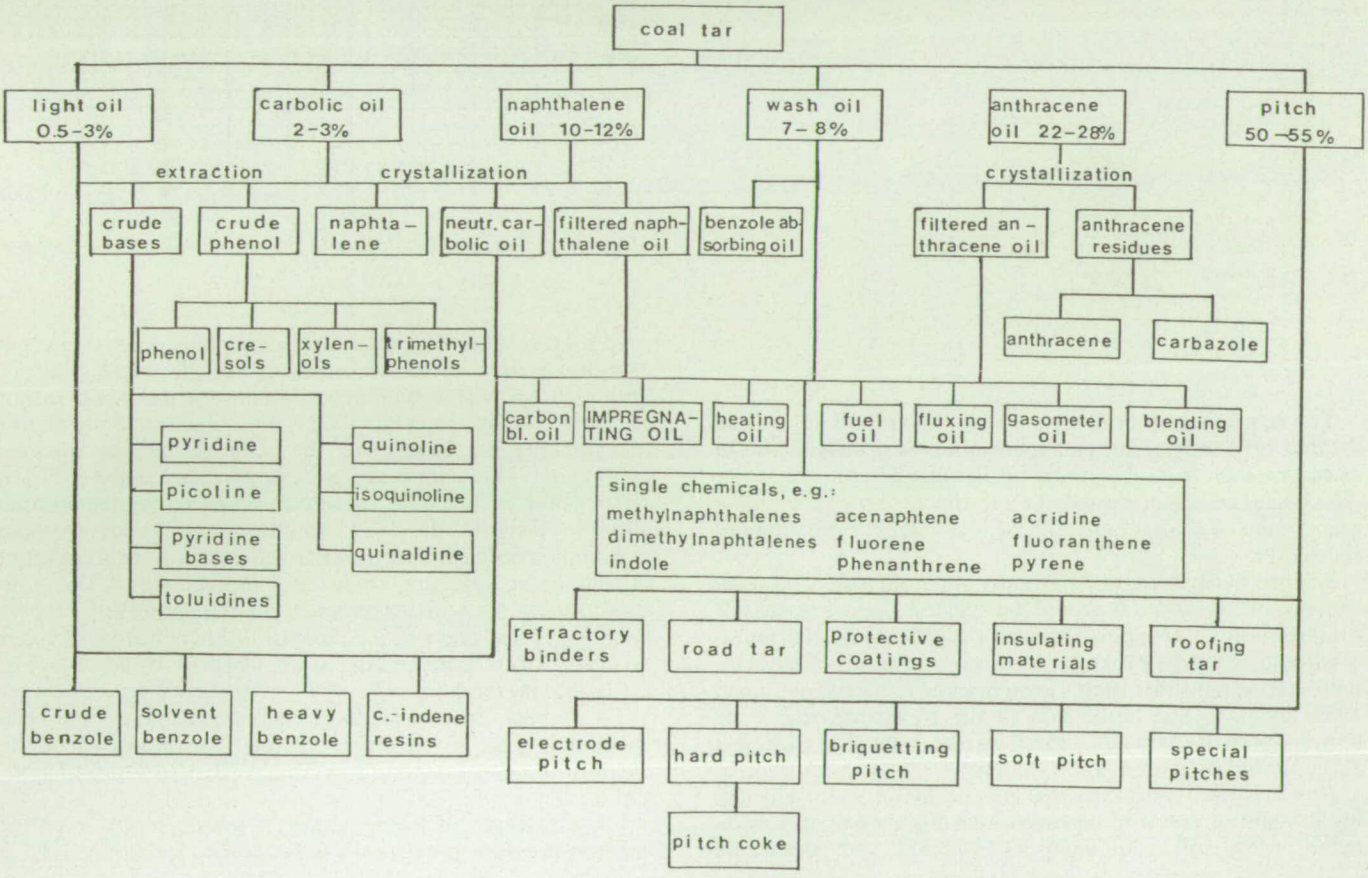


TABLE 4
Workup scheme of high temperature coal tar



100,000 tons in 1984 and are partly used as feedstocks for creosote.

Present Creosote Markets

In principle, about 35 per cent by weight of high temperature coal tar is available as feedstock for the manufacture of creosote from European sources. This provides a potential of 1 million tons of creosote. In the light of this potential, the actual use of creosote in Europe is smaller, we estimate it at just under 200,000 tons with the main volumes used in countries with important railroad sleeper impregnation.

Although quantities in the order of 50,000 tons of creosote are exported from Europe, mainly to the United States, the total use of creosote in Europe is still not more than roughly one-quarter of the potential from its coal tar sources.

It is shown in the following table (Table 4), that coal tar oils have a great versatility to meet various other specifications, as feedstocks for carbon black, washing oils, fluxing oils and fuel oils as some examples of present uses. Because of these alternative uses of tar oil feedstocks, the prices basis for creosote in Western Europe is related to the fuel oil price. Railroad sleepers certainly use most creosoted wood, with a production of 4–5 million pieces in Europe in 1984.

This quantity of 500,000 cubic metres of impregnated wood uses about 85,000 tons of creosote. Switchties are added separately using an additional 15,000 tons, so that the total creosote consumption for sleepers can be estimated at 100,000 tons or roughly 50 per cent of total creosote consumption in Europe. The consumption of creosote for poles in various applications is estimated at 60,000 tons, whereas the remainder of 40,000 tons of creosote is used for stakes, fenceposts, miscellaneous and manual applications.

Modern Creosote Specifications

Many specifications for coal tar creosote in various applications have been developed in the past which led to a confusing multitude of requirements in Europe as well as other countries. After earlier harmonisation attempts (Scandinavian Specifications, 1937 and Budapest Specifications, 1938) in 1982 the West European Institute for Wood Impregnation (W.E.I.) proposed a specification for two types of creosote (W.E.I., 1982, 2nd revised edition 1985), which has already been adopted by some European Rail – and Telecommunication administrations and will hopefully be followed by others with the aim of a fully harmonised creosote specification for all European Countries. This specification is shown in Table 5.

TABLE 5
W.E.I. Specifications for creosote

Specifications	*W.E.I. Type A*	*W.E.I. Type B*
Coal Tar Creosote	100%	100%
Density D 20/4 (g/ml)	1·04–1·15	1·02–1·15
Water Content (Vol.%)	≤ 1	≤ 1
Crystallisation Point (°C.)	≤23	≤23
Acid Content (Vol.%)	≤ 3	≤ 3
Drop Test	Traces	Traces
Boiling Analysis (Vol.%)		
Distillate to 235°C.	≤10	≤20
Distillate to 300°C.	20–40	40–60
Distillate to 355°C.	55–75	70–90

This progress in harmonising European specifications, has as a main effect on the product the reduction of the water soluble phenols content making creosote environmentally more acceptable and less toxic, and was made possible on the basis of preceding research work of Becker, Liese, Wälchli, Willeitner and other authors, who have shown that creosotes with reduced phenol contents performed as well as the earlier oils with a high percentage of phenols.

In Table 7, some of these results are quoted. Furthermore, practical experience from field trials of W.E.I. after 25 years of service with varying phenolic concentrations of up to 10 per cent in various types of creosotes essentially permit the same conclusion (Broese van Groenou, 1980). The effect on acute toxicity of creosote is shown in the toxicological results discussed later. It is interesting in this respect that already Tidy (1884) considered acids unimportant (Tidy, C. M., Report on the Description of creosote best suited for creosoting timber. App. of Boulton – on the antiseptic treatment of timber, London 1884) (cf. Wälchli, 1983).

TABLE 6
Influence of the content of phenols on the fungicidal activity of coal tar creosote (According to tests at B.A.M. 1958, E.M.P.A. 1958 and V.F.H. 1958)

Basidiomycetes used for tests	*Phenol concentration*	*Toxic Limit Values in kg/cbm at* B.A.M.	E.M.P.A.	V.F.H.
	0·5%	ca. 5·7	4·9...7·6	5·6
Coniophora	1·5%	8·4...13	5·6...9·2	5·9...9·3
Cerebella	4·5%	8·8...13	5·7...7·2	5·5...8·7
	0·5%	31...44	27...43	34...46
Lentinus	1·5%	42...63	40...58	45...60
Lepideus	4·5%	33...47	32...47	46...55

(Wälchli, 1983)

It should also be noted, that creosotes made from low temperature tar as produced in the U.K. contain a higher concentration of acids but these have a different composition than those from high temperature tar. However, the water soluble part is roughly comparable with the water soluble portion of high temperature coal tar creosote. Hence, the specification maximising acids content to 3 per cent by volume does not apply to creosotes made from low temperature tar.

New Developments of Creosote Feedstocks

Techniques for coal carbonisation, liquefraction and gasification, could provide new creosote feedstocks. As already mentioned, the use of low temperature tars for creosote manufacture is practiced in England and its use has been proven. Besides this, gasification tar oils of the SaSol coal gasification process are used for creosote manufacture in South Africa. The latter tar oils, although being coal tar oils are different from the mentioned traditional types of creosote and are difficult to use for wood impregnation as such. They are usually combined with about 20–30 per cent of a waxy oil (Waksol K) for improving leachability and improving durability of protection by reduction of evaporation. The requirements for these products are described in the South African Bureau of Standards specification (S.A.B.S. 539–1980, whereas under S.A.B.S. 538–1980 the traditional high temperature coke oven coal tar creosote also remains in use in South Africa).

Practical experience with the SaSol creosotes was recently reported (Pizzi, Conradie, Cockroft, 1984).

There is no practical experience yet reported of the wood protecting properties of the products generated in modern coal hydrogenation processes.

By various hydrogenation technologies, some 4 million tons of coal hydrogenation oils were produced as motor fuel in Germany until the end of World War II. Different modern processes of coal hydrogenation were developed and recently run in experimental facilities in England as well as in Germany;

research is also being done in other countries (Franck, Knop, 1979).

The process run in England is characterised as a two-stage process consisting of an extraction of coal with an oil and a hydrocracking step of the obtained coal solution under pressure, whereas the German process uses a direct catalytic hydrogenation of a coal slurry, and was run in an experimental facility with a capacity of about 120 t/d. of coal oil from 200 t/d. of coal. As the principle of the English process is to extract only part of coal with supercritical gases and tar oils the yield is only up to 33 per cent of organic matter in coal.

Wood Protecting Properties of Coal Conversion Oils

To develop some initial insight into the wood protecting properties of such products, we investigated oils from both processes for their toxicity against wood destroying basidiomycetes according to the wood block method in Kolle Flasks.

The whole straight run hydrogenation oils as well as distillation fractions thereof were tested. The following table contains the test results of those fractions, which come closest to the traditional creosote parameters. As the whole oil did not show significant differences from the fractions, its results are not included in the table. The fractions had boiling ranges from 200–350°C. and densities of 0·98 which is lower than coal tar creosote (1·04–1·12).

Chemical composition differs from traditional creosote, as was found by application of different analytical methods as G.C., H.P.L.C., I.R. and M.S. To summarise the character of hydrogenation oils, they are showing a much lower content of multi-ring aromatics as phenanthrene, anthracene, fluoranthene or pyrene than creosote, little naphthalene and a higher phenolics content in the case of the German oil, whereas the phenolics content in the English oil is low due to its different way of generation. Both oils show a comparatively high content of hydroaromatics and alkyl substituted aromatics, which is their most significant difference to traditional creosote oils. Some of their physical and chemical parameters are shown in the following Table 7, including their penetration properties in comparison to traditional creosote.

TABLE 7
Penetration tests of Coal Hydrogenation products (DIN 52 168) on pinus sylvestris

	Average (mm)
1. English Coal liquefaction middle oil	6
2. German Coal liquifaction middle oil	5·5
3. Coal Tar Creosote	5·0

Specifications of Coal Hydrogenation Products	*Boiling Range*	*Density*	*Phenols*
1. English middle oil	200–350°	0·98	0·1%
2. German middle oil	200–350°	0·98	14%
3. Coal Tar Creosote	200–350°	1·06	3%

The next table shows the results of Basidiomycetes tests of Coal Hydrogenation oils (Table 8).

Discussion of Results from Coal Conversion Oils

The results obtained in the experiments are in line with the previous knowledge about the biological activity in relation to the chemical composition and did not change very much whether the whole oil or a fraction within the distillation range of creosote was taken.

TABLE 8
Results of Basidiomycetes Tests of Coal Hydrogenation Products

	Coniophora Puteana	*Poria Monticola*	*Lentinus Lepideus*
I. Wood block tests in Kolle Flasks according to DIN 52 176 (kg/cbm)			
1. English Coal liquefaction middle oil	160...100	160...100	250...200
2. German Coal liquefaction middle oil	140...100	150...120	150...200
3. Coal Tar Creosote	−40	−40	−40
II. Wood block tests after Leaching (DIN 52 176/EN 84; kg/cbm)			
1. English Coal liquefaction middle oil	200...160	250...200	250...200
2. German Coal liquefaction middle oil	200...160	180...150	200...170
3. Coal Tar Creosote	110...90	160...110	160...110
III. Wood block tests after wind tunnel evaporation (DIN 52 176/EN 73; kg/cbm)			
1. English Coal liquefaction middle oil	200...160	250...200	250...200
2. German Coal liquefaction middle oil	200...160	200...160	200...170
3. Coal Tar Creosote	110...80	110...80	110...80

As the chemical composition with the higher content in hydroaromatics and alkylaromatics appeared to be a reason for the differences, an experiment was done adding a known fungicide i.e., xylenol to enhance the fungicidal properties, but no change was found, i.e. xylenol did not improve the fungicidal performance of the coal hydrogenation oils.

This is surprising on the basis of the analytically found ingredients in the German material e.g. certain phenols, naphthols and quinolines from which a better fungicidal effect would have been expected, but it performed only marginally better than the English oil, which does not contain significant amounts of acids or bases at all. On the other hand, this is in line with the findings mentioned before that phenols do not essentially contribute to fungicidal activity.

Another surprise is that the fungal toxicity of the hydrogenation oils, although weak in comparison with coal tar creosote; did not get weaker through leaching or wind tunnel evaporation, while, as expected, the coal tar creosote was considerably reduced in its toxic limit values after leaching resp. evaporation.

This difference is not explainable with distillation or vapour pressure differences as the coal hydrogenation oils were actually even somewhat 'lighter' than the coal tar creosote, so at least evaporation should have had an effectiveness reducing effect. It is hence possible to conclude that the new oils do not evaporate or leach from wood to a considerable extent, which could make them desirable formulating components for coal tar creosote.

However, as it is known, the wood protecting properties of creosotes cannot be completely described by small sample testing only. Tests with larger samples such as stakes under practical conditions in field trials will be necessary for more complete answers. Although the future of industrial coal conversion is still uncertain in several countries, for further demonstration of the hydrogenation technology on a larger scale, a 1 million ton per year coal hydrogenation facility is currently under discussion in Germany.

