



Brush Strokes



www.scanz.org.nz

SURFACE COATINGS ASSOCIATION NEW ZEALAND INC

MARCH 2012





Enabling the Coatings
Innovations of Tomorrow



Dow Coating Materials is committed to discovering breakthrough technologies and solving even the most complex problems.

INSPIRE	Inspiration is at the heart of every Dow Coating Materials story.
COLLABORATE	Fanning the flames of inspiration takes a lot of hands.
INNOVATE	To some, innovation might seem like magic, but for Dow Coating Materials, it's woven into every part of our business.
GROW	Personal, professional, financial, technological – any way you define it, growth is the single biggest goal of Dow Coating Materials. It's what we know. It's what we love. It's how we think.

For more information about Dow Coating Materials, please call 64 9 275 7154, or visit www.dow.coatings

Need Innovation? ISM have the solution!

Representing the leading brands in paint manufacture

ADDITIVES

Acrylic Microspheres
AMP95 and VOX 1000
Cellulosics
Bentone Clays
Biocides
"Green" options
Flow, levelling, defoamers
Wetting agents
Rheology Modifiers
Dispersants

RESINS

Acrylic polyols
Alkyds
Crosslinkers
Epoxies

Iso Free systems
Hydrocarbon resins
Phenolics
Silicones and Siloxanes
Solution polymers

PIGMENTS

AntiCorrosives
Cuprous Oxide
Flame Retardants
Fluorescents
Metallics
Mixed Metallic Oxides
Organic and Inorganics
Pearls
Titanium Dioxide
Ultramarines



ism

ISM NEW ZEALAND LTD, 71C MONTGOMERIE ROAD,
AIRPORT OAKS, MANUKAU CITY 2241, NEW ZEALAND
TELEPHONE: +64 9 275 0745 FACSIMILE: +64 9 275 0746

www.ismnz.com



For Your Specialty Chemical Needs

ECKART
Excellence in Effect Pigments

Transpek-Silox
Developing Chemicals. Defining Solutions.

Clariant
[Exactly your chemistry.]

MICHELMAN
FOUR COMPETITIVE EDGES™

KRONOS

Shell Surfactants

AMERICAN GILSONITE COMPANY

SNCZ
SPECIALIST IN INDUSTRIAL CHEMICALS

CM MP
Specialist of Industrial Minerals

Kamsons

FERRO
THE PERFORMANCE MATERIALS COMPANY

Auckland 09 444 4650 Brett, Janine, Glenys, Rod

Christchurch 03 338 8995 Mike, Jason

www.chemcolour.co.nz info@chemcolour.co.nz

ISO 9001:2000



CYTEC

Liquid Coating Resins & Additives

LANXESS
Shaping Chemistry

Bayferrox Iron Oxides

ISP

Biocides & Performance Additives

R. T. Vanderbilt
INDUSTRIAL MINERALS AND CHEMICALS

Mineral Fillers & Additives

Stepan

Surfactants & Enviro-friendly Solvents

Nick Bray
Nigel Garland

09 306 6091
09 306 6096

nick@alchemyagencies.co.nz
nigel@alchemyagencies.co.nz

www.alchemyagencies.co.nz



"Supplier for industrial solutions"

DSM Neoresins; Arch Chemical biocides; BASF Emulsions & solvents; Celanese solvents & monomers; Extender pigments; Orica chlorinated paraffins; Degussa catalysts; Haltermann Oils & solvents; Huntsman Tioxide; Kukdo Epoxies; Noveon additives; Lucite monomers; Magruder flushes; Penreco oils; Rockwood Oxides; Johnson Matthey organic titanates; Wolstenholme metallic pigments and much more...

Free phone 0800 22 22 77

<http://www.orica-chemicals.com>



Brushstrokes Editorial

We are now well into the new year and the weather is still adversely affected by the La Nina conditions that caused havoc over the Christmas New year period. It certainly caused me some drama that I could have done without. While the weather has restricted the opportunity to paint outside, it has had the benefit of stimulating growth in our primary industries with a consequent injection of much needed money into the economy. That can never be bad, even for the paint industry.

This year SCANZ is holding its 50th Conference at the Marlborough Convention Centre in Blenheim between the 19th and 21st of July. The theme of the conference is "Made in New Zealand" and the schedule of speakers will showcase the innovation and energy in the coatings industry from a national perspective. If you are lucky enough to see the research and development taking place in the CRI's, the universities and some of the more innovative and specialised companies in the industry you cannot help but be impressed at what is being tackled and achieved in our small little backwater of the world. So make a diary date for the conference and badger your company to let you attend (and pay for it of course, in fact bring your manager along as well).

The next few themes for Brushstrokes are Emulsions, Surfactants and Additives, Concrete Coatings and Adhesion and adhesives. I invite good technical articles on these or any coatings related subject suitable to print in the journal. Remember that the articles can have a strong commercial slant and showcase a company or its products so long as it contains good technical content and is not primarily just advertising.

In a similar vein, I need a couple of co-editors to help collect and assemble technical articles and stories about commercial side of the industry, people and changes, new products and new entrants into the market, changes in management or ownership, legislative and compliance issues or anything to do with the commercial activities in the industry. This is a chance to become more involved in

the organisation and to meet others in the industry that you might not otherwise meet. It is a case of many hands make light work. Give me a call or send me an email.

Don't forget that SCANZ has a close association with the University of Auckland. The Coatings and Polymer Science Course is still available. If you are interested, give Neil Edmonds a ring or send him an email at nr.edmonds@auckland.ac.nz. Similarly, our sister organisation in Australia runs an online course in paint technology that is available to members of SCANZ as well. Contact a member of the committee for the details.

...ED

WANTED

A couple of Co-editors for Brushstrokes to help with writing and collating articles.

The theme for the next issue is
"Emulsions"

Any technical, historical or market oriented articles on emulsions or dispersion polymers will be gratefully accepted.

Please send articles to cbolt@xtra.co.nz
or contact the editor on 021-897-844

Advertising enquiries: contact Marina on
021-781-968 or email her at
marina@apconz.co.nz

Visit the SCANZ website
www.scanz.org.nz



- | | |
|--------------------------------|--------------------|
| ● Binders | ● Surfactants |
| ● Rhodoline Defoamers | ● Water Repellents |
| ● Rhodoline Dispersants | ● Wetting Agents |
| ● Extenders: Tixosil & Tioxlex | ● Gensil Silicones |

New Zealand Manufacturer backed by Global Innovation

For more information contact:

Kevin Osten Ph (0274) 577 417 • kevin.osten@ap.rhodia.com • Customer Services: Ph (06) 368 9372 • Fax (06) 368 2071



Painted Memories

A selection of Historical Paint References compiled by Peter Walters

In July 1880 John Williams Benn, a furniture designer, skilled pencil artist and a Junior Partner of the London Furniture Wholesaler Lawes Randall & Co., published the first issue of the trade journal "The Cabinet Maker" in order to have a vehicle to expound his passion for the simpler furniture lines of the late 18th century masters, Thomas Chippendale, George Hepplewhite and Thomas Sheraton, in contrast to the over ornate style prevalent in the late Victorian era of the time.

In 1980 "The Cabinet Maker", with Timothy Benn, the great great grandson of John Benn, at the helm, celebrated a successful centenary of publication by printing a commemorative booklet, of which I am fortunate enough to possess a copy. The cover of this booklet reproduced the title in marquetry, the epitome of the cabinet makers art.

Cabinetry is the manufacture of wooden cabinets, shelves and furniture. Any output of the cabinet maker is not complete until it has received a protective surface coating. In acknowledgement of that fact the commemorative booklet contained a chapter on the changes in the finishing of furniture during the century of publication. This chapter was written by John Collier, a Lecturer in wood finishing at the London College of Furniture and author of the textbook "Wood Finishing"; Volume 6 of the Pergamon Series of Monographs on Furniture and Timber, first published in 1967 by Pergamon Press.

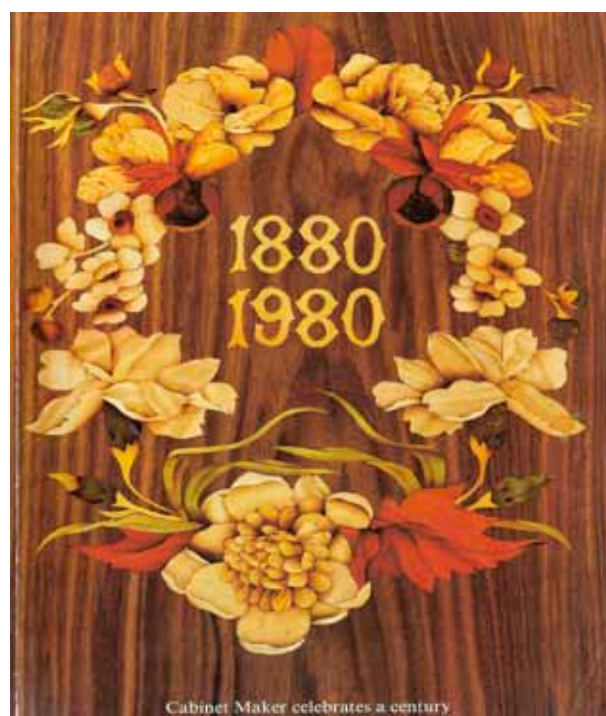
The critical importance of the finish that is applied to furniture is best highlighted in this excerpt from the autobiographical blank verse poem by the 1972 British Poet Laureate Sir John Betjeman, 1906-1984, "Summoned by Bells", where the author recounts his childhood impressions of the atmosphere in the furniture manufacturing and finishing sections of the family firm which manufactured, among other things, Victorian style furniture;

*"...The cabinet-maker's shop, all belts and wheels
And whining saws, would thrill me with the scream
Of tortured wood, starting a blackened plank
Under the cruel plane, and coming out
Sweet-scented, pink and smooth and richly grained;
While in a far off shed, caressingly,
French polishers, all whistling different tunes,
With reeking swabs would rub the coloured woods,
Bringing the figured surfaces to light;
Dark whirling walnut, deep and deeper brown,
And rare mahogany's pressed butterflies..."*

Furniture manufacture was an important part of British Industry in the late 19th century. The industry, particularly the manufacture of wooden chairs, was concentrated in High Wycombe, the largest town in Buckinghamshire just west north west of London. The Industry was so important to the town that when Queen Victoria visited the town in 1877, the council organised an arch of chairs to be erected over the High Street, with the words "Long live the Queen" printed boldly across the arch for the Queen to pass under.

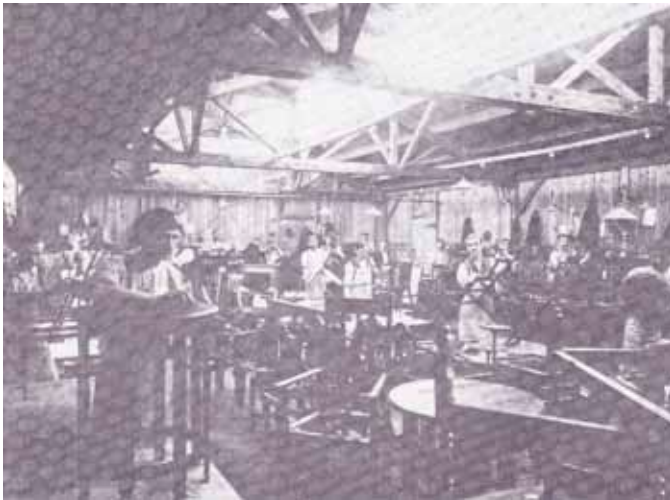


Reproduced, for Brush Strokes timber finishing theme, is the woodfinishing chapter from The Cabinet Makers centennial commemorative publication;



From Polish to Polyurethane - a century of woodfinishing

By John Collier



The old and the new. Above is a 1902 photograph of polishing work in a High Wycombe chair factory. Below, an endless loop of conveyor takes panels twice round automatically to finish both sides at Arenson International. Panels are being fed in on the left of the picture, and leave on the right.

IN A BOOK written in 1905, a definition of French polish is offered: "French polish — a cheap and nasty method used since 1851 to varnish poor-looking wood to disguise its inferiority. It is quicker than the old method of rubbing in oil and turpentine and beeswax. It is composed of shellac dissolved in methylated spirits with colouring matter added."

That all the treasures of Hepplewhite, Chippendale and Sheraton had been wax polished, as indeed had those of the French *ébénistes*, was a formidable tribute. Even as late as 1901 under the influence of the Guild Craftsmen 'The Studio' was able to write: 'To hate the French polisher is the beginning of wisdom'.

But all this was before quantity production of furniture. By 1880, French polishing was practically the only method of wood finishing. Oiling and waxing were for church furniture, the 'special' and for the craft purist. Indeed it had become a

much admired craft in its own right, though in my day French polishers were called the 'scum of the trade'. There was a dichotomy between the end result and the despised practitioner who polished it.

To be sure there was good and bad French polishing. At its best it set a standard of excellence in appearance never to be excelled. But there were many variations. It used to be said 'If you want a good finish, go to a pianoforte polisher. If you want a good colour, go to a cabinet polisher'. The same materials but different methods were employed. These were the days of 'trade secrets' and mysteries, of stale beer and cow dung and a host of private concoctions called recipes before the days of formulae.

At the lower end of the scale there were short cuts where the mop and the varnish pot came into play with a slick laying on of wet rubbers. There was no science: nobody ever learned more than his master. You learned from the piece-master or the foreman in the factory or under the arches or even on the pavement outside the cramped quarters of the cabinet maker in a London East End workshop or its equivalent in High Wycombe, Leeds, Liverpool or Manchester.

Beyond this there was little instruction. It was even many years before there was a City & Guilds examination for French polishing: not indeed before the day of the French polisher's supremacy was gone and the examination had to titled 'hand and spray polishing'. Technical education itself, of course, was a half-hearted affair subsidised by surplus funds from the brewers set up to finance failed publicans.

Technically there was little progress between 1850 and 1920. Quantity production had set in to a limited degree with a slight rise in living standards and an increasing demand for furniture, but the techniques remained the same. Thus with the introduction of improved wood cutting machinery and slick methods of assembly at one end, and the time-consuming French polishing process at the other, the scene was set for the notorious bottleneck in the polishing shop which bedevilled so many works managers, causing frustration and ulcers.

The situation was made more acute because many employers had themselves been wood machinists or cabinet makers but few, if any, had a clue about polishing or polishers. Perhaps polishers were the scum of the trade! In 1920 a very ordinary commercial grade upright piano was polished over a period of six months. A medium-quality suite of furniture would take weeks rather than days to finish. If ever we were to approach mass production, there would have to be change.

The change came about fortuitously. It had all happened before. The 'thin red line' of British imperialist forces had been coloured by shellac dye. Then invention of aniline dyes had meant that the market for shellac slumped until new uses were found for the natural resin by the development of French polishing.

Now, at the end of the first world war with the emergent demand for cars, for furniture and the beginnings of mass

production, new materials and processes were urgently required. And there was a material to hand.

During the war great quantities of cellulose acetate — aeroplane ‘dope’ — were produced. This had an immediate use for cable covering, but with slight modification of the production process it could be converted to cellulose nitrate which could form the highly volatile element in surface coatings which became known as nitrocellulose.

Together with this new surface coating material the means of applying it, the spray gun, was developed. The big market for the spraying on of nitrocellulose finishes was the car trade. But it soon tentatively seeped through to the pianoforte trade where the writer was one of the first to use it, and even more tentatively to the furniture trade.

The predominance of nitrocellulose finishes was to last unchallenged for 40 years or more. Speed of application was the winning feature. No longer did we carefully, painstakingly and slowly build up a film of shellac on the surface: ‘bodying-in’ and ‘bodying-up’ we called it. It called for craft skill. Now all was changed. In a few seconds it was possible to apply one or two coats of lacquer to give an adequate film thickness — not that we had ever thought in such terms before.

Then there was a hand process of ‘pulling-over’ to a finish. But this was simple and could be learned easily, it was said, as indeed could the preliminary spraying: an oversimplification that was to cost industry dearly in poorly finished jobs and waste of materials!.

The introduction of nitrocellulose, or NC, into the furniture trade was not welcomed by French polishers nor, indeed, by all of their masters. The critics were rampant. NC chipped, it bloomed, it cracked, it couldn’t be repaired, it marked in transport. There was a good deal of truth in some of the criticisms of the early lacquers, and there were other complications. Craftsmen did not want to become operatives and in any case they feared for their jobs. Employers were not always eager to install expensive plant and re-organise their works and their domestic economy. In addition, all other processes such as staining and colouring had to be recast so that the materials used were compatible with the new finish.

Nevertheless economic pressure prevailed. Factory production became almost exclusively based on NC. Meanwhile shopfitting and other in situ trades still depended on the French polisher. Architects, with new-found wisdom, specified French polishing as a mark of excellence. Thus it went on up to and including the mass sales of radio sets and television sets: everything from a lavatory seat to a tennis racquet was finished with ‘cellulose’.