Developments in formulating traditional creosotes with larger scale testing of stakes presently in progress are A.W.P.A.'s P.14 coal tar creosote, an addition of 2 per cent sulphur to P.1 creosote (Webb, 1983) and the development of 'Pigmented Emulsified Creosote' (P.E.C.) (Greaves, Chin, McCarthy, Watkins, 1985).

Both formulations improve creosote's environmental

acceptance, as they are suggested for a cleaner surface and in the case of P.E.C., also an evenly coloured surface of the wood. The addition of sulphur is also improving creosote's toxicity against lentinus lepideus in the case of A.W.P.A.'s P.14.

Lawniczak (1979) reported an improved penetration of 12–50 mm instead of 3–5 mm by formulation of creosote with styrenes and cumene derivatives as well as the possibility to run the impregnation process at room temperature.

The impregnation of heartwood, as can already be seen from the earlier quoted work of Hösli remains a goal worth while to achieve. The preceding examples of creosote development express the liveliness of this old, reliable product by the attention it continues to receive in science and industry.

Health and Environmental Aspects

Together with other wood preservatives creosote has also been the target of measures resulting from an increased environmental consciousness which has progressed much faster in recent years than in the decades before. This forces the wood preserving industry and the producers of wood preservatives to adapt the composition of their products and procedures to comply with the upcoming new regulations. In principle there are three areas of possible risks; the application in the impregnation process, by the use and finally by the disposal of the impregnated timber. For three wood preservatives, namely Arsenicals, Pentachlorophenol and Creosote, very thorough analyses of possible risks versus benefits were performed during the process of Rebuttable Presumption against Re-registration (R.P.A.R.) of the U.S. E.P.A. (Environmental Protection Agency). Consequently, the mentioned wood preservatives including creosote have been the subject of thorough recent toxicological and environmental research which is continuing. The main reason for concerns about creosote's toxicity is associated with its content of compounds of the class of polynuclear aromatic hydrocarbons (P.A.H.'s), a few of which, as Benzo-a-Pyrene (BaP.) are carcinogens in animal experiments. Analysis of P.A.H.'s in the environment has made rapid progress in recent years.

Acute Toxicity

At first I would like to discuss some newer data on acute toxicity which was obtained for a W.E.I. type creosote. They include also recent acute mammal toxicity data of creosotes major constituents and are summarised on the following table:

As can be seen, the acute toxicity and irritation effect of modern creosotes is very low. The fact, that in earlier published literature a considerably higher acute toxicity is mentioned, it may be possible to explain with the reduced phenol content of modern creosotes, but also by the apparent very low acute toxicities of major creosote ingredients in their isolated form. In an atmosphere saturated with creosote, no inhalation risk over an 8 hour period could be found (Willeitner/Dieter, 1984).

Chronic Toxicity

Animal studies to characterise chronic toxicity risk of creosote are summarised in the 'Registry of Toxic Effects of Chemical Substances' (R.T.E.C.S.) of the U.S. National Institute for Occupational Safety and Health (N.I.O.S.H.).

To produce chronic toxic effects, the following concentrations are mentioned in R.T.E.C.S. for creosote:

14 g/kg (male rat, oral, 91 days)
52 g/kg (female, pregnant rat, oral, 91 days)
131 g/kg (male mouse, oral, 91 days).

It is obvious, that these enormous concentrations differ by magnitudes from exposures to man possible by application of creosote for wood impregnation in any known process. The practical insignificance of these concentrations is further confirmed by the definition of A.C.G.I.H. (American Conference of Governmental – Industrial Hygienists), the association which produces the T.L.V. lists, that there is no practical significance of a carcinogen if more than 1·5 g/kg are needed to produce a carcinogenic effect.

P.A.H.'s in the Environment of Wood Preservation Plants

P.A.H.'s are of course not only found in coal tar. They are ubiquitous and occur everywhere where pyrolysis processes take place. In burning coal, operating an automobile, smoking meats and cooking food, in naturally occurring fires and even from volcanoes polycyclic aromatic hydrocarbons are generated. Although the air concentrations of single P.A.H. compounds as BaP. are in the nanogram range, today's techniques permit the measuring of these low concentrations reliably by combinations of chromatographic and spectroscopic methods. Air sampling is normally done with a glass-fibre silver membrane filter and charcoal adsorption. Much progress and new insight has been reported recently in environmental P.A.H. analysis (Grimmer, 1984; Andersson, Levin, Nilsson, 1983; Blome, 1983) but also in workplace exposure analysis.

TABLE 9
Acute Toxicity of Creosote and its Major Chemical Constituents

	Irritation Effects (Rabbit)			*Acute Toxicity (Rat)*		
	Primary Skin Irritation/24 h.		*Primary Eye Irritation*	*LD (Oral) mg/kg*	*LD (dermal) mg/kg*	*Inhalation risk 20°/8 h. saturated air*
	Draize Score Ind.	*Classification*	*Classification*			
Creosote DB (W.E.I. type A)	2·2	not irritating	not irritating	LD 50: 3,870	over 3,100	
Creosote Z (Carbolineum)	1·9	not irritating	not irritating	LD 50: 5,430	over 4,200	none
Acenaphthene	0·54	not irritating	not irritating	over 16,000		
Anthracene	0·79	not irritating	not irritating	over 16,000	over 1,320	
Carbazole	0·5	not irritating	not irritating	over 16,000		
Diphenylene oxide	0	not irritating	not irritating	over 16,000		
Fluoranthene	0·66	not irritating	not irritating	over 16,000		
Fluorene	0·33	not irritating	not irritating	over 16,000		
1-Methyl naphthalene	3·3	not irritating	not irritating	LD 50: 2,860		
2-Methyl naphthalene	4·1	not irritating	not irritating	LD 50: 3,900		
Naphthalene	1·8	not irritating	not irritating	over 16,000	over 16,000	none
Phenanthrene	0·7	not irritating	not irritating	over 16,000		
Pyrene	0·79	not irritating	not irritating	over 16,000		

Investigations by Huntingdon Research Centre (Germany) 1979–81

Concentrations of P.A.H.'s in the workplace environment of coke oven operations, aluminium plants as well as creosoting plants were recently measured and continue to be monitored.

The following table contains recent results from wood impregnation plants at locations in various countries:

TABLE 10
Airborne concentrations of polynuclear hydrocarbons in the working environment of wood creosoting plants

Author	*Year*	*Process*	*Concentration*	*Substance*	*Maximum permissible level (Country)*
Flickinger Lawrence	1982	Vacuum Pressure	0·1 mg/cbm	Benzene soluble** Particulate matter	(U.S.A.) 0·2
Flickinger Lawrence	1982	Vacuum Pressure	0·3 ug/cbm	Benzo-a-Pyrene	
Henningsson	1983	Vacuum Pressure	0·05 ug/cbm	Benzo-a-Pyrene	(Sweden) 5 ug/cbm
Andersson Levin Nilsson	1983	Handling impregnat Railroad ties	0·05 ug/cbm	Benzo-a-Pyrene	(Sweden) 5 ug/cbm
Rudling Rosen	1983	Vacuum Pressure	0·05 ug/cbm	Benzo-a-Pyrene	(Sweden) 5 ug/cbm
Rütgerswerke	1984	Vacuum Pressure	0·07 ug/cbm	Benzo-a-Pyrene	(W. Germany) 2 ug/cbm*
Rütgerswerke	1984	Hot-Cold trough impregnation	0·8 ug/cbm	Benzo-a-Pyrene	(W. Germany) 2 ug/cbm*

*Proposed maximum limit in Germany for continuous 8 hour workshift 2ug/cbm to constitute 'no exposure' short time maximum 5·2 ug/cbm (1 hour).
**Containing about 20% PAH's or 0·5 . . . 1% Benzo-a-Pyrene.

As a comparison, the next table shows airborne concentrations of BaP. in various locations in the environment:

TABLE 11
Airborne concentrations of Benzo-a-Pyrene in the environment at various locations (Blome, 1983)

Location	*BaP. concentration (ug/cbm)*
Ruhr-area (Industrial)	0·001 . . . 0·3
Countryside	0·007
Auto-emission	6 . . . 69
Small heating units	0·001 . . . 1·300
Passengers in cars	0·001 . . . 0·016
Passengers in aeroplanes	0·085 . . . 0·15
Guests in restaurants	0·03 . . . 0·14

(According to: H. Blome, B.I.A. Report 3/83, Sankt Augustin, W. Germany)

When comparing these values with air concentrations of P.A.H.'s in wood impregnating plants as shown in the previous table a comparable magnitude of concentrations can be found. As can also be seen, the limit values set in the mentioned countries for BaP. or P.A.H.'s are not reached or exceeded in one case.

Measuring BaP. as an indicating compound for P.A.H.'s has proven a practical method to obtain reproducible results at these extremely low concentrations. Andersson, Levin, Nilsson (1983) showed that an approximate correlation exists between P.A.H.'s and the benzene soluble portion containing normally 20 per cent of identifiable P.A.H.'s or 0·5–1 per cent of Benzo-a-Pyrene, which could qualify BaP. as a guidance compound in estimating total P.A.H.'s

Research of the airborne concentrations of vapourisable compounds of creosote, which are mainly responsible for its odour, such as indene, naphthalene, methylnaphthalene etc., was done recently by Ingram, McGinnis, Prince, Gjovik and Webb (1984) using wood blocks as testing samples.

In these investigations the relationship of the rate of evaporation and the vapour pressure of the compounds was again confirmed. From the acute toxicity data mentioned earlier for these compounds, it can be seen that only those with very low acute toxicities vapourise to a measurable extent. Various types of coatings based on synthetic resins or pitch can significantly reduce vapourisation of creosote components from treated wood.

Epidemiological Studies

Epidemiological studies of wood creosoting were recently done in Norway, Sweden, the U.S. and West Germany.

An extensive written survey of 90 firms in West Germany in 1980/81 was published by Willeitner and Dieter (1984). This study represents practically the total quantity of creosote used for wood impregnation in Germany after World War II.

In the participating firms, about 1,800 employees were handling creosote in 1980, whereas the average number of persons for the period of 1950–1969 was 2,350. Of the 90 companies, 59 firms impregnated timber, the others used creosote in other ways, mainly by filling to smaller containers and formulating.

Thirty-six firms had used creosotes for more than 50 years, four of them for more than 100 years. The oldest company had used creosote for wood impregnation since 1860.

The results of this survey are summarised in the following table:

TABLE 12
Experience about possible health effects when handling creosote

Number of firms contacted	*Time periods separately surveyed*			
	1980	*1979-1970*	*1969-1950*	*Before 1950*
Total	90	89	86	52
Impregnation plants	59	59	57	33
Other creosote users	31	30	29	19
Persons employed handling creosote (avg. p.a.)	1,800	1,800	2,350	2,550
Creosote used for Wood impregnation (t) (avg.)	40,000	42,000	34,000	10,000
No statement about acute Health effects	1	1	1	1
No diseases noticed (%)	80	80	78	71
Primary skin irritations noticed (%)	19	19	21	27
– of which only under direct sun exposure (%)	71	16	67	71
– others (%)	29	24	33	29
Chronic health effects (%)	0	0	0	0
No chronic health effects observed (%)	100	100	100	100

The results of a study of the Norwegian Cancer Research Institute on the occurrence of specific types of cancer in an impregnation plant is summarised in the following table:

TABLE 13
Comparative survey about the observed and expected occurrence of specific types of cancer in an impregnation plant. (According to Norwegian Cancer Research Institute, 1981)

Form of Cancer	*Observed Cases*	*Expected Cases*
Stomach Mucous Membrane	4	6·24
Colon	3	3·25
Small intestine	3	2·11
Pancreas	3	1·81
Lungs	2	5·04
Bladder	6	8·10
Lymphatic Glands	3	1·37
Other Forms	13	16·50
Total	37	44·52

The Norwegian study covers a work population of 665 male employees during the period of January 1, 1953 to January 1, 1980. The evaluation does not include 218 persons, who were employed after 1970 or had been employed for a period of less than 18 months, hence the evaluation is based on 447 male employees.

This study is particularly interesting as it analyses the different types of cancer with the conclusion that also by the different cancer types, no increased cancer risk has been observed.

In the U.S., an epidemiological study was done on 329 creosote workers (Flickinger, Lawrence, 1981). Also this study did not show an increased cancer risk. Hence, recent toxicological, environmental and epidemiological findings do not indicate the need for further restrictions of creosote, as it obviously can be handled safely for wood impregnation under present conditions.

What would be the consequences if the currently still ongoing legislative efforts to impose additional restrictions on creosote were to be enforced?

In the U.S.A. if the E.P.A. requirements were to be enforced, the application of creosote as well as P.C.P. and Arsenicals would be restricted to application by certified applicators. Additional personal protection measures would become mandatory, such as the wearing of impermeable gloves and coveralls in impregnation plants and when handling impregnated wood.

Furthermore, a consumer awareness programme would be introduced with specific handling precautions and application restrictions for creosote impregnated wood.

In Sweden and Denmark, there are toxic legislation efforts to classify creosote into the class of a highly toxic and carcinogenic material, with new labelling requirements in Sweden to be effective by the beginning of 1986. Many organisations, such as W.E.I., have already commented that these presently proposed regulations are unnecessary in the light of our modern knowledge of creosote. A different approach is taken in Finland, Norway and Germany, where classification is or will be based on BaP. content.

Finland for example limits the content of BaP. to a maximum of 500 p.p.m. in heavy creosote. Benzo-a-Pyrene will be used as a guidance substance for toxic classification of pyrolysis products in Germany where the new proposed legislation is expected to go into effect by January 1, 1986.

In our present time of increased environmental consciousness, the development of modern methods of environmental analysis methods can be used to show that creosote and its application for wood preservation does not present any unreasonable risks, when properly handled.

Wood preservation is essential to preserve our valuable forest reserves and creosote continues to be a very important factor in this effort.

Although conventional creosote has maintained this position for well over 100 years it can be seen from new activities in technical and environmental fields that 'the old old product is still very lively'.

This attention creosote receives from scientific and industrial communities is an indication that its future will be as interesting as its long history.

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DISCUSSION ON PAPER 6

Chairman: Mr. G. O. Hutchison

THE CHAIRMAN: Ladies and Gentlemen, I am sure that you, like me, were very interested in that paper. As we are running fairly short of time I think we will go straight into any questions that anybody would like to put to Dr. Löhnert.

MR. S. SHOOP (Harry Stanger Limited): Because of the time I should like to restrict myself just to health and safety aspects. I should like to congratulate the authors on what I regard as an important, timely and useful paper. Its importance will be that most people will refer to this as a key document in the future. It is timely. We only have to look at today's papers to know what is under attack. Even our gin and tonics are under attack as being unsafe and when you come to things like creosote you have people who listen to old wives' tales who accept and take for granted that creosote is dangerous and do not look at the evidence.

We now have seen the evidence, evidence that has been produced not on the basis of theoretical considerations or laboratory results, but on the basis of material that has been used in the field, not solely in our grandfathers' time, the so-called 'Grandfathers' clause'. We are talking of something which was used in the time of our great, great, great, great-grandfathers' time. There is 150 years of experience in creosoting, which shows that it can be used safely.

It is useful. We know of a case, the B.W.P.A. had an example, of a man who had a house where the inside timbers were creosoted — something which you should not do because the smell is unpleasant, but that is the worst that can be said of creosote being used indoors — and eight months afterwards someone went to that house where two months earlier the creosoted timber had been varnished, and the following morning, having been in the house for just four hours, he complained of weakness of the lower limbs. If you look at the paper you will see on page 20 that in an atmosphere saturated with creosote no inhalation risk over an eight hour period could be found, and that would be very, very useful in this particular case.

THE CHAIRMAN: Can you come to your question, please.

MR. S. SHOOP (Harry Stanger Limited): There is no question, I am just making a point on how useful the document is. Very, very briefly I would like to draw attention to page 20, speaking of the toxicity of older creosote you find in the published literature, when you look up the documents on the toxicity of creosote make sure it is coal tar creosote because more or less all the text-books like Pattie and Sachs are referring to the wrong creosote which is wood creosote, which is entirely phenolic as opposed to coal tar creosote which has only very few phenols in it.

DR. G. LÖHNERT: Thank you very much for your comments. I think there might be a possibility that this was a different type which was showing the higher toxicity in the past, it is not excluded that it might have been wood creosote.

MR. W. D. BETTS (Director, British Tar Industry Association): If I might be just permitted a brief comment. I will try and keep it brief in view of the limited time available. The British Tar Industry Association along with its French and German counterparts has been looking at the potential hazards of tar products in general, which of course includes creosote. They have also been assessing the risks. I think it is important to draw a distinction between potential hazard and actual risk for those who interpret the thinking of what appears from the environmental lobby. The potential hazard, as Dr. Löhnert has illustrated, is really based on animal studies where excessive doses of components in coal tar or coal tar itself are applied to the skins of animals. The relevance of these results to human beings is far from clear, but it does set a potential hazard. As has already been stated in fact the American Conference of Government Industrial Hygienists regard the levels which are shown for coal tar materials as not constituting an acceptable occupational risk, in other words it is not a real occupational risk.

In terms of risks, it is important to define this really as the product of the seriousness of an event if it occurs multiplied by the likelihood that it will occur. It is very encouraging that the view we have come to is that although there may be a potential hazard in coal tar materials and creosote this is not realised in practice, in other words, the risk is very small. If the risk occurred it can be serious but the likelihood of the risk occurring is very small indeed. It is very gratifying that the results of the German study conform to the views that we, ourselves, have come to.

Again the Health and Safety Executive Officers in the United Kingdom realise this. They have approved, through the Pesticides Safety Precautions Scheme, the use of creosote for both professional and domestic use provided it is applied within the recommendations that they have issued. These are just simple and sensible precautions which should be taken during application.

THE CHAIRMAN: Does anybody have a question. (Laughter).

MR. I. B. WAUGH (Collinda Limited): There have been articles recently in our trade press stating that creosote oils have been banned for use in the retail trade in Germany. Is this the case or is this an exaggeration? I wonder if Dr Löhnert can add

anything to this.

DR. G. LÖHNERT: I have no basis for confirming that. That is not the case. Creosote is in the retail trade for general application in Germany.

THE CHAIRMAN: We have time for one more question if there is one (No response). Can I thank Dr Löhnert, I am sure, on your behalf for a very excellent paper on such an interesting subject as creosote and also thank you, the audience, for your questions and involvement in the paper. Thank you, Dr Löhnert. *(Applause).*

APPRAISAL OF FUNGICIDAL EMULSIONS FOR IN SITU TREATMENT

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Introduction

The practice of treating building timber before installation to protect it from rot and insect attack in-service is not a new one. It has its roots in antiquity (Richardson 1978) and has been widespread in Europe for the last 150 years.

The practice of applying protective treatments to installed building-timbers is rather more recent and does not appear to have become widespread in the UK until the 1950's.

The development which greatly facilitated 'in-situ' treatment was the appearance of organic solvent borne preservatives. Prior to their advent, the wood preserver had available to him only creosote and water borne preservatives. For reasons such as its colour and odour, the potential for using creosote within an existing building was severely limited. Whilst water borne preservatives did not have these drawbacks, they did not penetrate the timber to any appreciable depth when applied by brush or spray. The appearance of colourless preservatives which penetrated the timber well, and rapidly lost what little odour they had, therefore represented a significant advance.

Today, perhaps 15–20 million litres of organic solvent wood preservatives are used each year in the UK for the in situ treatment of building timber. Few wood preservers would argue however that remedial spray treatments are other than making the best of a less than ideal situation. No in situ treatment can ever be as satisfactory as a pre-installation, total immersion treatment. Not only do pre-installation treatments protect all surfaces of the timber, they almost inevitably result in deeper penetration of preservative than brush or spray application. This latter point is particularly pertinent to the present discussion. Adequate penetration is a 'holy-grail' of timber preservation and its importance is stressed in many publications (e.g. Coggins, 1980, BWPA Leaflet No. 4).

There are two principal reasons why deep penetration of preservatives is so very desirable. Firstly, there is evidence which has suggested that penetration to a minimum depth of a few millimetres is essential for a preservative to function. Baker & Taylor (1967) published results which showed that an apparently adequate loading of insecticide in timber failed to prevent emergence of *Anobium* if the treated layer was only 1 mm thick. Evidence from mycological tests has also indicated that a thin layer of toxic chemical may not always present a barrier to colonisation by fungi (Blow 1981). The well documented ability of *Serpula lacrymans* to grow in 'search' of nutrient through conditions which are not themselves nutritious (Findlay 1962, Coggins 1980) also points to the desirability of deep penetration.

A second reason which is cited as evidence that deep penetration is desirable is that like most complex organic molecules, the biocides used in organic solvent preservatives have a finite, albeit very low, vapour pressure. The implication of this is that these chemicals are very slowly lost from treated timber.

Work has shown (Morgan & Purslow 1973, Purslow 1974, Orsler & Stone 1981) that this loss is, however, virtually confined to the outer two millimetres or so of timber and so even in the long term gives little cause for concern if adequate penetration of biocides extends beyond this depth.

Emulsion Treatments

Although organic solvent preservatives have long dominated the in-situ treatment industry, increasing prominence has been given in recent years to low oil-content emulsified formulations (Woodhouse 1976, Orsler & Stone 1981). These are formulations in which a very highly concentrated organic solvent preservative is finely dispersed or 'emulsified' into water. The dispersion is stabilised with 'surfactants' or 'emulsifiers' to prevent it reverting to separate oil and water phases.

On face value, there are three principal advantages and two principal disadvantages to using emulsified formulations for in-situ treatment. The apparent advantages are reduced odour, reduced cost and reduced fire risk. The apparent disadvantages are the need to handle concentrated preservatives and reduced penetration.

Considering first the apparent advantages of using emulsions for in situ treatment, it is certainly a fact that the odour associated with organic solvent preservatives can be reduced if the volume of organic solvent used is reduced, as is the case when an emulsified treatment liquid is used. This reduction in odour is widely perceived as an advantage, in that persistent odours can be a source of irritation to householders etc.

However, a note of caution needs also to be struck. Comparative absence of odour is not, of course, synonymous with comparative absence of toxic chemicals and should not therefore be used as an 'excuse' to avoid limiting the use and occupation of treated regions for 48 hours after treatment, or otherwise cutting back on the safety precautions specified by HSE.

In the context of odour, it may also be noted that certain fungicides, such as T.B.T.O., themselves have an odour. This of course is not diminished by reducing the solvent-content of a formulation and in some circumstances, it may even become more apparent. Possibly as a reflection of this, a certain amount of remedial treatment is today performed with products containing only 5 g/l T.B.T.O. whereas throughout the pre-treatment industry, formulations containing 8 g/l (or, more usually, its equivalent) are used. The relative efficacy of the former formulations is obviously intrinsically lower than that of 'full-strength' formulations.

A second apparent advantage of using emulsions is the saving in solvent and hence in raw materials costs. However, whilst a cost differential between organic solvent preservative and emulsified versions thereof usually exists, it is less substantial than might at first be expected. As has already been stated, the oil-phase of an emulsified formulation has to be more highly concentrated than 'normal' and in some cases more costly solvents have to be used in order to achieve this. Secondly, it is necessary to incorporate emulsifiers to stabilise the emulsion whilst it is being applied, and the cost of these is not encountered when traditional organic solvent preservatives are formulated.

Finally, certain biocides, most notably pentachlorophenol (P.C.P.) do not readily lend themselves to incorporation into emulsifiable concentrates. In consequence, more expensive biocides such as tributyl tin oxide (T.B.T.O.) and pentachlorophenylaurate (P.C.P.L.) are used in emulsions.

A third apparent advantage of using emulsified preservative formulations is that of reduced fire risk. This reduction in the risk of a fire associated with the preservative is virtually total. This is not to say that emulsified formulations may be used with any less care. From the point of view of operator safety, disruption of electricity supplies for instance is more vital than ever because water conducts electricity.

A disadvantage associated with using emulsified formulations arises from the fact that that they are frequently supplied

as concentrates. This not only introduces the need for much greater care and security if these materials are taken to site, it also greatly increases the number of people in the wood preservation industry who handle concentrated mixtures of biocides.

A second apparent disadvantage of using emulsified preservatives which was mentioned above was that of reduced penetration. There are two principal reasons for supposing that the penetration of emulsions will be inferior to that of organic solvents. The first of these arises from the fact that it is reasonable to suppose that the flow characteristics of an emulsion will be dominated by the flow characteristics of the 'continuous phase' i.e. of the water.To the timber preserver, it is a matter of common experience that water enters timber a great deal more slowly than does organic solvent.

The second reason for anticipating that the flow of emulsions into timber will be restricted may be derived by extrapolation from the work of Kelso et al (1963). It has long been known that the rate at which water will flow through a piece of timber diminishes with time (Ewart 1905, Anderson et al 1941) and over the years several explanations were advanced to account for this (Buckman et al 1935, Huber & Mertz 1958). However, in 1963 Kelso published results from which he showed that diminution of flow rate occurs as a consequence of the formation of air bubbles within the timber. These bubbles become lodged at constrictions in the flow path through the timber (e.g. at the pit membrane) and then occlude these openings thereby preventing or severely limiting further flow, unless a substantial pressure is applied.

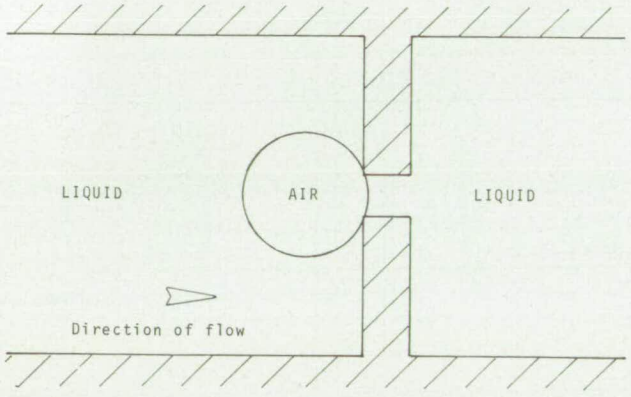

Fig. 1. Schematic diagram of air bubble blocking a constriction in a flow path.

Mathematical discussions of the above phenomenon can be found elsehwere (Siau, 1971). Suffice it here to observe that there is a clear analogy between a volume of water containing air bubbles and a volume of water containing oil droplets. Therefore it appears possible, indeed, almost inevitable, that unless a substantial external pressure can be applied, the flow of an emulsion into timber will be poorer than the flow of a simple solution of water borne preservative. Moreover, there appears to be a real possibility that the oil phase of an emulsion (which is the carrier for the timber preservative chemicals) may be filtered out in the most superficial layers of the timber.

Effect of surfactants on flow

The above argument for the intrinsically poor penetration potential of emulsions must be considered alongside the strong possibility that the surfactants which are present to stabilise any emulsion may profoundly influence penetration as a result of the way in which they change the properties of the surface of the liquid. Penetration of a surface — applied timber treatment liquid occurs largely as a result of capillary forces and is described by the Washburn equation.

$$1 = \left(\frac{r\ t\ T\ \mathrm{Cos}\ \theta}{2\ \eta}\right)^{1/2}$$ Washburn Equation Equation 1

where 1 = distance travelled by liquid in time t
r = radius of capillary
T = surface tension of liquid
$\mathrm{Cos}\ \theta$ = cosine of contact angle between liquid surface and capillary wall
η = viscosity

It may be seen that two properties of a liquid's surface are included in the above equation, namely, the surface tension and the contact angle. With respect to these two characteristics flow into timber will proceed most rapidly when the surface tension is high and the contact angle is low (i.e. when the Cosine of the contact angle is high).

Many surfactants decrease the surface tension of liquids and so their presence in an emulsified system might be expected to reduce the surface tension of the continuous phase (the water) and reduce the rate of flow into timber. At the same time many surfactants reduce the contact angle between water and timber (i.e. they are wetting agents) and their presence would therefore be expected to enhance flow into timber.

A study of the effect of a particular surfactant or blend of surfactants on the surface tension and contact angle of a liquid should enable its effect on flow to be predicted. However, preliminary work indicated that this may not always be so. Rather it appears that other factors may also exert an influence.

In order to attempt to elucidate the effect of surfactants on flow, a largely empirical programme of investigation was undertaken. This programme involved the examination of the penetration characteristics of a range of 'solutions' of surfactants in water, into dry pine sapwood. In addition to this the penetration of several emulsions was also studied. In association with this work, measurements of changes in surface tension, viscosity and contact angle were also made.

Investigations were limited to dry timber (moisture content ca. 12 per cent), despite the fact that the reality of in situ treatment is that timber is not always dry at time of treatment. This limitation was decided upon partly because of the technical complexities introduced by experimenting with wet timber and partly because there seemed to be no theoretical reason why penetration of the active ingredients in emulsions into wet timber should proceed more easily than into timber which was dry.

Selection of surfactants and assessment of their effects on the physical properties of water.