Concurrently, however, a new industrial development was maturing: the introduction of the so-called ‘plastics’. Already in odd corners of the trade there were available special finishes for special purposes such as heat resistance. They were based on phenolic resins, the first of the wholly synthetic resins, modified for use as a surface coating. They were the

harbinger of a revolution.

New techniques had to be learned. Such materials did not dry wholly by the evaporation of solvents but also by a process of polymerisation induced by a catalyst. They were ‘chemical finishes’, two-component finishes where mixing had to take place just before application. Conceptions such as ‘pot-life’ and ‘shelf-life’ had to be embraced.

These early ‘plastic’ finishes had obvious disadvantages. They were dark in colour. They sometimes reacted violently with the chemicals in the wood. Stains and fillers needed to be specially formulated. There was no easy way to process them: they were utilitarian rather than decorative. And they were expensive.

The matter might have remained there but for the introduction of laminated plastics. These set a new standard of resistance to moisture, heat and chemical attack. Blessed with these qualities in her kitchen, the housewife thought it not unreasonable to ask that her coffee table should resist the heat and possible spillage of coffee, and why can’t the sideboard be resistant to alcohol?

For the benefit of the non-specialist, it is perhaps worth stating that both French polish and nitrocellulose films are water permeable, and are easily softened by solvents and heat. French polish is a simple solution, and nitrocellulose is a colloidal solution. In the process of drying by evaporation the solids remain the same: they are ‘reversible’ finishes. The dried film is quickly re-dissolved by the addition of solvents. Hence its vulnerability.

The ‘plastic’ lacquers are quite different, for here the solids are converted into a new film formed by the action of a catalyst or some other additive. To various degrees the surface coating is resistant to heat, moisture and solvents — almost like a laminated plastic surface.

To a large extent the earlier snags had been ironed out. The acid catalysed finishes, or AC, were now water-white and the pot life had been modified to make them more conveniently usable. At first, urea-formaldehyde resins were used. Later came the introduction of melamines — similar to the resin used in laminated plastics.

These finishes did have quite a vogue, a situation that was made easier by the public acceptance of matt finishes straight from the spray gun, the growing popularity of teak being a contributory factor. But acceptance was not universal for two reasons. In production the pre-mixing of the lacquer was always a hazard in terms of human error, and the material was not suitable for a gloss finish where this was required.

In consequence of these problems there evolved a hybrid range of finishes that took their place in the scene. NC lacquers had not stood still: they had been modified and upgraded to a significant degree. At the same time there was the development of pre-catalysed lacquers by various manoeuvres (which involved the inclusion of a proportion of NC lacquer in many cases). Thus there was often little to choose between the

upgraded NC and the down-graded AC lacquer. This, it has to be said, is still the position.

Then a new material emerged: the polyurethanes. They are a high quality surface coating; perhaps the best available. Some would say they are too good for normal furniture. Some of us were sold on them and did our best to popularise them, but even with the modifications that were soon introduced, this, the toughest finish available even now, failed to capture more than a small corner of the market. The term was full of mystery and magic which was exploited by the paint trade, but has never been adequately explored by the furniture trade.

These were days of high excitement. Other parts of the trade seemed to be static, but at the finishing end there always seemed to be something new, a multiplicity of solvents, a plethora of resins: alkyds, urea-formaldehyde, melamine-formaldehyde, epoxies, acrylics, polyesters and polyurethanes.

Foremen and managers went to evening classes to learn the new language. There were lectures, demonstrations and discussions, seminars and symposiums. Good was it in that day to be alive!

With glossy finishes there is a different story. The finishing of the case-work for the now booming television industry absorbed the tradition of the pianoforte trade for a full high-gloss finish. To meet this demand, and for other purposes, the polyester finish was devised. Of Germanic origin and with a full blast of enthusiastic recommendation it was to solve all our problems.

There is no doubt but that, properly applied and processed, it is capable of providing a full-gloss finish comparable with the best vitriol-finished French polish, and with infinitely greater durability. It has not swept the board, partly because the demand for a full gloss has declined and partly because the proper use of polyesters demands a complete commitment right from the design stage of the article to be treated.

At this point it is worthwhile to underline what has happened. The despised craft has become a science embracing concepts that were certainly not current in the days of my apprenticeship. In short, the chemist has taken over. There used to be three solvents — water, methylated spirit and turps. There was one resin — shellac. And there were numerous sundries like vegetable dyes and crude alkalis like lime and caustic soda. Now there are hundreds of solvents and thousands of resins. There are elaborate chemical concepts and complicated formulae. Above all there is measurement. A handful of this and a cupful of that is no longer good enough.

And now enters a new dimension. The spray gun had become ubiquitous but now engineering is applied to surface coating in a big way. The roller coater and the curtain coater are introduced, making possible a controlled deposit, measured at first in ounces per square foot but now in grammes per square metre. Conveyor belts are linked with the machines and we learn to measure metres per second as well as grammes per square metre.

Some of us evolve a concept of starting at one end of the line with a board in the white and taking it off at the other perfectly and uniformly finished and dry for packing. It is done. But not without further developments: forced drying — convection heating, infra-red, ultra-violet, gamma rays. Even laser beams enter our theories. The physicist joins the engineer and the chemist.

Meanwhile there are parallel developments. Grain printing is devised and finds a place in the line. This leads to the development of foils and then of printed wood grain papers and even to the added refinement of grain pits to give verisimilitude. Some furniture is advertised as “real wood”.

There are pertinacious attempts to rationalise the application of the two-component lacquers by means of dual-feed guns and the application of dissimilar coatings, wet on wet, subsequently to react. Hot lacquer and airless spray take a corner of the market.

All these developments involve modifications to the materials employed and increasing collusion between plant manufacturer, lacquer manufacturer and the user. But the net result is that we have passed from craft production to mechanisation and in some cases to automation. And the silicon chip is round the corner.

Now entirely new factors are being introduced into the equation. We are becoming more aware of the toxic effects of some of the materials we have adopted. Polyesters and polyurethanes were always suspect, but we easily allowed ourselves to be lulled into acquiescence. On the other hand there are those who perhaps scare too easily: even the humble can of paraffin is now suspect.

Probably the most important new factor, however, is the oil crisis. This has led to renewed interest in water-based finishes or, to be more precise, water -thinnable, emulsified lacquers. Another line of approach is that of alcohol-based materials, perhaps acid catalysed. Now is this not where we came in? ‘French polish composed of shellac dissolved in methylated spirit....’!



An Introduction to Timber Preservation

by Michael Behr, Rebain International (NZ) Ltd

Wood from timber plantations is a renewable natural resource, aesthetically pleasing, and is a versatile material that can provide a cost-effective alternative to man-made products such as steel. Wood is an organic substrate consisting mainly of cellulose and lignin which is decayed over time by microorganisms that utilise one or both of these compounds as a nutrient source. Air-breathing living organisms need five basic requirements to survive: oxygen in the form of air, water, nutrients, a temperature range and time. Remove one of these elements and the organism cannot exist. Over the centuries man has devised hurdles to slow microbial decay. Hurdles set to prevent microbial spoilage can be observed in everyday life. Take a block of butter for example. One of the hurdles that delay the onset of spoilage is the addition of salt, which acts as a natural preservative. Second is the packaging. The wrapper provides a physical barrier between the microorganisms and the butter. A third hurdle is refrigeration. Whilst cold temperatures do not necessarily destroy microorganisms, it reduces the chance of dormant spores on the butter from germinating. Timber preservatives constitute a hurdle intended to exclude decay agents such as fungi, termites and wood boring insects from using wood as a nutrient source, thus increasing the durability of the wood and extending service life.

The earliest wood preservatives include tars which are manufactured from organic substrates such as wood and coal. The first use of preservatives included the tarring of wooden hulls of ships, and later the use of creosote to treat railway sleepers and utility poles. Various types of wood preservatives have been developed and improved on over time and several options are now available in the market place. There are two broad types of timber preservatives, these being water-borne and solvent-borne formulations. Several countries, including New Zealand and Australia, follow a Hazard Class rating system from Hazard Class H1 through to Hazard Class H6

depending on the end application of the timber, and the level of protection required during service. Water-borne preservatives are represented in Hazard Class 1 through to Hazard Class 6, whereas solvent-borne preservatives are represented within Hazard Class 1 through to Hazard Class 3. In the United States the rating system is similar to our Hazard Class system but is called the "Use Category System" or UCS.

The Hazard Class rating system used in Australasia:

Hazard Class H1:

Is the treatment level for low hazard applications where the timber is not exposed to the elements i.e. inside, above ground and in a dry environment. In New Zealand the major use for timber in H1 is for house framing elements with over 90% of houses being built using timber frames. Timber used in compliance with the New Zealand Building Code [Standards New Zealand (2003): NZS3602: Timber and wood-based products for use in building] should in theory preclude moisture ingress. However, on occasion, the frame may be exposed to moisture over time, for example due to the neglect of building maintenance or damage to the building envelope caused by extreme weather events. Class H1 is divided into two categories, class H1.1 and H1.2.

H1.1 is for timber used in a dry environment requiring protection against wood boring insects.

H1.2 is for timber protected from the weather, but where there is the possibility of moisture ingress which increases the risk of fungal decay.

The insect resistance imparted by the preservatives in Classes H1.1 and H1.2 is for wood boring insects, and excludes protection against termites.



Head Office
5 Lockhart Place, Mt Wellington, Auckland 1060, New Zealand
P.O. Box 62274, Mt Wellington, Auckland 1641, New Zealand
Tel +64 9 914 7010 Fax +64 9 914 7014
Email: sibelconz@sibelco.co.nz

Nationwide Stockists of: Barytes, Calcite, Cement, Clay, Diatomaceous Earth, Feldspar, Gypsum, Iron Oxide Pigment, Magnesium Oxide, Mica, Miclay, Nepheline Syenite, Pumice, Pyrophyllite, Silica, Slate, Talc & Wollastonite
www.sibelco.co.nz

Hazard Class H2:

This is for the Australian market and is for applications such as house framing, flooring and trusses. Insecticides such as Permethrin (a synthetic pyrethroid) are included in the preservative formulation to protect against termite attack.

Hazard Class H3:

Is for applications where timber is exposed to the weather, but is not in ground contact i.e. outside and above ground level. This class is also divided into two categories H3.1 and H3.2.

H3.1 is for timber used outdoors, above the ground, exposed to weather where the timber is set in a vertical orientation.

H3.2 as above, but where the timber is set in a horizontal position and at risk from water entrapment.

In 2011 the Department of Building and Housing New Zealand combined the different Hazard Class levels H1.1, H1.2 and H3.1 (which cover the treatment requirements for framing timber within the building envelope) and rationalised into a single hazard class called H1.2 (amended standard H1.2-NZS3640:2003).

Hazard Class H4:

Is for areas where timber is in contact with the ground resulting in a high fungal decay hazard. Examples of use include fencing posts and landscaping timber.

Hazard Class H5:

Is for ground contact areas where there is a serious decay hazard due to wet soil. Applications include structural poles, engineered retaining walls and pilings.

Hazard Class H6:

For marine water exposure, or ground contact in estuarine locations. Marine borer pose a severe hazard to timber in this environment. Typical uses include quayside piles, jetty poles and landings.

Types of preservatives used in the Hazard Classes:

Water-borne:

Well established preservatives include liquid boron and glycol borate formulations. Boron-based preservatives offer broad spectrum efficacy against decay fungi, wood boring insects and termites, and has the benefit of low mammalian toxicity. Glycol borates formulated in a monoethylene glycol carrier offer an advantage over purely water-based boron in that the treatment has less affect on the dimensional stability of the timber, less instance of raising the wood grain, and allows

the formulation to penetrate deeply into the wood substrate. Borates can be applied as a dip treatment or by the vacuum pressure impregnation process. Boron treated timber is dyed pink in colour. The Department of Building and Housing New Zealand supports the use of boron for the new Hazard Class H1.2 for timber framing elements within the building envelope. Reference: www.dbh.govt.nz/consultingon-timber-treatment-discussion-6

Alkaline Copper Quaternary (AQC) preservative is based on Copper combined with a quaternary ammonium compound and is applied to wood by pressure treatment. AQC provides long term protection against decay fungi, borer and termites. Timber is treated with AQC preservatives at different loadings cover Hazard Classes H1 through to H5.

Chromated Copper Arsenate (CCA) is a water-borne preservative that provides long term wood protection and is applied to timber by pressure treatment. CCA is an effective fungicide and termiticide, and covers the entire Hazard Class H1 to H6 (depending on retention levels and depth of preservative penetration set for the timber). CCA treated timber has a characteristic light green colour.

Solvent-borne:

Light Organic Solvent Preservative (LOSP) systems vary according to the active ingredients with which they are formulated. LOSP provides protection for timber used indoors, and outdoors above the ground. LOSP formulations contain an insecticide for Hazard Class H1.1, or a fungicide and an insecticide for H1.2. For Hazard Class H3.1 LOSP contains the fungicides Propiconazole and Tebuconazole and the insecticide Permethrin. LOSP may also contain water repelling compounds such as petroleum resin and/or paraffin wax. LOSP is applied to timber by the vacuum impregnation process.

The predominant wood species used in New Zealand:

Radiata pine (*Pinus radiata*) is the dominant plantation species in New Zealand and Douglas-fir (*Pseudotsuga menziesii*) the second most planted forestry species. Radiata pine is a versatile species and suitable for a wide variety of end-use applications and can be treated for Hazard Class H1 through to H6. Radiata takes stain well and is easy to coat, and it bonds well with structural adhesives. Douglas-fir is predominantly used as a framing timber and is not suitable for ground contact or marine exposure. Reference: www.nzwood.co.nz

The future of Wood Preservation and the opportunity for involvement of SCANZ members:

The International Research Group on Wood Protection (a former OECD group of experts) was formed in 1969 as an independent research group focused on generating knowledge of the science of wood deterioration. Today IRG comprises of researchers and commercial participants in the field of Wood Protection who meet once a year in a different location around the world

to provide an opportunity for the members to share ideas and novel solutions for the sustainability of wood products.

The 42nd annual IRG conference was held in Queenstown, New Zealand in 2011, where over 20 countries were represented. Local attendees included delegates from forest products research institutions such as SCION, the Department of Building and Housing NZ, Ministry of Science and Innovation, and commercial participants such as the timber treatment companies, chemical raw material suppliers and independent consultants.

At IRG, the presentation of research papers is split into Working Parties (WP) which covers different group subjects. Each WP session runs for an hour and a half and usually includes four to five presentations. The author has fifteen to twenty minutes to present their work, and then five minutes of questions from the audience. At IRG42 almost one hundred papers were presented over a four day period. Examples of WP groups include "Prediction of service life", "New wood protecting chemicals", "Chemical wood modification", and "Sustainability and Environment". The Working Party relevant to SCANZ members is WP 4.5: "Coatings, hydrophobic treatments and surface aspects". This WP was the least represented of all group sessions with only three papers being submitted and just a solitary coatings company was represented at IRG42, that delegate being from Akzo Decorative Paints, Sweden. Membership to the IRG is open to all interested parties and new participants are welcome, so this may be a good opportunity for SCANZ members to become involved

in IRG bringing with it an understanding of the advances in new timber treatment products, and increased awareness of the hurdles that may be faced when coating an ever evolving substrate. This year IRG43 is being held from the 6th - 10th May in Kuala Lumpur, Malaysia and IRG44 is being held the following year in Stockholm, Sweden.

For further reading on wood products, timber preservation and upcoming events please visit the following websites:

www.nzwood.co.nz

www.irg-wp.com

www.scionresearch.com

www.branz.co.nz

www.woodpreservationevents.com

About the Author:



Michael Behr was born in Durban, South Africa. He attended Durban High School and then completed a National Diploma in Microbiology at the Durban Institute of Technology. Michael migrated to New Zealand in 2005 and joined Rebain International later that year as a Technical Sales Representative. Michael has 18 years' experience supplying raw materials to the Timber Preservation Industry.

The Surface Coatings Association of New Zealand



Annual Conference

19th to 21st July 2012

At the Marlborough Convention Centre
in Blenheim

Registration forms and conference programme will be available soon.

Check the website for information and electronic registration forms.

www.scanz.org.nz

New approaches for solvent-free waterborne polyurethanes

Speaker: Dirk Mestach - Authors: Dirk Mestach, Jan Goossen and Derrick Twene

Company: Nuplex Resins BV, The Netherlands - Contact dirk.mestach@nuplexresins.com

Abstract

When it comes to having high performance environmentally acceptable coatings, waterborne polyurethanes are the first choice. Waterborne polyurethanes can either be one- or two-component systems or binders curing by ultra-violet radiation. Until now waterborne polyurethanes however often contain N-methyl pyrrolidone (NMP), a solvent that is used in the processing of the resin. Due to upcoming European legislation, products containing more than 5 % NMP will have to be labeled as being irritant and toxic (Xi: R36/37/38, T: R 61). In this paper some novel NMP-free waterborne polyurethanes are discussed and their performance is compared with NMP containing products.