The selection of surfactants to be included in the test programme was made to cover as wide a range of chemical types as possible, whilst also restricting work to surfactants which might be used in wood preservative emulsions. Of the surfactants (ca. 70) originally screened 15 were selected for testing (Table 1) on the basis that these were found to be at least partially successful at stabilising an emulsion of water and white spirit.

Measurements of surface tension were made using a modification of the 'drop weight' method, in which drops of test liquid were allowed slowly to develop at, and fall from, the tip of a standard laboratory burette, and the mass of each drop was determined. From this an estimate of the surface tension was calculated using published equations (Adam 1941).

An assessment of the advancing contact angle of each surfactant solution against planed pine sapwood was made using the tilting plate method. This technique involves partially submerging a sample of dry timber in the test solution and adjusting the angle between the timber sample and the surface of the liquid until the meniscus on one side curves neither up nor down. The surface of the liquid therefore remains flat as the timber sample is plunged more deeply into it.

TABLE 1
Generic Chemical Descriptions of Surfactants Selected for Testing

Surfactant Reference Code	*Cation*	*Anionic Surfactants* *Anion*
A	Sodium	Alkane sulphonate
B	Sodium	Alkane sulphonate
C	Amine	Alkylaryl sulphonate
D	Sodium	Dodecyl benzene sulphonate
E	Isopropylamine	Dodecyl benzene sulphonate
F	Isopropylamine	Dodecyl benzene sulphonate
G	Sodium	Alkylaryl polyether sulphonate
H	Sodium	Olefine sulphonate
J	Sodium	Oleophilic sulphonate
K	Sodium	Dioctyl sulphosuccinate
L	Sodium	Di — isooctyl sulphosuccinate
M	Sodium	N — methyl N — tall oil acid taurate
	Nonionic Surfactants	
N	Ethoxylated linear C_{14} fatty alcohol	
P	Ethoxylated unsaturated fatty acid	
Q	Ethoxylated lanolin derivative	

A 5% m/m "solution" of each of these 15 surfactants was prepared and certain physical characteristics of each were measured (Table 2).

TABLE 2
Properties of 5% m/m 'solutions' of the surfactants described in Table 1, in deionised water

Surfactant Reference Code	*Surface Tension (dynes/cm)*	*Contact Angle against planed pine*	*Viscosity cp*	*Solubility**
A	29	18	1	h
B	26	16	1	h
C	28	37	16	m
D	30	22	1	l
E	28	33	3	l
F	29	27	3	l
G	31	16	1	m
H	33	20	1	h
J	35	23	1	m
K	25	23	6	m
L	26	21	4	m
M	32	20	1	h
N	31	24	10	m
P	37	25	7	m
Q	46	40	1	m

*h = 5% m/m — totally soluble in water
m = 5% m/m — forms homogeneous suspension in water
l = 5% m/m — does not form homogeneous mixture

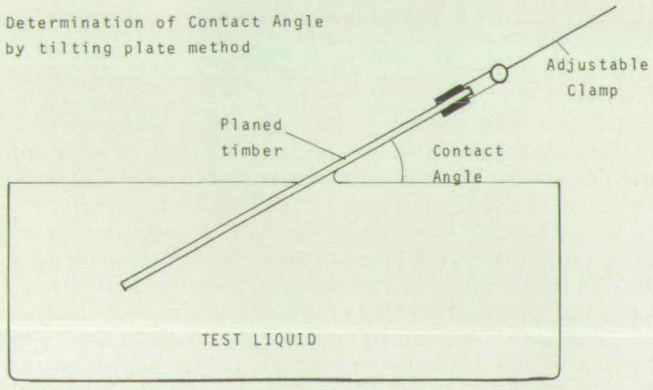

Fig. 2. Determination of Contact Angle by tilting plate method.

The viscosity of each test solution was determined using an Ostwald viscometer.

Lateral penetration into timber

To examine the penetration of liquids laterally into dry Corsican pine sapwood a specially constructed 'flow meter' which is represented diagrammatically in Fig. 3 was used. In essence, this consisted of a tube, one end of which could be clamped firmly against and vertically above, a sample of timber. This tube was equipped with a small hole near its base such that it could be filled from the bottom with test liquid, thus avoiding air bubbles becoming trapped at the timber's surface.When this hole was closed, the rate at which liquid entered the sample of timber was monitored by observing the rate at which the liquid within the tube fell.

For this latter purpose the upper part of the tube was constructed of glass so as to be transparent. In addition the diameter of the tube was not uniform along its length. Rather, the diameter of the lower end of the tube was comparatively large (33 mm) to allow liquid to enter the timber over a large area, whilst the diameter of the sight glass was comparatively small (4 mm) in order that small amounts of liquid entering the timber were visible as relatively large vertical movements of the upper surface of the test liquid.

Samples of timber for use in the flow meter were prepared from rough sawn lengths of dry Corsican pine measuring ca. 45 × 33 mm in cross-section. One sapwood surface of each beam was designated the 'test face' and was planed smooth.

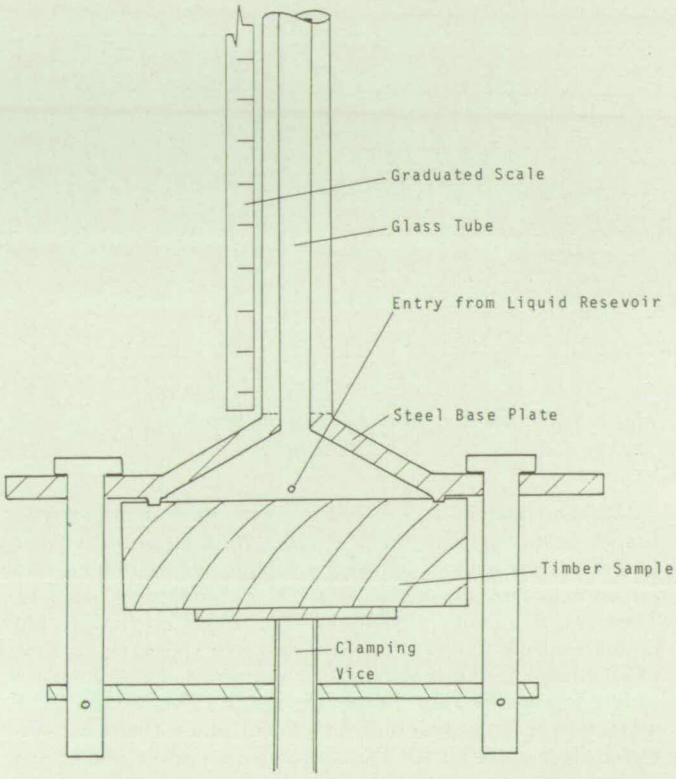

Fig. 3. Flow meter used to determine rate of entry of test liquids into timber samples.

Each length was then cut into sequentially numbered pieces, each ca. 100 mm long. The transverse surfaces of each piece were sealed with PVA adhesive. From this sequential series, samples were selected alternately for treatment with water (which was used as the reference liquid) or with a test liquid. Five alternate samples were treated with each test liquid, although if exceptionally variable results were obtained, this

number was increased. Samples containing knots or splits were not used.

Prior to use on each occasion, the flow meter was cleaned and its reservoir was charged with test liquid. One sample of timber at a time was positioned with 'test surface' under the conical opening of the base plate of the flow tester. The clamping vice was tightened to a standard torque (achieved by applying ca. 2.4 Nm to a 3/8" BSF thread). This clamping pressure pressed the hard metal ring around the opening of the base plate (Fig. 3) into the surface of the timber, thereby forming a seal.

When the sample had been clamped into place, the needle valve between the liquid reservoir and the conical chamber was opened to allow liquid to move by gravity from the reservoir into the conical chamber and up the sight glass. At the moment the liquid level in the reservoir started to drop, a stopwatch was started. When the liquid reached a convenient height near the top of the sight glass, the needle valve was closed and a pressure of 100 kPa was applied to the liquid. The passage of the meniscus down the sight glass was monitored throughout a five minute period. The average distance moved by the surface of each test liquid was expressed as a percentage of the average obtained with water on the matched, alternate samples and the results are presented in Table 3.

In the experimentation described above, an applied pressure was employed in order to expedite the movement of the liquid through the timber. Whilst this does not model precisely the situation in which preservative liquid is applied by brush or spray to the surface of timber, it is considered that the pressure used was too small to introduce significant distortion to the relativity of the movements between the water and surfactant solutions. However, the use of an applied pressure precluded the inclusion of comparative results for white spirit, because under these test conditions this liquid entered the timber too quickly for quantitative results to be recorded.

TABLE 3

Relative volumes of lateral flow of 5% m/m aqueous 'solutions' of surfactants applied at 100 kPa to pine sapwood. Results expressed relative to 'water = 100%'

Surfactant Reference Code	*Relative volume entering timber during 5 minute test period (water = 100%)*
A	92%
B	95%
C	57%
D	11%
E	59%
F	31%
G	17%
H	44%
J	31%
K	52%
L	18%
M	63%
N	33%
P	65%
Q	05%

Discussion of 'surfactant-solution' penetration data

From Table 3, it is clear that none of the surfactants tested enhanced the flow of water laterally into pine sapwood. Indeed, all the surfactants actually led to decreased flow, although with the two alkane sulphonates the decrease was only marginal.

No apparent correlation could be established between flow into timber and either contact angle, surface tension or solution viscosity. It was observed that the greatest flow occurred with the two most soluble surfactants i.e. the alkane sulphonates. This observation highlighted the possibility that excess surfactant in suspension in the water might impede flow and give rise to results such as those observed. To check this possibility one of the alkyl aryl sulphonate surfactants was evaluated at lower concentrations but the results of this work (Table 4) did not indicate that excess surfactant could in general be implicated as a factor impeding flow.

In the apparent absence of a correlation between the physical characteristics of the surfactant solutions and their flow characteristics, it was concluded that the factor exerting the dominant influence on flow was related to the chemical interaction between the liquid and the wood substance. However, in view of the fact that the fundamental aim of this empirical study was to identify surfactants which substantially enhance flow of water into timber, more detailed investigation of the mechanism underlying the above results was considered to be outside the scope of the present investigation and was not pursued.

TABLE 4

Relative volumes of lateral flow of aqueous solutions of an alkyl aryl sulphonate surfactant (reference code C in Tables 1–3) applied at 100 kPa to pine sapwood. Results expressed relative to 'water = 100%'

Concentration of surfactant % m/m	*Relative volume entering timber during 5 minute test period*
1	57%
2	65%
4	59%
5	57%

Flow meter — Penetration of emulsions

Because the relevance of this work to the treatment of timber with wood preservative emulsions was of foremost interest, the flow meter investigations outlined above were extended to examine the flow characteristics of white spirit-in-water emulsions, stabilised with the surfactants listed in Table 1. For most of this part of the investigation the ratio of water and white spirit was held constant at 10 per cent m/m white spirit and 85 per cent m/m water, the remainder of the mixture (5 per cent m/m) being surfactant. The rate of entry of each of these emulsions into Corsican pine sapwood was compared with that of water in the manner already described and the results are presented in Table 5.

TABLE 5

Relative volumes of lateral flow of oil-in-water emulsions (10% white spirit, 85% water, 5% surfactant) applied at 100 kPa to pine sapwood. Results expressed relative to 'water = 100%'

Reference code of surfactant used to stabilise the emulsion	*Relative volume entering timber during 5 minute test period*
A	48%
B	101%
C	61%
D	51%
E	35%
F	73%
G	75%
H	45%
J	41%
K	36%
L	87%
M	28%
N	37%
P	26%
Q	29%

As with the surfactant 'solutions', the results obtained showed great variability between systems with only one emul-

sion entering the timber as quickly as water, and no readily discernible pattern emerging. The flow of five of the emulsions tested was less than that displayed by the corresponding surfactant 'solutions' but the converse occurred with the remaining ten. There was no apparent correlation between this behaviour and the chemical type of the surfactant present.

End grain penetration tests

The results derived from work with the flow meter were, to a large extent, unexpected and are difficult to interpret. Additional experimentation was therefore undertaken using a different technique in order to verify, or otherwise, the results obtained using the flow meter. This additional work employed the standard end-grain penetration test which is described in BS 5707 Part 1.

For each test, five 25 mm × 25 mm sticks of knot free pine measuring 150 mm in length were conditioned at 22°C and 70% RH for at least 7 days prior to testing. After this time each stick was cross-cut at its mid point and one of the two newly exposed transverse surfaces of each stick was placed in a 5 mm depth of decalin to which had been added 0.5 per cent m/m of Waxolene blue A dye. Simultaneously the other new transverse face of each stick was placed in a similar depth of either surfactant solution (to which had been added 0.5 per cent m/m of water blue dye) or emulsion (to the oil phase of which 0.5% m/m Waxolene blue A dye had been added). All the test samples were left in the dye solutions for 3 minutes before being removed, drained vertically for 5 minutes and then placed horizontally to dry for at least 7 days. After this drying period, all the samples were sawn longitudinally at right angles to the growth rings and the average depth of penetration of dye within the central 15 mm of each sample was determined by taking the average of the maximum and minimum distances travelled by the liquid. The results obtained for each liquid are expressed in Table 6 in terms of depth of penetration relative to the depth of penetration occurring with decalin, as given by Equation 2.

$$P = \frac{DP}{DX} \times 100 \qquad \text{Equation 2}$$

where P = penetration factor (%)
DP = mean penetration of test liquid
DX = mean penetration of reference liquid decalin

This test was used to examine the penetration of water, white spirit, five of the emulsions tested in the flow meter and three proprietary dual-purpose wood preservative emulsions (Table 6).

In addition, the effects of the quantity of solvent in the emulsions, quantity of surfactant used to stabilise the emulsion and the hydrophile lipophile balance (HLB value) of the surfactant were also examined and the results of these tests are presented in Tables 7, 8 and 9.

From Table 6 it can be seen that the relative depth of end grain penetration by decalin and white spirit is 1:1.3 whereas the relativity between decalin and water is 1:0.17 i.e. the white spirit penetrated about 7.5 times more deeply than the water. The five emulsions tested showed between 0.09 and 0.13 the flow of decalin with an average value of 0.11. Thus the average penetration observed with the five emulsions was approximately 65% of the penetration of water. The corresponding average value for these five emulsions in the flow meter was 49%.

Although the correlation, in detail, between the two techniques used is not particularly close, the overall indications are very similar indeed, in that they both indicate that in similar conditions all the emulsions tested penetrate timber less deeply than water. The results from the three proprietary dual purpose emulsions indicate that they behave in the same way as the other emulsions tested.