Introduction

Waterborne polyurethanes are amongst the binders of choice when it comes to high quality and demanding applications. Waterborne polyurethanes can be formulated into environmentally acceptable coatings containing low amounts of volatile organic components (VOC). Due to the nature of the polymer backbone of polyurethanes they are both hard and flexible, making them ideal for use in scratch resistant, hard wearing coatings. These properties are the result of inter- and intra chain interactions between polyurethane chains. These interactions are attributed to hydrogen bonding between the urethane and the urea linkages in the polymer backbone (figure 1).

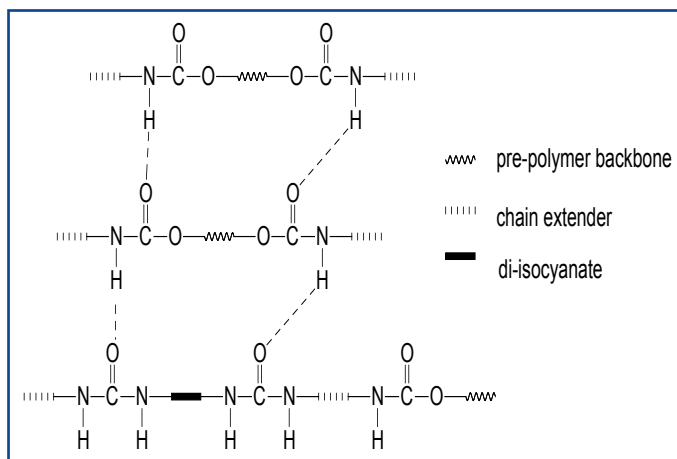


Figure 1. Hydrogen bonding between polyurethane chains.

Waterborne polyurethanes can be used both in one and two component and in radiation curing coatings. The polyurethanes can be either thermoplastic or (self) crosslinking.

Irrespective of the application the general synthesis route for a polyurethane dispersion is as follows: a polymeric diol, for example a polyester, polyether or polycarbonate diol is reacted with a hydrophilizing diol and a diisocyanate. Depending on the ratio between the diols and the diisocyanate the polyurethane thus obtained can be either isocyanate or hydroxyl functional. In the case the polyurethane is isocyanate functional it is often referred to as a polyurethane pre-polymer. The polyurethane is then dispersed into water either directly or by means of phase-inversion. If the polyurethane is NCO-functional it can be chain extended using a diamine after the dispersion process. Optionally a chain stopper can be used to react with the NCO-functionality. This chain stopper can be used to introduce functional groups for example for crosslinking of the polyurethane after drying of the coating. A schematic representation of the process is given in figure 2.

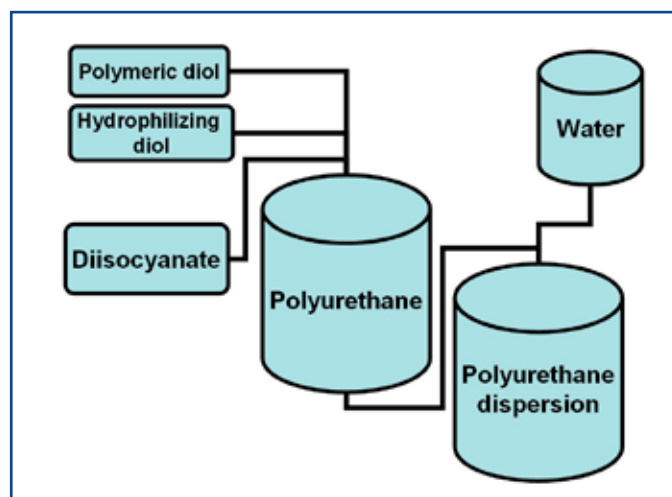


Figure 2. Process for polyurethane dispersion production.

In most waterborne polyurethanes used in the coatings industry, at least part of the hydrophilizing diol is dimethylol propionic acid (DMPA, figure 3).

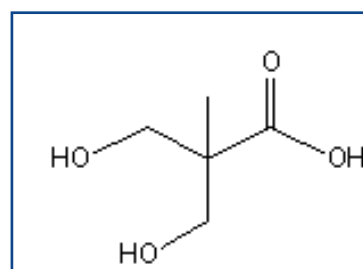


Figure 3. Dimethylol propionic acid (DMPA)

The hindered carboxylic acid group in DMPA is less reactive than most acid groups. Therefore DMPA reacts as a diol. The free acid group can be neutralized with

a base and makes the polyurethane water dispersible.

Until recently waterborne polyurethanes generally contained a certain amount of volatile organic solvents. These organic solvents are used in the synthesis of the polyurethane dispersion in order to reduce the (pre-) polymer viscosity but also to aid in the dissolving of DMPA in the polyols prior to the addition of the diisocyanate. Not all solvents can be used for this as they have to be a-protic (non reactive with isocyanates) and hydrolytically stable. This limits the choice to ketones, (cyclic) ethers and some amines and amides. The solubility of DMPA in these solvents varies strongly¹ (table 1) and until recently N-Methyl-2-pyrrolidone (NMP, figure 4) was the preferred solvent.

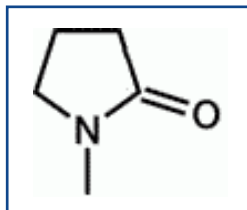


Figure 4. N-Methyl-2-pyrrolidone (NMP)

Table 1. Solubility of DMPA in solvents.

Solvent	Solubility (g/ 100 g solvent)
Acetone	0
Methyl ethyl ketone	2,2
Diethylene glycol diethylether	1,12
Tetrahydrofurane	4,7
1,4 Dioxane	13,5
N-Methyl morpholine	103
N,N-Dimethyl formamide	63,9
N-Methyl pyrrolidone	54

A problem associated with NMP is the fact that it can not be removed by distillation after dispersing the polyurethane in water. It therefore remains in the polyurethane-dispersion and functions as coalescing aid. The classification of NMP as “toxicologically questionable” is currently being discussed by the European Union. It is proposed that products containing more than 0.5 % NMP will have to be labeled as being irritant and toxic (Xi: R36/37/38, T: R 61). In the United States, California Proposition 65 requires special labeling of products containing NMP while other states and countries may follow. Therefore a worldwide need to replace or eliminate NMP from polyurethane dispersions exists.

Alternatives for N-Methyl Pyrrolidone

Several approaches have been used to replace NMP in the manufacture of polyurethane dispersions. A straight forward replacement of NMP by N-Ethyl-Pyrrolidone (NEP) is suggested by some companies². Even though it is claimed that NEP is an interesting alternative and that the toxicological profile is favorable compared to that of NMP, we do not see this as a sustainable option.

Other manufacturers have modified the well known acetone process³. An important problem associated with the acetone

process is the fact that the solubility of DMPA in acetone is virtually zero. Neutralizing the carboxylic acid group of DMPA with triethyl amine, however, raises the solubility⁴ considerably. A drawback of this process is that large amounts of acetone have to be stripped from the polyurethane after it has been dispersed. In order to get an economically feasible process, the acetone has to be recycled and used again. In view of the low flashpoint of acetone, some producers prefer to work with methylethyl ketone (MEK). Another way to increase the solubility of DMPA in the reaction mixture is to cap the hydroxyl groups with ε-caprolactone.

This modification converts the crystalline material in a soft waxy material with a low melting point and an enhanced solubility⁵. A draw-back of this route is that the hard diisocyanate-DMPA-diisocyanate segment now becomes a soft segment. Therefore the polyurethane has to be completely redesigned in order to obtain the desired coating properties.

A last solution for the production of solvent-free polyurethane dispersions is to use an ethylenically unsaturated monomer as a temporary solvent in the polyurethane synthesis. Esters of methacrylic acid are most suitable for this. These “solvents” are emulsion polymerized after the polyurethane is dispersed into water by adding a suitable initiator such as a persulphate or a hydroperoxide in combination with a reducing agent. Optionally additional monomers can be added at this stage. This synthesis route leads to hybrid urethane-acrylic dispersions. This approach however does not solve the DMPA-solubility problem as methacrylic esters are relatively poor solvents for DMPA.

Chemists at Nuplex Resins now have developed a proprietary technology that allows for the production of NMP-free polyurethane dispersions with the use of only small quantities of auxiliary process solvents. These solvents can be virtually completely removed after the production of the dispersion. Key to this process is the in-house development of polyol building-blocks that assist in dissolving the DMPA.

In order to demonstrate that the polyurethane dispersions prepared according to the novel process have equal or superior properties compared to NMP containing products a comparison was made between the first product we developed, Setaqua PU-1 (more details are given later) and two well known NMP-containing products from competitors. All products are anionic, aliphatic, polyester based polyurethanes. The minimal film-formation temperature for all binders was below 0 °C. Information on these binders is given in table 2.

Table 2. Typical resin properties.

	Setaqua PU-1	Comp 1	Comp 2.
Total solids (% w/w)	36	40	40
pH	8	7,5	8
% NMP	0	5,3	4,5

All polyurethane dispersions were formulated into a simple clear varnish using 4 % butyl glycol as a co-solvent. Figure 5

shows the hardness development for the different binders.

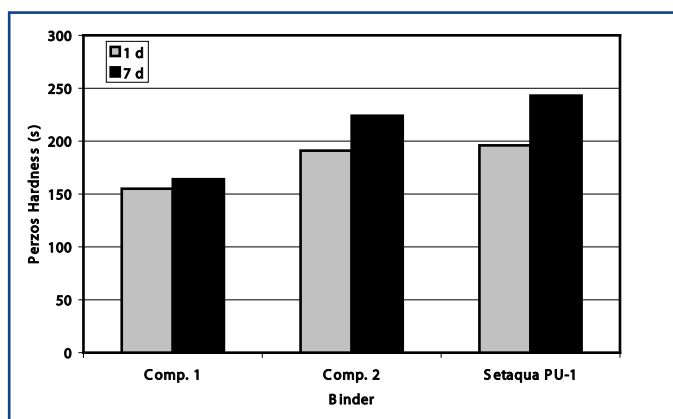


Figure 5. Hardness development of polyurethane dispersions as a function of drying time.

It can be seen that using an NMP-free polyurethane dispersion does not detract from the early hardness development. After one week of drying at ambient temperature, the hardness is superior to that of the NMP-containing types. This can be attributed to the plasticizing effect that NMP has on the film. In order to investigate if the film-formation was not hindered by the absence of NMP, chemical resistance properties were determined after seven days of drying at ambient temperature (table 3).

Table 3. Chemical resistance (DIN 68 861 1B)

Substance	Time	Comp. 1	Comp. 2	Setaqua PU-1
Coffee	16 h	3	2	3
Tea	16 h	5	2	2
Atrix® hand cream	16 h	2	1	2
Mustard	5 h	3	2	1
Water	16 h	0	3	0
Acetone	10 s	1	0	0
Red wine	5 h	3	4	2
Ammonia (10 %)	2 min	0	0	0
Sweat	5 h	3	3	0
Lipstick	16 h	4	4	2
Black ink	16 h	5	5	4
Olive oil	16 h	0	0	0

As can be seen from this table, the resistance properties are comparable or even better. Summarizing it was proven that the newly developed NMP-free technology allows us to synthesize polyurethane dispersions that have all of the benefits of the NMP containing types.

Types of solvent-free polyurethane dispersions.

Using the new synthesis process several types of polyurethane dispersions were developed:

- chain extended high molecular weight polyurethane dispersions (Setaqua PU-1)
- low molecular weight fatty acid modified polyurethane dispersions (Setaqua PU-2)
- self-crosslinking urethane-acrylic dispersions (Setaqua UA)

The high molecular weight polyurethane dispersions are most frequently used in combination with acrylic dispersions. Main purpose is to improve the mechanical properties of the acrylics. Common applications can be found in industrial wood-coatings. The chain extended polyurethane dispersions however can also be used as main binders in both one- and two-component coatings. Applications are parquet, furniture and plastic coatings. Crosslinkers such as polyaziridines or water-dispersible polyisocyanates can be used to enhance the performance.

Fatty acid modified polyurethane dispersions are a very versatile class of binders that find application in both decorative and industrial coatings. Because of their relatively low molecular weight they offer excellent flow and leveling. For wood-primers or sealers they allow good wetting and penetration of the wood. When used for decorative applications, such as in Do-It-Yourself trim-paints, they offer good wet-edge and open time.

Because of the fatty acid modification the hardness and chemical resistance properties build-up after drying of the coating.

Most of the fatty acid modified polyurethane dispersions still contain free hydroxyl groups. These can be used for reaction with for example water-dispersible polyisocyanates. Once again this boosts the performance of the coating.

Self-crosslinking urethane-acrylic dispersions offer synergistic properties compared to simple physical blends of polyurethane and acrylic dispersions. Applications are once again numerous ranging from parquet finishes to decorative enamels.

In the remainder of the paper some application examples will be given for the novel binders.

One component parquet lacquer based on a chain extended high molecular weight polyurethane dispersion.

Parquet floors are currently in fashion. Besides factory finished parquet, a lot of parquet floors are being coated after installation. The parquet lacquers used for this must meet a number of criteria: they must be non-yellowing and have a high chemical resistance. Furthermore they must have fair abrasion resistance. For the application point of view they must be fast drying and have a low odor. These lacquers can be based on PU-1 as a sole binder, but most commonly the polyurethane is combined with an acrylic dispersion. Combining a polyurethane with an acrylic dispersion not only results in the improvement of a number of coating properties but also brings economical benefits. In the following one component formulations we therefore also evaluated blends of Setaqua PU-1 with a self-crosslinking, surfactant free acrylic (Setaqua XL) and a thermoplastic acrylic (Setaqua TP) dispersion. The properties of these co-binders are given in table 4.

Table 4. Properties of acrylic co-binders.

Property	TP	XL	Unit
Non-Volatiles	43 - 45	39 - 41	%
pH	7 - 8.5	7 - 9	
Minimal film-formation temperature	15	14	°C

In the one component parquet lacquer the binder was either PU-1 pure, a blend with 30 % (w/w) of XL or TP and a blend containing up to 70 % XL. The blend of PU-1 with 70 % TP was not compatible (hazy films). The actual formulations used are given in table 5.

Table 5. One component parquet lacquer.

Formulation	PU-1	+ 30 % XL	+ 30 % TP	+ 70 % XL
Setaqua PU-1	120	85,3	85,3	36,5
Setaqua XL		36,2		84
Setaqua TP			32,7	
Butyl glycol	4,5		6,2	
Dipropylene glycol methyl ether		2,7		3,3
Propylene Glycol Butyl Ether		2,7		3,3
Defoaming agent	0,4	0,4	0,4	0,4
Low foam leveling agent (100 % active)				
Demineralized water	7,9	4,5	4,5	4,5

It has to be noted that the levels of co-solvent used in the formulations is not constant. The amount of co-solvent was based on the minimal film-formation temperature (MFT) of the binder combination.

Films of the varnishes were applied onto glass (dry film thickness ca. 30 micron). The films were allowed to dry at ambient temperature (23 °C) and the hardness was measured after one and seven days. The results are shown in figure 6.

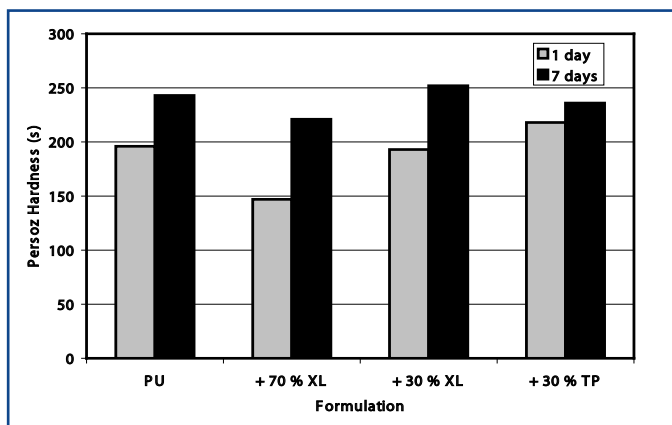


Figure 6. Hardness development for polyurethane and polyurethane-acrylic parquet varnishes.

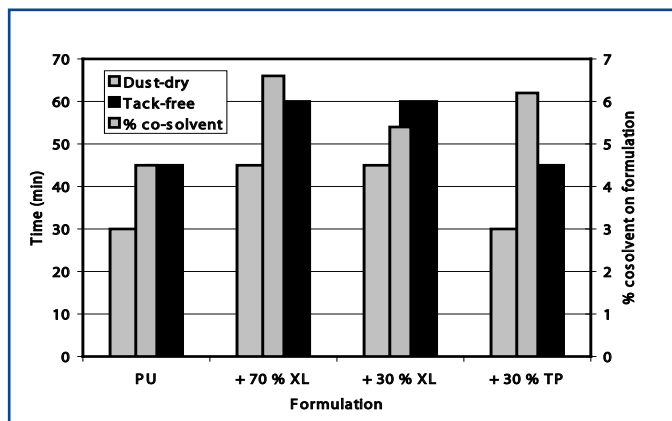


Figure 7. Dust-dry and tack-free times of parquet varnishes.