TABLE 6
Results of 'BS 5707 end grain penetration tests' using white spirit, water and a selection of emulsions

Test liquid		*Relative % penetration (Decalin = 100%)*
White spirit (10%) in water (85%)	A	12
Emulsions stabilised with 5%	C	9
Surfactant as indicated: (for	F	13
surfactant reference codes, see	N	12
Table 1)	P	11
Proprietary emulsion	X	16
Proprietary emulsion	Y	16
Proprietary emulsion	Z	10
Water		17
White Spirit		129

TABLE 7
Effect of quantity of white spirit in an emulsion on its penetration into timber, as determined using the BS 5707 end grain penetration test. All emulsions stabilised with 5% of surfactant, Reference Code C.

% of white spirit in test liquid	*Relative % penetration (Decalin = 100%)*
0	8
10	9
35	15
55	41
70	63
85	81
90	116
100	129

TABLE 8
Effect of quantity of surfactant 'C' used to stabilise a 10% white spirit in water emulsion on penetration into pine sapwood, as determined using the BS 5707 end grain penetration test

% of Surfactant C in emulsion	*Relative % penetration (Decalin = 100%)*
2	9
4	12
5	9
6	7
8	9

TABLE 9
Effect of HLB value of surfactant mixture on the penetration of 5% m/m 'solution' of surfactant in water into pine sapwood as determined using the BS 5707 end grain penetration test

*HLB value**	*Relative % penetration (Decalin = 100%)*
4	11
7	11
11	11
14	12
17	14

* HLB values obtained by mixing a polyoxyethylene sorbitan ester and a sorbitan mono oleate in varying ratios.

Of the three additional aspects investigated using the end grain penetration test, the quantity of surfactant present and its HLB value appeared to have rather little effect on penetra-

tion (Tables 8 & 9) but there was a marked positive correlation between the volume of organic solvent present and the penetration which occurred (Table 7). This last finding is consistent with the conclusions of Pearce (1978) and is, of course, also consistent with the deep penetration which occurs when bodied mayonnaise emulsions, which are typically 80 per cent organic phase, are used.

Uptake at refusal

During in situ application of wood preservative liquid, treatment should always be carried out to achieve a manufacturer's recommended minimum coverage, and is frequently done 'to refusal' i.e. until the surface of the timber is running with preservative and will absorb no more. The results reported above highlighted the possibility, indeed the probability, that the volume of liquid which a piece of timber will absorb during an in situ treatment is likely to be greater when an organic solvent preservative is used than when an emulsion is applied. To investigate whether this is indeed the case, an experiment was performed in which matched pieces of timber were selected and weighed. One surface of each piece was sprayed with either organic solvent or an emulsion preservative for 30 seconds. The excess preservative was allowed to run off and then each panel was re-weighed. From its weight, the volume of liquid absorbed by the sample was calculated and the volumes so determined are presented in Table 10.

TABLE 10
Volumes of four proprietary dual purpose preservatives retained by timber from three sources during 30 seconds spraying

Test Liquid	*Substrate* *Rough sawn whitewood (80 years old)* ml/m^2	*Fine sawn pine* ml/m^2	*Planed pine* ml/m^2
Organic solvent preservative	470	380	190
Proprietary Emulsion X	350	300	180
Proprietary Emulsion Y	380	200	160
Proprietary Emulsion Z	320	170	160

From the results in Table 10, it is clear that the volumetric absorption of preservative is likely to be less during treatment-to-refusal with emulsions than with organic solvent preservatives. It would appear therefore than in practice it may well be more difficult and time consuming to apply an effective and uniformly distributed volume of preservative using emulsion type materials.

Distribution

The distribution of insecticide following emulsion and organic solvent preservative treatments has been examined using chemical analysis by several workers (Orsler & Berry 1982, Orsler & Stone 1982).

The distribution of fungicide appears to have been less extensively studied perhaps as a consequence of the fact that there is no reason for expecting that fungicides and insecticides will be distributed differently. Using a bioassay technique, Ingleby (1982) compared the distributions of P.C.P.L. in pine sapwood and demonstrated distribution profiles similar to those revealed in insecticide distribution studies.

To supplement the existing data on distribution profiles, the present work included analysis of timber which had been treated with emulsion and organic solvent formulations containing 1.8 per cent m/m Tri butyl tin naphthenate (T.B.T.N.) The emulsion contained 9.8 per cent m/m organic phase. Representative analytical results are presented in Figure 4. The emulsion used in this part of the work was stabilised with a nonyl phenol ethoxylate surfactant.

The results (Fig. 4) are consistent with the findings of earlier workers, in that they demonstrate that higher levels of biocide are deposited more deeply into the timber when organic solvent preservatives are applied than when emulsion formulations are used. Interestingly, neither in this investigation, nor in any of the previous investigations cited, do the analytical results display as much difference in penetration between the two systems as the end grain penetration test results would indicate might exist. The end grain penetration tests indicate that organic solvent preservatives penetrated 10–14 times more deeply than emulsified formulations, whereas the analytical results do not indicate such a differential.

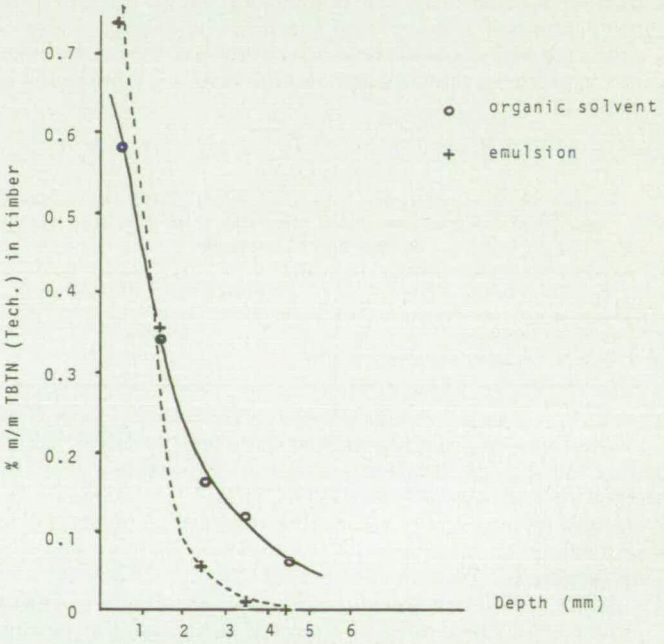

Fig. 4. Distribution of Tri butyl tin naphthenate in pine sapwood surface treated with 300 g/m² organic solvent and emulsion formulations containing 1.8% m/m T.B.T.N.

Without further experimentation it is not possible to conclude with certainty whether this inconsistency arises from the fact that for some reason, such as the limited volume applied, the organic solvent did not penetrate further, or whether the preservative penetrated, after which the biocides were redistributed during drying, in a manner similar to that reported by Jensen & Imsgard (1982). Whatever the underlying mechanism, the picture which nevertheless emerges clearly from this and other studies is one of deeper deposition of biocides following treatment with organic solvent preservative solutions.

At the beginning of this paper, the desirability of obtaining deep penetration was discussed in terms of efficacy, both short and long term. To attempt to assess the significance of the differences in biocide distribution which have been shown to occur following treatment with emulsions and organic solvent preservatives, a programme of biological investigations was undertaken.

Slice tests

Techniques for investigating the depth of fungicide penetration in a piece of preservative treated timber have been described by Sutter (1978) and a 'transferse slice test' was set up employing a technique similar to that used by this worker. In this test matched, near tangential, surfaces of pine sapwood were treated with 250 g/m² of emulsion and organic solvent preservatives containing 1.8 per cent m/m T.B.T. Naphthen-

ate. (The emulsion comprised 2.8 per cent by mass organic phase and was stabilised with a nonyl phenol ethoxylate). Treatment was effected by spreading treating liquid evenly over the upper horizontal surface using a pipette.

After 3 weeks drying, 4 emulsion and 4 organic solvent-treated slices measuring 60 × 40 mm and 5 mm thick were cut well away from the originally exposed end grain. After sterilizing by gamma radiation the slices were exposed in pairs to *Coniophora puteana* FPRL 11E cultured in a 100 mm square plastic petri dish containing malt extract agar (4 per cent m/m dry powdered malt).

Two similarly treated slices were positioned on a sterile plastic gauze which rested on the growing fungus. Incubation was at 22 ± 1°C and 70 ± 5% RH. After 6 weeks the slices were oven dried at 103°C overnight and examined for depth of protection below the treated surface. The average depth of protected timber below the central portion of the treated edge of each slide was determined and the results are presented in Table 11.

TABLE 11

Average depth of protection with 1.8% m/mT.B.T.N. formulation applied at 250 g/m² and tested using the 'transverse-slice test' method and *C. puteana*

Treating Liquid	*Average depth of protection*
T.B.T.N. Emulsion	3 mm
T.B.T.N. Organic solvent	5 mm

This transverse slice test method was relatively easy to undertake and showed differences in depth of protection given by emulsion and organic formulations. However to eliminate the element of subjectivity involved in establishing the depths of protection, an alternative, less subjective method was also investigated.

Sutter (1978) developed a method in which thin pieces of timber were cut parallel to a treated surface and at varying depths below it. By assessing results in terms of weight loss this technique appeared to eliminate the subjectivity referred to above and so a test was undertaken using this approach. Matched pine sapwood, near tangential, surfaces were treated in the same way as previously described for the transverse slice test with emulsion and organic solvent formulations containing 1.8 per cent m/m T.B.T.N. The emulsion stabilisation system was the same as already outlined in connection with the analytical work.

After the treated blocks had dried each was cut up to give several 30 × 10 mm pieces which were further cut to give 2.0 mm thick slices taken from different depths below the treated surface. These slices together with control slices cut from matched untreated timber were sterilised by gamma radiation and exposed to *Coniophora puteana* (FPRL 11E) growing at 22°C and 70 per cent RH on malt extract agar. The samples were then removed, cleaned and oven dried overnight at 103°C. The weight lost by each slice was then calculated and the results are presented in Table 12.

With both the emulsion and the organic solvent treatments only the outer 2 mm samples were totally protected from decay. It can however be seen that with the organic solvent formulation some protection was evident in the 3-5 mm sample (23.7 per cent weight loss compared with an average of ca. 30 per cent with controls). With the emulsion, the greatest depth at which some protection was recorded was in the 1-3 mm sample (14.9 per cent weight loss).

TABLE 12

Average weight losses for 2 mm thick slices, removed from different depths below a pine sapwood surface treated with 250 g/m² of 1.8% m/m T.B.T.N. and exposed to *C. puteana* for 6 weeks

Depth	*Average weight loss %*	
	Emulsion	*Organic Solvent*
0-2 mm	2	1
1-3 mm	15	10
2-4 mm	39	20
3-5 mm	35	24
4-6 mm	40	34
5-7 mm	43	42
6-8 mm	47	36
Controls	27	32

Surface Challenge Tests

It can be argued that the slice tests outlined above have limited value in predicting the relative efficacy of different systems of preservative treatment. This is because the way in which the 'biological challenge' is applied is not a good simulation of practical exposure. It is the protection afforded by the whole profile of biocide within the timber which is of practical relevance. Because of this, it can be argued that evaluation of a surface applied treatment may best be done using a test technique in which the surface of a piece of treated timber is exposed to, or 'challenged' by, wood destroying fungus.

'Surface-challenge' tests have been used for some years in the Fosroc Laboratories. These have simply involved securing open petri-dish cultures of wood destroying fungi against samples of timber and assessing the degree of attack which ensued.

However, certain technical problems are associated with this approach. Consequently as part of this present investigation work was undertaken to refine this procedure. This work is still in hand, and has not yet yielded definitive results. The progress which has so far been made is described below.

The surface challenge procedure described above had three principal attendant drawbacks. Firstly, presumably largely because of the proximity of the malt extract agar food source, the test was excessively severe. Secondly, problems arose in connection with limiting growth to within the area covered by the petri dish. Thirdly, the whole system was very prone to contamination.

A continuing progression of modifications to the original procedure has so far led to the system represented diagrammatically in Figure 5 which overcomes the difficulties outlined above. To conduct an evaluation using this system, test blocks are prepared, and stuck onto the lid-and-tube assemblies. These assemblies together with the gauzes, plastic bags and feeder blocks are then sterilised by gamma radiation. The sterile materials are then aseptically placed onto fresh active cultures of *Coniophora puteana* and the whole assemblies are incubated inside loosely tied sterile plastic bags at 22°C and 70 per cent RH.

So far, two methods of assessing the results have been tried. Initially the test blocks were examined regularly throughout the incubation period for evidence of fungal growth penetrating the treated surface of the block. This method of assessment was used to evaluate the performance of two loadings of two T.B.T.N. formulations and the results obtained are summarised in Table 13.

Both formulations contained 1.8 per cent m/m T.B.T.N. One was a solution in organic solvent whilst the other was an emulsion containing 9.8 per cent organic phase and stabilised with a nonyl phenol ethoxylate surfactant.

The results in Table 13 demonstrate that, even in this very severe test, 150 g/m² of surface applied preservative (half a typical 'commercial' application rate) totally prevented decay both before and after ageing. Although in many respects this is a most satisfactory result, a method of assessing and comparing

formulations yields useful data only if conditions in which failure occurs can be produced. In consequence of this the method of setting up and assessing the test was modified. To set up the test a range of biocide application rates was tested for a fixed exposure period.

Variation of the biocide application rate was effected by using a fixed concentration of each treating liquid and varying its application rate between 50 and 125 g/m^2.

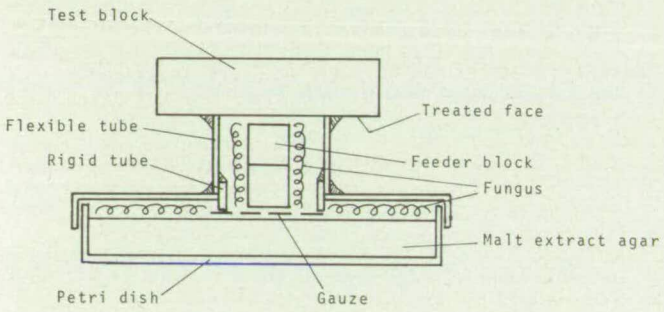

Fig. 5. Surface challenge test system.

TABLE 13
Performance during surface challenging tests of blocks treated with 1.8% T.B.T.N. in emulsion and in organic solvent

Formulation	*Application Rate g/m^2*	*Blocks not aged before testing*	*Blocks aged 6 weeks at 40°C before testing*
1.8% m/m TBTN in white spirit	150 300	No failures after 8 weeks	No failures after 8 weeks
1.8% m/m TBTN in emulsion	150 300		
Controls		All failed by 4 weeks	

Three replicates of each application rate were set up and their performances, both before and after ageing, were assessed by cross-cutting them after 6 weeks exposure to fungus.

To assess the results obtained, the blocks were examined to identify both the highest biocide application rate at which decay was observed and the lowest application rate at which all the replicate blocks remained sound. The results obtained are summarised in Table 14.

TABLE 14
'Toxic limits' indicated by surface-challenge tests of blocks treated with varying quantities of T.B.T.N. (applied as 1.8% m/m T.B.T.N. in either emulsion or organic solvent) and aged at 40°C for 0, 6 or 12 weeks

Formulation	*'Toxic Limits' — g/m^2 T.B.T.N.*		
	Unaged	*Aged: 6 weeks*	*Aged: 12 weeks*
TBTN solution in white spirit	<0.9	near 2.25	near 2.25
TBTN emulsion	<0.9	near 2.25	near 2.25

From Table 14 it can be seen that no failures of unaged material occurred even where the loading of biocide was 0.9 g/m^2. This loading of biocide was equally effective when applied both in emulsion and in organic solvent carriers, as indeed should be expected in the absence of factors such as surface damage or ageing.

After a 6 week period of ageing at 40°C in a ventilated oven, the toxic threshold rose to approximately 2.25 g/m^2 for both the emulsion and organic solvent treatments, and a similar threshold was also noted for both sets of treatments after 12 weeks ageing.

On face value, the results indicate that the effect of ageing on the performance of both emulsion and organic solvent preservatives is similar. However, two possible factors associated with the design of the experimental system have also to be considered before definitive conclusions can be drawn.

The first of these factors relates to the severity of the biological challenge. In seeking to reconcile the resulted obtained with the analytical results it becomes apparent that in tests where the severity of the biological challenge is such that abnormally high loadings of biocide are required to prevent decay, a differential will not be revealed between two loadings of preservative which are both below this abnormally high level. In other words, it could well be that the levels of biocide which are deposited several millimetres below the surface by organic solvent treatments are adequate to provide significant protection in practice but are inadequate to provide protection in the abnormally severe conditions of the above test.

A second possible reason why the test results presented in Table 14 may be giving a distorted impression of the relative efficacy of emulsion and organic solvent treatments is related to the fact that differences in application rates were achieved by adjusting the volumes of preservative applied. Thus 50/g/m^2 of treating solution were used to deposit 0.9 g/m^2 of T.B.T.N. whilst 125 g/m^2 of treating solution were used to apply 2.25 g/m^2 of T.B.T.N. Analytical results have been presented which confirm that, when near-commercial quantities of formulated product are applied, organic solvent preservatives penetrate more deeply than emulsion formulations. It cannot however be taken for granted that the same occurs when very much lower volumes of product are applied. If the application rate is so low that the depth of penetration achieved is limited more by the volume applied than by the characteristics of the treating liquid, a material difference between the penetration of the two types of formulation in question may not occur. This, of course, would lead to similar performance of both types of formulations in biological tests.

For future testing of emulsions in our laboratories, the test procedure will be modified such that 'commercial' loadings of formulated preservative will be applied and the relative long-term efficacy of these treatments will be assessed by biological-challenge after a range of periods of ageing. This approach will avoid the second of the two problems discussed above. Overcoming the problem of an unrealistically severe biological challenge is however rather less straightforward, and it may be that this will always be a problem associated with accelerated biological testing.

Conclusions

This investigation set out to investigate the relative penetration and fungicidal efficacy of surface-applied emulsion and organic solvent wood preservatives. From the results obtained it is clear that, notwithstanding claims to the contrary which are sometimes made, organic solvent formulations penetrate timber more readily than emulsions and at commercial application rates the penetration of organic solvent formulations was superior to that of emulsified formulations. In both of the two 'slice' tests, this superior penetration was apparent in the form of deeper protection against decay.

As an adjunct to the 'slice' tests for assessing fungicidal efficacy, a surface challenge test has also been developed and whilst the technical detail of this test requires further refinement, results already available confirm the efficacy of surface-applied fungicidal treatments.

During this investigation it was noted that, apparently to reduce odour problems, a certain amount of in situ treatment is being done with emulsion formulations which contain significantly less fungicide than is used in organic solvent pre-

treatment formulations and which are therefore intrinsically less effective. In view of the fact that in situ treatment can never be as thorough as pretreatment, the use of low concentration formulations can only be justified for situations where the likelihood of decay is remote and its consequences are of little importance. Full strength, organic solvent (or bodied mayonnaise) formulations should be used when maximum possible penetration of effective levels of fungicide is required.

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DISCUSSION ON PAPER 7

Chairman: Mr J M Baker

THE CHAIRMAN: Although we have not run over the total time the discussion time is rather short so I will throw the paper open straightaway to discussion with the usual request, please, for name, affiliation and could you please speak up.

MR. J. DAVID (Catomance Limited): May I take you back to the first assumption, which was in the Washburn Equation, that time did not matter. I assume that if you are using a volatile solvent as the oil phase with water then time does not matter because it will evaporate and disappear. If you use an oil phase which is not volatile and which remains on the timber you have a time which may be from 48 hours with white spirit to, it may be, 30 years. In that case I would suggest that time does matter. Have you considered that possibility?

MR. L. D. A. SAUNDERS: Yes, indeed we have. Obviously as you saw in the presentation it is not one that we have considered experimentally. One of the underlying thoughts which we had in designing what we did was a consideration of what would be required to satisfy criteria which are being laid down, or are under discussion for being laid down, as standards to describe emulsions. During the discussions which I have heard, and obviously I have not heard all of them, there has been no suggestion that one has to put in clauses concerning the type of solvent used, the type of surfactant used or whatever. So, yes, while I will certainly take your point, that if you get the solvent right you might very well get penetration going on with time in the way you do not with volatile organic solvent, if that is important to the performance of the emulsion then that must be embodied in any document which seeks to set down what a good emulsion is.

MR. B. A. RICHARDSON (Penarth Research International Limited): There is an awful lot of useful information in this paper and it takes a little bit of digesting, so I wonder whether I could make three related comments which might lead to a question.

If you refer to Table 7, this is where the penetration is proportional to the solvent concentration in the emulsion. You would not expect white spirit to be absorbed into wet wood, that is wood wetted by the emulsion water of course. So one of the pre-requisites of this type of penetration is that the emulsifier will coat the wood and protect it so that, in fact, the white spirit can penetrate. So that, in fact, this relationship only exists with certain types of surfactant; it cannot always be reproduced. However, if you have the right type of surfactant this is the relationship which we find always occurs.

Then if you go on to Figure 4, can I suggest that the Tributyltin naphthenate probably hydrolyses and is present as a mixture of T.B.T.O. and a small amount of naphthenic acid in the emulsion, because there is certainly evidence that this is the type of situation which occurs. Incidentally, I would suggest that the small amount of naphtenic acid is actually quite a useful stabiliser for emulsion when you are using T.B.T.O. So it has a useful side function in this particular situation.

Finally in the case of Table 12 the penetration with Tributyltin naphthenate in organic solvent is really not much and actually I suggest that the results are indicating the

degree of filtration or the absorption that is occurring. I imagine, for instance, that the solvent in the emulsion is actually penetrating very much further than the T.B.T. is penetrating and that perhaps the results are indicating the difference between T.B.T.N. in organic solvent and T.B.T.O. in emulsion. Once again the hydrolyses may account for the difference.

Those are just three comments based upon our own observations which I should like to make from what I have noticed in the paper.

Thank you very much for presenting these observations for all of us. They are very helpful.

DR. W. P. K. FINDLAY (Consultant): I want to ask two very simple questions. I am not a physicist and I do not pretend to understand the reasons for capilliary entry of fluids but I understand that the primary purpose of emulsions is to put a large quantity on so that penetration can go on considerably longer than with a solution which will only be a small quantity at each application. So with one application of emulsion you will get the same effect as with several applications of solvent preservative. Secondly, surely one of the major reasons is that it reduces the fire risk enormously. Am I right that those are the two principle reasons for using emulsions?

MR. L. D. A. SAUNDERS: If I can take the second of those propositions first. Yes, it certainly does reduce the fire risk enormously. Regarding the first proposition, your suggestion is not my understanding of the reason why mobile sprayable emulsions are used. Certainly it is my understanding that your suggestion is the reason why *mayonnaise* type emulsions are used and I think the logic of that is very sound. However, particularly with formulations which do not contain so much biocide as organic solvent formulations, your first suggestion is not my understanding of why emulsions are used.

DR. W. P. K. FINDLAY: I am thinking of the mayonnaise type.

DR. F. IMSGARD (Gori Research Limited, Denmark): I have a question concerning the moisture content in wood and to what extent that affects the penetration of the emulsion. If you treat relatively dry wood the water will suck into the wall of the capillary rather fast and what you are left with is probably a product where the viscosity could go up very high and you end up with rather a gel which is what you find when you remove your water from the emulsion. I should also like to comment on what Mr Richardson said. T.B.T.N. does not hydrolyse in water emulsion and it will stay for years.

MR. L. D. A. SAUNDERS: If I can come back to your question. No, we did not look at the effect of the moisture content of the timber which we were treating. As I indicated in the paper we felt that dealing with damp timber, or wet timber, introduced an added degree of technical complexity, and we were not prepared to commit the resources to deal with the problems that tend to accompany that sort of work. We therefore limited ourselves to dry timber although, of course, we recognise that the reality of life is that in in-situ treatments we are not always treating dry timber.

THE CHAIRMAN: I do not know whether you heard, Barry, the last remark which was about hydrolyses and T.B.T. naphthenate. Perhaps you can take that up outside the session.

MR. B. A. RICHARDSON (Penarth Research International Limited): I think it is a difference of opinion.

THE CHAIRMAN: That is rather more daunting.

DR. J. W. W. MORGAN (Princes Risborough Laboratory): I should like to make one comment on which I invite the speakers to make their own observations and ask one question. The comment relates to the use of the Rideal Washburn Equation which I understood to be an equation which describes capillary flow. You did say, in fact, that you applied pressure of something like one atmosphere, where I would expect a totally different set of equations to apply, which were less dependent upon the surface characteristics of the liquid. Nonetheless you proved your point in subsequent observations.

The question concerns the comment made at the end, that the depth of penetration was not adequate to prevent fungal attack in your fungal tests. I was just wondering whether you had any opinions on what depth of penetration you would have expected to protect the timber.

MR. D. P. BLOW: I think that really depends on the biocide that you are using. As one of the slides showed, if you were using an AAC, for example, there were quite considerable depths of apparent protection but the fungus still seemed able to grow through this treatment. An adequate depth of penetration for an AAC may be, for example, 10 mm while for a more toxic fungicide 3 mm might be sufficient. I think it is a matter of considering each biocide independently.

MR. L. B. WOODHOUSE (Cementone-Beaver Limited): I should like to put to you a view on a question I think you posed about why there are different rates of toxicant between insecticide and fungicide. In the case of insecticide it is accepted that the solvent, the system with the organic solvent material, plays a part in the eradication kill, and I believe that people use additional insecticide to make up for that lack of kill because there is very little organic solvent. In the case of fungicide treatments it is not quite the same because they are not used as eradicant treatments, only as a preventative treatment whereas, of course, insecticides are used as eradicants.

Secondly, I was very pleased to see you highlight the effect of the higher oil quantities which certainly would bear out our own findings, that the higher the oil content the better the penetration.

MR. L. D. A. SAUNDERS: Thank you, Lewis, for the information about why higher insecticide levels are used; that is logical. It still, to my mind, leaves open the question as to why lower fungicide levels are considered acceptable in emulsions. I still do not have a feel for that.

THE CHAIRMAN: I think we have time for one quick question only.

DR. A. F. BRAVERY (Princes Risborough Laboratory): I have a comment which relates to a point John Morgan made, if I could just put it in a slightly different way. It seems to me that the bioassay technique you were using in your first two approaches, the Peter Sutter slice test, is a good way of determining compliance with a requirement for a given depth of protection but it does not take us very far down the road towards deciding what level you should set as that requirement in the first place. That is a similar point to the one John was making. You also made the comment in your paper that you were worried about the severity, the reality of the test in relation to severity of the attack. What do you see as ways in which you can manipulate the severity to make it more realistic in relation to the sort of challenges that might occur in practice.

MR. D. P. BLOW: I am sure you will appreciate it is difficult in a biological laboratory test to make the fungal-challenge equivalent to that expected in practice. There are in practice a variety of situations and conditions where remedially-treated timber could be challenged by fungus.

What we were trying to do was to reproduce the sort of situation where one has treated a piece of timber but nearby there remains an active source of fungus that can challenge the treatment. To make the surface challenge test more relevant while still using the same type of procedure one could reduce the nutrient available to the fungus. This would be done by using water agar in place of malt extract agar. Those are my only thoughts on that subject at the present time.

THE CHAIRMAN: I am sorry to break it off with the discussion still running although I think it is a good way to go. I think we have heard a paper this afternoon which is provocative in its ideas and which has been presented with great flair. We have also had a very lively discussion which I am sure will be continued outside the meeting. Can I, on behalf of you all, thank our two speakers for the paper. *(Applause).*

RESEARCH AND DEVELOPMENT IN WOOD PRESERVATION AS AN ADJUNCT TO CUSTOMER SERVICE

by A. R. M. Barr
Catomance Limited

Introduction

In this paper the in-house laboratory testing and the formulating of wood preservatives are presented against a background of customer service.

The industrial biologist working in the fields of technical service and product developments associated with wood preservation has not only be to innovative in his scientific work but must also develop skills of detection and diplomacy to help him when dealing with those who have only a peripheral or incomplete knowledge of the subject.

The great value of a comprehensive laboratory back-up service is that it enables the manufacturer, not only to assess more accurately market demands, but to formulate his products to suit the ever-changing requirements of his customers.

To understand the nature and complexity of problems thrown up in this field a sound knowledge of the biology of the attacking organisms, the anatomy of wood and the chemistry and physics of wood preservatives is necessary. When considering research and development work the influence of the environment on the preservative and the preservative on the environment is also of particular importance.

Laboratory Practice — Customer Service

(a) Analysis of Customer 'Demands'

An analysis of our laboratory records over a five year period in respect of remedial treatment customer demands gave the following breakdown (Table 1) of mycological, entomological and chemical based requests expressed in percentage terms.

A closer examination of the work done by the biologist reveals that of the 11per cent insect identifications carried out in the laboratory 37 per cent of these were associated with wood-boring insects and the remaining 63 per cent with general household insect pests. Anobium punctatum accounted for 23 per cent, Xestobium rufovillosum for 10 per cent and weevil, wharf borer, powder post beetle and bark borer made up the remaining 4 per cent of the wood boring insects.

The percentage occurrence of household insect pests is listed along with the wood-boring insects in Table 2.

Of the 35.1 per cent of investigations into insect activity in wood, 89 per cent of these were accredited to Anobium punctatum, 9 per cent to Xestobium rufovillosum and 2 per cent to Weevil and Wharf Borer, Table 3.