The coatings were also applied onto oak veneer (150 micron wet layer thickness) and the dust-dry and tack-free times were recorded. The results are shown in figure 7 above.

It is quite surprising to notice that the addition of 30 % TP-1 does not influence the drying times, even though the level of co-solvent in the polyurethane-acrylic blend is higher. Blends with the self-crosslinking acrylic have longer drying times although still sufficiently short for this application.

Chemical resistance properties of the dried varnishes were determined (on oak veneer 2 layers after drying for 7 days at ambient temperature). The results are given in table 6.

Table 6. Chemical resistance properties of parquet varnish (DIN 68 861 1B)

Substance	Contact time	PU-1	+ 70 % XL	+ 30 % XL	+ 30 % TP
Coffee	16h	3	1	3	3
Tea	16h	2	0	1	1
Atrix® hand cream	16h	2	0	2	3
Water	16h	0	0	0	3
Lipstick	16h	2	1	2	3
Black ink	16h	4	3	4	4
Olive oil	16h	0	0	0	1
Mustard	5h	1	0	2	2
Red wine	5h	2	0	0	0
Sweat	5h	0	0	0	5
Ethanol/water	1h	5	2	5	5
Ammonia 10 %	2 min	0	0	0	0

Blending of the thermoplastic acrylic with PU-1 does not offer too much with respect to chemical properties. Some resistance properties even deteriorate. Blends with the self-crosslinking acrylic on the other hand offer interesting improvements in properties. Especially the blend composed of 30 % PU-1 and 70 % XL performs well.

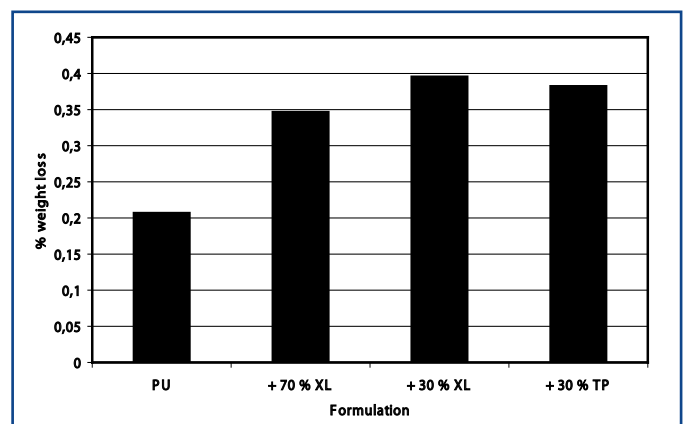


Figure 8. Abrasion resistance of parquet varnishes (after 7 days drying at ambient temperature).

Finally the abrasion resistance was determined (Taber Abrader, test-wheel CS-17, load 1000 grams). Results are given in figure 8. The pure polyurethane formulation obviously has the best abrasion resistance, but adding an acrylic dispersion only

has a minimal negative effect. Difference between the abrasion results of the blended binders is negligible.

Air-drying polyurethane metal primer based on Setaqua PU-2

Air-drying, fatty acid modified polyurethane dispersions are very well suited for industrially applied metal coatings. Until now these types of coatings often contained NMP. We developed a low VOC NMP-free metal primer formulation and investigated its main properties. The primer formulation is given in table 7.

Table 7. Air-drying polyurethane primer

	Component	Weight
Paste	Demineralized water	9,8
	Acrylic based dispersant	0,6
	Defoamer	0,4
	Butyl glycol	3,2
	Titanium dioxide	5,5
	Dolomite	4,9
	Zinc oxide	1,5
	Zinc phosphate	8,6
	Talc	8,6
	Mica	5
	Transparent iron oxide	1,1
	Fumed silica	0,3
Let-down	Setaqua PU-2	41,2
	Calcium-drier	0,2
	Corrosion inhibitor (50 % in demineralized water)	0,8
	Cobalt-drier (33 % aqueous solution)	1,1
	Polyurethane thickener (solution in water / butyl glycol)	0,8

Having good adhesion is crucial for a primer, test were performed on a number of different metal substrates. Results are given in table 8.

Table 8. Adhesion of primer based on Setaqua PU-2.

Substrate	Adhesion (Gitterschit)	Water-spot test*	
	ASTM D 3359	15 min.	1 hr
Cold rolled steel	1	0	0
Zinc plated steel (thermal)	1	0	0
Aluminum (Alu 2S)	0	0	0
Bonder panel	0	0	0
Aluminum Q-panel	0	0	0
Zinc plated steel (electrolytic)	0	0	0

* 0 is good, 5 is bad

Primers based on Setaqua PU-2 can be easily over-coated with both one and two component water-borne and solvent-borne topcoats. Even the primer as such shows very good salt-spray resistance. Test results are given in table 9.

Table 9. Salt-spray results: primer based on Setaqua PU-2.

Topcoat	Hours salt-spray	100	250	500	750	1000
primer as such	Blistering	-	-	f 4-2	f 4-2	f 6-4
	Under rusting (%)	-	-	-	-	none
	Adhesion* (mm)	-	-	-	-	2-4
	Discoloration	none	none	none	none	none
water borne 2K urethane coating	Blistering	none	none	none	m 4-2	f 8-6
	Under rusting (%)	-	-	-	-	none
	Adhesion (mm)	-	-	-	4	0
	Discoloration	none	none	none	none	slight
waterborne one component	Blistering	-	-	-	-	none
	Under rusting (%)	-	-	-	-	none
	Adhesion (mm)	-	-	-	5	2-3
	Discoloration	none	none	none	Mod.	slight
solvent-borne one component	Blistering	-	-	-	-	f 8-6
	Under rusting (%)	-	-	-	-	none
	Adhesion (mm)	-	-	-	3	0
	Discoloration	none	none	none	none	slight

* Around scratch

Furniture lacquer based on Setaqua UA.

Urethane-acrylic dispersions offer advantages over simple blends of a polyurethane dispersion and an acrylic dispersion. Because of the fact that the acrylic part is polymerized in the presence of the dispersed polyurethane, grafting reactions occur resulting in the formation of real hybrid particles where the polyurethane and the acrylic polymer chains are present in one particle. This is clearly shown in figure 9 where atomic force microscopy picture of a film cast from Setaqua UA is shown.

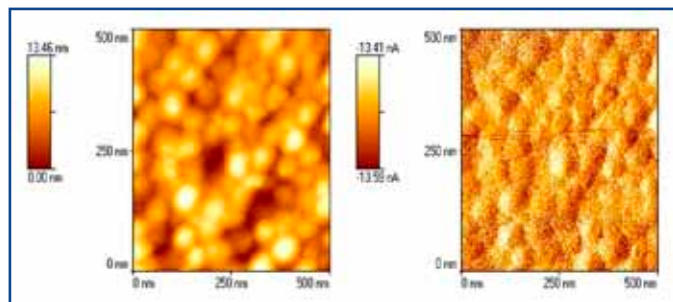


Figure 9. Atomic force microscopy on Setaqua UA (left: topographic, right: tapping mode).

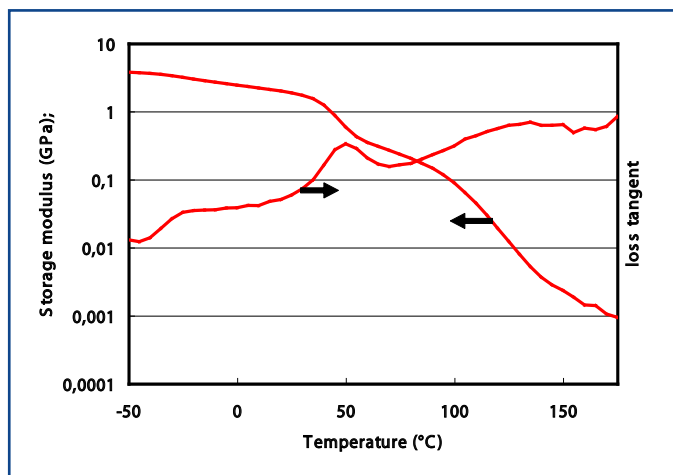


Figure 10. Dynamic Mechanical Thermal Analysis on Setaqua UA (freq. 11 Hz.) after drying at ambient temperature for 7 days.

The acrylic-urethane hybrid polymer is modified with carbonyl groups in order to cross-link via the reaction with a polyhydrazide component. As described in numerous previous papers, it takes about one week at ambient temperature to reach full conversion. Dynamical Mechanical Thermal Analysis (DMTA) was used to study the mechanical properties after crosslinking (figure 10).

Even though only one type of particle can be seen using AFM, the DMTA plot shows different transitions, suggesting a core-shell like morphology.