Wet rot fungi made up for 45 per cent of the specimens of decay organisms examined; 29 per cent were Serpula lacrymans and the remaining 26 per cent were divided between soft rot fungi and non-wood-rotting fungi, Table 4.

(b) Case History

It is clear from this appraisal that much of the time spent by our industrial biologists is given over to looking at specimens of

TABLE 1
Analysis of Laboratory Records

Biologist			*Chemist*
Insect Identification	*Fungus Identification*	*Insect Activity and Chemical Analysis*	*Salts Analysis in Plaster/Brickwork/Mortar*
11.0%	21.8%	35.1%	32.1%

TABLE 2
Percentage of insect types identified from a five year spread of customer requests.

Wood-boring insects		*Household insect pests*	
Furniture Beetle (Anobium punctatum)	23%	Carpet Beetles (Anthrenus spp./Attagenus spp.)	19%
Death Watch Beetle (Xestobium rufovillosum)	10%	Biscuit Beetle (Stegobium paniceum)	16%
Wood-boring Weevil (Europhryum sp./Pentarthrum sp.)	4%	Mealworm Beetle (Tenebrio molitor)	6%
Wharf Borer (Nacerdes melanura)		Spider Beetle (Ptinus sp./Niptus sp./Gibbium sp.)	3%
Powder Post Beetle (Lyctus brunneus)		Garden Weevil (Otiorrhynchus sp.)	2%
Bark Borer (Scolytidae)		Ground Beetle (Harpalus rufipens)	4%
		Plaster Beetle (Cryptophagus sp./Lathridius sp.)	4%
		Flies/Bugs/Moths (Diptera/Hemiptera/Lepidoptera)	13%
		Wasps/Bees/Others (Hymenoptera)	2%

decayed or insect infested timber with the view to identifying as accurately as possible the cause and reason for biological failure. Identification techniques, therefore, play an important role in the day-to-day running of the customer service side of laboratory work. The accuracy of an identification is often dependent upon the amount of background information supplied with the specimen, and case history and specimen presentation are, therefore, a fundamental part of this work.

TABLE 3
Examination of wood samples for evidence of active infestation; figures in brackets indicate the percentage of infestations which were found to be active.

Furniture Beetle	*Death Watch Beetle*	*Weevil/Wharf Borer*
89% (12%)	9% (2%)	2% (2%)

TABLE 4
Percentage of fungal types identified from a five year spread of customer requests.

Wet Rot	*Dry Rot*	*Soft Rot/Non-Wood-Rotting Fungi*
45%	29%	26%

Whenever a sample is submitted for laboratory examination it is extremely useful, and in some cases essential, to have as much background information as possible if an accurate appraisal of the situation is to be achieved. Information relating to the type of property (e.g. domestic, commercial, vacant, inhabited, age, etc), the situation from which the sample was taken (e.g. floor, roof void, upstairs, downstairs or in my lady's chamber!), the structure (e.g. rafter, joist, skirting board, etc), the conditions regarding the building (e.g. ventilation, dampness, weatherproofness, heating, etc) and the colour, texture and distribution of the agents of decay should always accompany any sample for laboratory examination. Site inspection reports are, therefore, vital to this form of customer service and we expect they should follow closely the format which we have developed over the years:–

(1) Address of Property
(2) Type of Property: Terraced/Detached/Semi-Detached/Commercial/Domestic
(3) Treated or Untreated Timber:
    If Treated:
    (a) Which Timbers were treated
    (b) Date of treatment, if known
    (c) Name of Company who carried out treatment
    (d) Name of Product used in treating timber
(4) Why were the timbers treated
    (a) Dry Rot attack
    (b) Wet Rot attack
    (c) Insect Infestation
        Type of Infestation
(5) Nature of Complaint/Reason for site inspection
(6) Sample taken for laboratory examination
    (a) Sample type:Fungus/Insect
    (b) Substrate Type: Wood/Brickwork/Composite
    (c) Source: Skirting Board/Wall/Ceiling
    (d) Situation: Roof Void/Cellar/Kitchen
    (e) State: Ventilation/Dampness/Temperature
    (f) Structure: Colour/Texture/Distribution

(c) Techniques

Having completed the site inspection report and obtained the specimens for laboratory examination, they should be despatched to the laboratory as soon as possible after selection since the natural processes of deterioration which are often accelerated through the act of packaging can render specimens completely unrecognisable. Separate correctly labelled containers such as bags or boxes should be used for each specimen so as to avoid any confusion due to cross contamination. White card or paper strips with the relevant background information printed in pencil (ink is not satisfactory as it may run and become illegible if the material is water or solvent laden) should be inserted in each package. Specimens should be packed in such a way as to avoid damage in transit, for example, fragile insect specimens should be placed in matchboxes containing tissue paper.

An adhesive tape impression technique may be usefully employed when it is not possible to send a representative sample of the decay to the laboratory. Here an adhesive cellulose tape such as 'Sellotape' is pressed into intimate contact with the surface with suspected fungal decay and then carefully peeled off and stretched, adhesive side downwards, over the empty tray of the matchbox. The tray is then returned to the matchbox sleeve and, after labelling, is ready for posting to the laboratory. Air-tight containers such as plastic bags suit materials requiring moisture content determinations such as plaster or brickwork (information in such cases to be affixed to the outside of the package and *not* enclosed with the sample) but should be avoided at all costs as a means of packaging biological specimens unless such specimens are to be examined the same day otherwise the only 'specimen' to be examined is often just a spoonfull of dirty water.

Laboratory Practice — In-House Service

(a) Analysis of Departmental 'Demands'

When we look at the results of our examinations, as set out in Table 2, we find that they colour the views of the marketing executives which set analysis of customer service demands against marketing constraints such as availability of raw materials and acceptability of suitable biocides and helps the industrial biologist to structure his research and development programme. The oil crisis of the late sixties which brought about a dramatic increase in the price of organic solvents was directly responsible for the development of water based emulsion formulations for the remedial treatment of timber against insect and fungal invasion.

Simple oil in water emulsions of fungicides and insecticides were found to be unwieldy and self-emulsifying concentrates were developed with improved emulsion stability and wetting out properties built into the formulation.

'Bats in the belfry' gave a push to the development of permethrin based formulations for the in-situ treatment of timber since the commonly used insecticides were found to be unacceptable.

The concept of co-solvency of insecticide and fungicide to enhance the retention of the contact insecticide has developed as a result of a better understanding of formulation in respect of penetration and permanency.

(b) Accelerated Test for Ready to Use Formulations

Marketing and development having agreed a formulation, there is no guarantee (if you'll forgive the expression) that it will work. Bioassay techniques for in-house evaluation of remedial treatment formulations are not intended primarily to give information about toxic limits but to indicate to us in comparative terms whether or not a treatment is capable of imparting resistance to the treated substrate.

We are not trying to pass or fail a 'test' but to ensure that a change will not vitiate years of field experience. The evaluation thus covers a range of tests many of which are modified and developed from standard tests in our own laboratories.

In most cases wood, in the form of wood blocks (Pinus sylvestris) or wood veneers (Fagus sylvatica), is used as the substrate. Internal standards are always included (5 per cent pentachlorophenol for fungus tests and 0.5 per cent gamma-

hexachlorocyclohexane for insect tests) together with untreated viability controls in assays of this type. The most common form of accelerated bioassay for fungicidal activity is the agar plate test using either a wood-rotting basidiomycete (Coniophora puteana) or a soft rot fungus (Chaetomium globosum) as the assay organism. Blocks or veneers of wood usually after a three minute dip treatment in the preservative formulation are air dried (minimum 48 hours for veneers and up to 28 days for wood blocks) before being subjected to the assay procedure.

Soft rot evaluation is usually carried out in Petri dishes using a mineral agar (carbon source for fungal growth supplied by the test specimen) with direct contact between agar and specimen. The test, after artificial infection of the treated and untreated specimens by spraying with a spore suspension of the test fungus in sterile water, is made at 28°C over a period of not more than 14 days.

With wood-rotting basidiomycetes the test differs in five respects: (1) the treated and untreated test specimens are supported on sterile plastic frames and are therefore not in direct contact with the agar, (2) the agar contains all the growth requirement for the development of the test fungus, (3) infection is by hyphal contact rather than through spore germination, (4) the temperature is six degrees lower at 22°C, and (5) the incubation period is usually 28 days rather than 14 days.

The activity of the insecticide in a formulation is gauged by the ability of a treated surface to bring about knockdown and kill of adult beetles. We choose adult Stegobium paniceum beetles between one and two weeks of age which are brought into contact with the surface of samples of treated and untreated wood by presentation in a 25 mm × 10 mm cross section glass cell. The glass cell containing five adult beetles is placed open end in contact with the wood sample and held in place with a rubber band. The time to knock down is recorded and the test is continued for a total of 24 hours. At the end of the test period the beetles are removed from the test system and placed in sterile 50 mm Petri dishes and the percentage kill calculated after a 6 hour recovery period (this period being a working day).

Information on the life expectancy of the active ingredient of wood preservative formulations is also of considerable importance and bioassay tests run in conjunction with accelerated ageing procedures are also a useful part of in-house testing. Heat ageing at 40°C for periods of up to and including 12 weeks in an air circulating oven is one such procedure which is particularly relevant to remedial treatment formulations. Edge sealed wooden blocks are quantitively treated by pipetting a known volume of a preservative formulation on to one face of the block. The blocks are then air dried at room temperature for 28 days before being half sectioned through the treated face, one half for accelerated ageing and the other for comparative analysis. The sample for comparative analysis is sealed in aluminium foil and held at room temperature until the ageing test has been completed. The 'aged' and 'unaged' specimens are finally conditioned by being exposed to room temperature for 7 days before chemical and biological evaluation.

(c) Screening Tests for Candidate Wood Preservative Chemicals

The laboratory procedure for screening candidate chemicals for biological activity has evolved because the nature of our involvement in materials preservation is rather wider than that of a company dealing only in wood preservatives. The range of materials to be protected includes not only cellulose in the form of wood, paper and textiles but also covers leather, plastics, non-cellulosic textiles, paint and adhesives. Information on the activity of candidate chemicals against macro-fungi, micro-fungi, bacteria actinomycetes, yeasts and in some instances algae must be obtained from a simple, rapid yet meaningful set of tests. Such tests must, therefore, employ an easy to treat, quick drying, uniform substrate to support the candidate chemical. An APV Carlson 50 mm diameter grade W/2 cellulose food filter has been found to have the right characteristics of uniformity of composition, drying properties and availability in that it is an off-the-shelf item. The 2.5 mm thick filter discs are also sufficiently robust to stand up to the rigours of some of the test procedures particularly when water soluble candidate chemicals are being evaluated.

The choice of test organisms has developed out of two main considerations, one the ease of culturing and two their occurrence as biodeteriogens over a wide range of material types; as indicated by the materials listed in brackets after each organism. Coniophora puteana (wood), has therefore been chosen to represent the macro-fungi and is used in the form of a mycelium challenge test. Chaetomium globosum (wood, paper, textiles, plastics), Aureobasidium pullulans (wood, textiles, plastics, paint), Aspergillus terreus (plastics, electronic equipment, vegetable matter), Paecilomyces variotii (leather, plastics, textiles both cellulosic and non-cellulosic), Penicillium funiculosum (textiles, paper, plastics, vegetable matter) are the micro-fungi used as a mixed spore challenge in a mineral agar plate test.

The Gram-negative Pseudomonas aeruginosa and a Gram-positive Bacillus species (paint, adhesives and cellulosic and non-cellulosic textiles) are used in a zone of inhibition test on nutrient agar plates as a means of assessing activity against bacteria.

Streptomyces rubrireticuli (rubber, plastics, wool) is used in a zone of inhibition plate test for assessing the activity against actinomycetes.

Activity against yeast is assessed using a sugar fermenting malt agar plate test with Saccharomyces cerevisiae (ubiquitous) as the test organism.

Algistatic activity is assessed in a tube culture test using an Oscillatoria species as the test organism.

(d) A Technique for Assessing the Influence of Formulation on Active Ingredient Activity

In the last few years it has become increasingly more important to have as wide an understanding as possible about the influence of formulations on activity and availability of insecticides used in wood preservatives. A test has been developed in our laboratory to help to obtain this kind of information. It is based on a closed cell 24 hour contact technique using Stegobium paniceum as the test insect.

This beetle was chosen for a number of reasons: (1) it belongs to the same family, Anobidae, as its two congeners Anobium punctatum and Xestobium rufovillosum, (2) it is of the same order of weight and body size as Anobium punctatum, and (3) its life cycle under laboratory conditions of 60 per cent relative humidity at 30°C is completed in 7 to 8 weeks.

The test is carried out inside a 125 mm × 35 mm diameter glass tube closed at one end by standing upright in the bottom half of a 50 mm glass Petri dish and at the other end by sealing with an APV Carlson 50 mm diameter cellulose food filter with glass ring. The whole assembly is held in place by the use of a strong elastic band — (Fig. 1). Before assembly, one half of the inside surface of the glass tube is coated with an emulsion of polytetrafluoroethylene (PTFE) and air dried at 120°C for 1 hour. The test is conducted witht he PTFE coated half of the glass tube on top so that its end is closed by the filter disc and glass ring. Five beetles, one to two weeks of age, are introduced into the system before securing the assembly with the elastic band.

When assessing the influence of an organic solvent alone on the activity of the adult beetles, two results can be achieved using this method: (1) the effect of contact with the solvent vapour only, and (2) the effect of contact with the solvent liquid. The solvent under investigation is introduced into the system by pipetting a known volume on the surface of the filter disc in the area enclosed by the glass ring. For a solvent vapour

only assessment the assembly is maintained in the upright position, i.e. with the filter disc at the top end of the assembly. In this position the beetles can only climb half way up the wall of the glass tube as they cannot adhere to the P.T.F.E. coating and hence only come into contact with the vapour of the solvent.

The time to knock down is recorded and the test is continued for a total of 24 hours. At the end of this period the beetles are removed from the assembly and placed in a sterile 50 mm glass Petri dish for a recovery period of 6 hours. After this time the percentage mortality for solvent vapour contact is calculated.

For liquid solvent contact the procedure is repeated; the only difference being that, in this case, the assembly is inverted. In this position the beetles can only come into contact with the solvent saturated filter disc since the P.T.F.E. coating prevents them from escaping into the other half of the tube. Once again, the time to knock down is recorded and the percentage mortality for liquid solvent contact calculated for a 24 hour exposure with a 6 hour recovery period.

The following tables give some indication of the influence of hydrocarbon solvents on the activity of adult beetles and illustrates one use of this technique.

Influence of Solvent-type on Beetle Activity

TABLE 5
Solvent Vapour Contact

Solvent Type	*Aromatic Content*	*Time to Knock Down*	*% Mortality*
White Spirit	⩾ 1%	> 90 minutes	Nil
White Spirit	⩽ 25%	45 minutes	Nil
White Spirit	⩽ 90%	20 minutes	20%
Xylene	100%	5 minutes	40%
Control (Air)	—	—	Nil

TABLE 6
Liquid Solvent Contact

Solvent Type	*Aromatic Content*	*Time to Knock Down*	*% Mortality*
White Spirit	⩾ 1%	>90 minutes	20%
White Spirit	⩽ 25%	6 minutes	80%
White Spirit	⩽ 90%	6 minutes	80%
Xylene	100%	4 minutes	100%
Control (Air)	—	—	Nil

(e) Special Tests for Updating Background Knowledge on Wood Preservation in the Remedial Environment

From time to time special problems arise from our reading of the literature or an observation which has no obvious explanation. One example to illustrate this arose from discussion on health hazards to operatives.

Mould spores have long been recognised as a source of allergens but work in Poland has drawn attention to the possible clinical hazards of fungal flora in the houses of people suffering from neoplastic diseases. Recent work by Blyth and Hardy reported on by Austwick in his paper "Human Mycotoxicosis — Past, Present and Future" indicates that the inhalation of fungal propagules of organisms producing mycotoxins may lead to clinical syndromes.

Since microbial succession is the natural order of decay, an investigation was undertaken to examine the nature and type of those organisms responsible for the lysis of the fruit body and vegetative growth of the wood rotting basidiomycete Serpula lacrymans. Many of the fungi producing mycotoxins grow saprophytically on dead or dying vegetable matter. Tests were, therefore, undertaken on growths of Serpula lacrymans from twenty different sites throughout the British Isles to try to establish the nature and type of the organisms responsible for this decay process. Identification of the organisms associated with the lysis of Serpula lacrymans was achieved using a selective agar plate isolation technique and the isolates were subcultured for identification purposes. Table 7 gives the frequency of fungal species isolated from the twenty specimens of Serpula lacrymans.

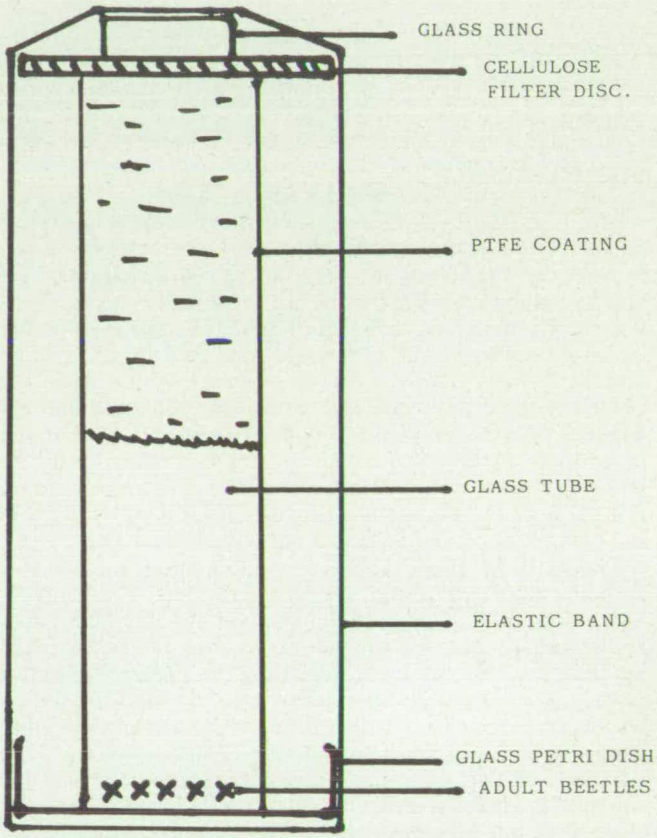

Fig. 1. Test assembly for assessing formulation influence on insect activity

TABLE 7
Micro-organisms isolated from specimens of *Serpula lacrymans*

Micro-organisms	*Frequency of Occurrence (in percentage of total number of specimens examined)*
Penicillium citrinum	35.0
P. paxilli	40.0
Penicillium spp. (not typed)	25.0
Fusarium sp.	25.0
Stachybotrys atra	5.0
Trichoderma viride	15.0
Pseudomonas spp.	100.0

In this investigation, three micro-fungi known to produce mycotoxins, namely, Penicillium citrinum, Stachybotrys atra, and Trichoderma viride, together with a possible fourth in the form of a Fusarium species, were found to be associated with the natural decay of Serpula lacrymans. This work will be published shortly in detail elsewhere but it underlines the importance of wearing protective clothing when working with fungal decay before chemicals are applied.

The work covered by this paper can be seen to offer challenges to extend our knowledge of the biology of the problems presented and the opportunities which the application of a little ingenuity can produce.

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DISCUSSION ON PAPER 8

Chairman: Mr P. D. North

THE CHAIRMAN: May we have any questions or comments, please.

MR. K. FEARNLEY (K Fearnley Limited): I must express surprise, and I think also on behalf of several people here, that remedial treatment companies should send such simple specimens for identification.

THE CHAIRMAN: Absolutely; I entirely agree.

MR. J. M. BRICKNELL (Fosroc Limited): It was a very interesting paper. I am very interested in the number of samples you get, in particular the insects you have sent to you for identification and to comment on whether or not the attacks were active. I was surprised, in fact, that a lot of remedial companies bother because usually the surveyor sees it and they just bore holes and say: "Thank goodness for that, we can treat the place" but obviously there are some who do want to look and find out whether the attack is active or not. It can be very hard on site certainly to determine whether an attack is active. What do you do in the laboratory? If the companies get a negative result is it really much help to them because surely if they had taken the next piece of timber that could have been active.

MR. A. R. M. BARR: That is a very fair comment. What we do in the laboratory, John, is a destructive test. The sample is broken up, the frass is collected and laid out on a filter paper and it is observed to see whether in fact there are any traces of movement within the frass, indicating the presence of active larvae. Also during the destructive breakdown of the timber we are looking to see whether or not there are any live adult beetles present within the wood. Yes, I agree with you. The sample is all that we get and how representative it is of the situation is always a difficulty. We also do chemical analysis along with our biological evaluations to see whether or not there are, in fact, pesticide residues still left in the timber but we are entirely in the hands of the surveyor in respect of how representative the particular specimen is of the environment that he is examining.

MR. A. C. OLIVER (Bucks College of Higher Education): I was also very interested in your list or organisms, the insects and fungi that you were finding. I was surprised that you had not had any Longhorn, but we will let that pass. I would have thought that they would have cropped up in five years.

MR. A. R. M. BARR: In terms of Longhorn, Alan, we have only had two suspected specimens of Longhorn. We sent both cases to Risborough and on both occasions they were found to be forest Longhorn. Never, in five years have we had a sample of timber that had Longhorn in it.

MR. A. C. OLIVER: I meant Longhorn of any variety. My question really is whether you could be more specific on wet rot, whether you can give individual indications of the species.

MR. A. R. M. BARR: The species that we find growing on the surface of decayed timber? Well we frequently find Chaetomium globosum which is strongly cellulitic. We often find a variety of Penicillium species, many of which have no ability to degrade cellulose whatsoever and therefore must be growing on the breakdown products of the timber that has been decayed or on the organism which is responsible for the timber decay in the first place. We frequently find Trichoderma. Again the species of Trichoderma that we find is not one which is strongly cellulitic. We also find a variety of (Cladisporium) species and it is this species that turns up more often than any other.

MR. A. C. OLIVER: My question was really on wet rots rather than soft rots.

MR. A. R. M. BARR: Wet rots. Sorry, my apologies. In the case of wet rots I have not done a breakdown of the difference between Coniophora and Fibroporia and the like. Most of what we see is probably Coniophora Puteana. We see more of that certainly than any of the other wet rot species.

THE CHAIRMAN: Could I just make a possible suggestion about the Longhorn situation. It could be that attack by that creature is so obvious that nobody even needs to send it in for identification. That is only a suggestion.

MR. J. G. MWANGI (Imperial College): It is well documented in the literature that Chaetomium globosum is not a good test organism for softwoods, especially pine. What do you think about that?

MR. A. R. M. BARR: A point which I did not raise and a point which is, in fact, raised in my paper is that the Company deals not only with the preservation of timber but with the preservation of a very wide range of materials. Our screening tests use Chaetomium globosum on many occasions because of the fact it is an organism which colonises a wide variety of cellulosic materials. I cannot comment because I am not aware of the fact that it has been documented in the literature as not being particularly aggressive towards timber. David has his hand up?

DR. D. J. DICKINSON (Imperial College): On the point of soft rot — are you ready for another question?

MR. A. R. M. BARR: I am sorry, my apologies, I thought you were indicating that you had something to add as far as Chaetomium globosum and the timber decay situation is concerned. I believe that Chaetomium — and Alan will probably help me in this situation — is an organism that is often found growing on timber in the cooling tower situation. So it is an organism which requires very wet conditions in timber indeed.

DR. D. J. DICKINSON: I have a question relating to soft rot. I am assuming that most of the occurrences of sapwood soft rot you are getting are coming from properties if they are from the remedial treatment industry. What sort of locations within the properties are you getting the occurrences of soft rot from?

MR. A. R. M. BARR: I have not looked at it in that way, David, and I could not truthfully comment.

DR. A. F. BRAVERY: Could I make a comment about your isolation work from the Serpula fruit bodies and then pose a question. The fact that you isolated these organisms at all and the fact that they came from the fruit body is relevant but their origin must have been in the air originally. The significance of them in terms of health risk will therefore depend on the concentration of them which builds up in the air. I think it is fairly well documented already that you really need very large concentrations of spores before they can be associated directly with a potential health risk and there are techniques for the measurement of those concentrations in the atmosphere. However, they are quite difficult and time consuming to use. Would I be right in assuming from your description that you actually have not been able to go as far as to measure concentrations in the air?

MR. A. R. M. BARR: Quite right. All we did was an initial investigation to see what organisms were responsible for the breakdown of Serpula in a biological succession situation.

DR. A. F. BRAVERY (Princes Risborough Laboratory): If I might ask one question in relation to the Stegobium knockdown test which is intriguing. How do you correlate the results with the wood boring insect activity? You did make the point yourself that you see it as an adult beetle knockdown situation

and not a measurement of potential activity against larvae. I was just intrigued to know what relationship you saw between it and the use of wood preservative formulations in the remedial practical situation.

MR. A. R. M. BARR: At the moment, Tony, the test is still in its early stages of development. We are using it only to look at organic solvent activity, and what influence the organic solvent has on a contact insecticide or an ingestion insecticide embodied into a formulation is the next stage in this work. We have not done any comparative trials whatsoever against wood boring organisms. It is only an indication of how the organic solvent may behave towards a beetle. Whether that can be truly related when one is looking at another species of insect is something that we have not, as yet, gone into. We do intend to try some correlations with adult Anobium to see whether or not we get a parallel situation. It is in the pipeline.

MR. J. M. BAKER (Princes Risborough Laboratory): Perhaps to save you some time I can say that it does not correlate very well. Certainly not with the organic phosphate compounds or cabonates. We did look at it with a research student fifteen years ago. It is a very attractive insect to use for bioassay but unfortunately you do not get the same ranking order as you do with Anobium. So beware.

MR. A. R. M. BARR: Thank you.

THE CHAIRMAN: Could we have one final question. *(No response)*. Because we have run over time, not because of Alan but because of previous activities and I know that the President is terrible when roused or kept waiting I think it is time that we brought this question time to a close. As I expected, Alan, it was a stimulating and most enjoyable paper. I hope as a result of it you will be getting better specimens sent into you, if that is the right phrase. I am able to reveal that when he was a child he wanted to be a bank clerk, which is a most ridiculous idea and I, for one, am very glad that he did not become a bank clerk. I hope you will join me in thanking him for a most enjoyable ending paper to this Convention. *(Applause)*.

CLOSING REMARKS BY PRESIDENT

As the hour is getting on, Ladies and Gentlemen, I will be brief in my closing remarks. It is, of course, a pleasure for the honourable President to bring to an end the formal part of the 36th Annual Convention of the B.W.P.A. at Casmbridge. I have been particularly impressed this year by the quality of the papers and also the very professional way in which they have been presented. This has been complemented by the stimulating question and answer periods. We have no doubt been assisted by the modern equipment, after we had overcome initial difficulties during the first paper, of this excellent new venue. The Peterhouse Theatre has proved to be a most suitable alternative to our usual meeting place in Ben't Street and I hope it will be acceptable as a regular future venue. Possibly the seats are a little harder and older than the University Lecture Romm but we will look into that one. They have probably also served their purpose. *(Laughter)*.

There are two presentations which had that little bit extra this year: Paper number 5 on Tin Compounds from Germany and Denmark. I think the snappy change from speaker to slide operator and back again kept things flowing very nicely. The other paper was John Levy's solo performance on work at Imperial College past, present and future.I am sure that we could have wished to ask him some questions on that, but some other time perhaps.

In thanking the authors for their papers I should also like to combine this with recognition of the quiet efficiency of the Chairman of each session. This assists considerably in the smooth flow of the convention. Ladies and Gentlemen, may I ask you now collectively, as you have done individually, to recognise the contribution of the Authors of the papers and the Chairman of the sessions. *(Applause)*.

All this would not have been possible without the devoted and painstaking work over many months and during the Convention of the B.W.P.A. permanent staff. I can assure you that almost as one Convention is finished work on the next one is beginning and already the date for the next year has been pencilled in. I would not normaly pick out any individual member of the B.W.P.A. because thay work together as a team, but I think as most of you know it would not be possible for me this year to aviod particular reference to Jack Bick and Jean Riman. They have already completed what will be their last Cambridge Convention, at least as organisers-in-chief. Most of you know, I am sure, that they are taking well earned retirement at the end of the year. There will be other occasions nearer the time when we can convey in more detail our deep felt thanks for their services over many years. However, today I offer them on your behalf a long and happy retirement and a wish that we may see them at future Conventions as relaxed delegates and not tied to the demands of the job. *(Cries of 'Hear, Hear')*. May I ask you to show your appreciation in the usual way. *(Applause)*.

I have no doubt that you will not want me to keep you any longer from a little bit of relaxation and leisure time in which you may want to make that final contact or that purchase which you promised yourself. I look forward to seeing you this evening at St. Catherine's enjoying our belated British summer before coming into Dinner. Thank you very much indeed. *(Applause)*.

THE BRITISH WOOD PRESERVING ASSOCIATION
1985 ANNUAL CONVENTION — 25/28th JUNE

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