A simple clear furniture lacquer was formulated using the recipe given in table 10.

Table 10. Clear furniture lacquer.

Component	Weight
Setaqua UA	50
Butylglycol/H ₂ O (1:1)	3
Tributoxy-ethylphosphate	0,5
Surface control additive	0.12
Thickener solution	1

The coating, applied at a wet layer thickness of 150 micron showed a hardness of 150 s Persoz after only one day of drying at ambient temperature. After one week hardness had gone up to 200 s. Persoz, indicating full crosslinking had taken place.

Chemical resistance properties were tested after 2 and 7 days of drying. The results are given in table 11.

Table 11. Chemical resistance (DIN 68 861 1B)

Days after application		2	7
Substance	contact time		
Acetone	10 s	1	1
Ethanol	2 min	1	1
Ethanol / demineralized water 1:1	1 h	1	0

Lipstick	16 h	2	2
Black ink	16 h	3	2
Demineralized water-water	16 h	0	0
Mustard	16 h	2	0

As it can be seen from table 11, resistance properties are quite satisfactory after short drying times and excellent after full cure has been obtained.

Summary

Novel types of solvent free polyurethanes and urethane-acrylic hybrids have been discussed. Through careful selection of the polyol building blocks the use of N-Methyl pyrrolidone can be avoided. The performance of these binders has been compared to conventional NMP containing types in a selection of coating applications. Performance levels that match or exceed those of NMP-containing types have been found for both industrial and decorative applications, clearly illustrating the versatile nature of these water-borne polyurethanes.

Acknowledgements

The authors would like to thank Anneke van der Zande, Fred Bakx and Rob Adolfs for the resins synthesis work and Robert van Egmond and Annemarie Bastiaenen for the paint evaluation work presented in this paper.

References (Endnotes)

1. "A complete guide to DMPA brand of dimethylol propionic acid", Geo Specialty Chemicals, 1999.
2. Ott. K. et al, Patent Application WO2005090447 A2 to BASF Aktiengesellschaft, 2005.
3. The Bayer Scientific Magazine, issue 17, p 92, 2005 (Internet: http://www.research.bayer.com/medien/pages/4003/wood_coating.pdf)
4. Schurmann, H., Bung J., VanAlsten H., US Patent 4,096,127 to Akzona Inc., 1978.
5. Scriven R.L., Chang W., US Patent 4,066,591 and 4,147,679 to PPG Industries Inc. 1979.



Coatings that Michelman has successfully tested for repulpability and their applications include:

- VaporCoat® 330C** – a wax replacement solution typically used on roll wrap, produce boxes, poultry boxes and anywhere packaged goods require protection from water and/or moisture vapor.
- Michem® Coat 40EAF** - another wax replacement coating that is water resistant and also demonstrates some grease resistance. Typically used on fruit, vegetable and protein/meat boxes.
- Nomar™ 70AF** - a water based, abrasion resistant coating, generally used to provide abrasion protection for gas flushed food packaging or small appliances.
- Coating X300AF™** - another waterborne coating that provides a high level of water resistance and good moisture resistance on kraft paper. It is used to protect food products from excessive moisture, freezer burn and sticking.
- MaxWhite™ 17** - a decorative white coating that provides excellent brightness before and after wax applications.



Surface Coatings of New Zealand

Wellington Christmas Dinner 2011

There ain't a lady living in the land that we'd swap for our dear Emily

Fourteen members and past-members turned up at Petone's Bistro107 on the first evening of December to celebrate Emily's finally receiving her 25 year certificate.

National President Richard Calvin arrived in full regalia to make the presentation. Everyone appreciated his attendance and his words of praise for Emily's efforts over the years on behalf of SCANZ and of the industry.

Richard made the point that by becoming a branch, the Wellington Section had freed itself of having to find a committee each year and could instead mount events as it wished.

The key points of the evening were:

- After waiting for more than a year, Emily finally received her certificate.
- Once again Bistro 107 proved it could provide a five star three course meal for \$30.00 (yes you read that right).
- The Wellington Branch proved to the National President it is still alive and kicking – just not having monthly meetings.
- Alan Thorburn can still end up with more glasses than an optometrist.



Emily receiving her 25 year certificate



Ex-presidential perks



*The President of SCANZ,
Richard Calvin, down for dinner
in Wellington*



The High Table



The low table - Alan and Dave close to "Lights Out"



The proof of the pudding

Using OMA and UV-Vis spectroscopy to predict the performance of wood coatings in outdoor-use

by F Bulian, A Matellon A Melchior, O Menotti, M Tolazzi, A Spagna & M Tanelli

Organic coatings are widely used in order to protect wood from degradation, in particular in outdoor applications. Wood degradation involves a number of complex reactions promoted by the interaction of wood with external factors such as oxygen, solar radiation, water, pollutants etc.

Coatings protect the wood, acting like a shield between it and external environment. However, being organic polymers, coatings are themselves subjected to weathering. Coating degradation is due to complex chemical-physical phenomena as a consequence of the interaction with environmental factors.

In particular, the chemical modifications of coating materials in outdoor applications are caused by the UV region of the spectrum of the solar radiation^{4,5} which promotes a complex series of photochemical reactions.

The effects of weathering lead to important changes in the material at molecular level (oxidations, radical formation, changes in polymer structure, changes in molecular weight distribution). These chemical modifications can be detected at a macroscopic level as change of colour, change of gloss, cracking, chalking, etc.

In addition to these chemical changes, some physical phenomena can also occur as an increase in molecular packing and loss of solvent (with a consequent reduction in volume and formation of internal stresses) which contribute to the degradation process. The final effect of coating degradation is the loss of protective performance for the substrate.

Research directions and problems

The ageing problems of coatings drive research towards two main directions:

- development of new formulations more resistant to weathering;
- setting up new test methods to predict coating durability.

As far as the first issue is concerned, coating formulators use different strategies in order to guarantee long durability of the coatings, taking into account various resin types, UV absorbers, radical scavengers and different types of pigments.

The development of an adequate test method is quite complex and many efforts are made in this field by researchers, as well as by standardisation committees.

In this area, the researchers should set out to achieve two goals:

- setting up a fast and reliable test procedure;
- simulating the stress levels of the material found in practical usage conditions.

Nowadays, wood coatings for exterior use are mostly tested following the European standard EN 927-3, which is based on a natural weathering test. However, this method presents two major drawbacks.

The first concerns the fact that one year is required for the completion of a natural weathering test, which is in conflict with the requirements of the manufacturers, who need a rapid evaluation of a new coating. Sometimes an even longer period of time is required, especially when different products are being compared.

The second limitation arises from the evaluation criteria, which are based on visual assessments of the exposed samples, not on physical measurements of parameters characterising coating degradation. At the end of the trial, the panels are evaluated for a range of parameters according to different standards:

- change of gloss -ISO 2813;
- change of colour -ISO 7724;
- chalking -ISO 4628-6;
- blistering -ISO 4628-2;
- flaking -ISO 4628-5;
- cracking -ISO 4628-4;
- adhesion -ISO 2409;
- general appearance.

According to each of the standards mentioned above, the coating; receive a score which is used to evaluate the performance and the conformity of wood coatings.

The value of accelerated testing

Another way to test a coating relies on laboratory-based test methods where adequate and relevant scientific

instruments are used. In this case, accelerated artificial weathering is carried out under controlled conditions of UV irradiance, temperature and relative humidity, with the optional possibility of simulating environmental condition through cycles of water spray and condensation.

This kind of test is relatively fast (for instance, in the European standard EN 927-6, the artificial trial takes 2016 hours [84 days] instead of one year for the natural one) and allows the monitoring of weathering processes under reproducible conditions. The limits of such methods are again the subjective evaluation criteria and the dependency of the overall results also on the wooden substrate necessarily used.

In this work, the authors will present results from the use of rapid weathering methods and their evaluation by laboratory measuring techniques, which represent objective results which can be used by formulators in particular to improve the performance of wood coatings. With such a new approach, possible improvements to wood coatings can be effectively measured.

This procedure, partially developed in previous work, where non-commercial products were used, was adopted in order to check coating variations at molecular level during weathering trials: in principle, chemical and structural variations (eg; mechanical and spectroscopic properties) could be directly related to coating durability.

Thermoplastic organic polymers with visco-elastic properties are widely used as coating films for wood protection. Consequently, their mechanical behaviour is similar both to solid materials (elastic properties) and to liquid substances (viscous properties). This complex mechanical behaviour can be studied in depth by using dynamic mechanical analysis (DMA)

The data obtained from DMA showed that the absolute value of T_g is not the only parameter related to the coating durability, but the "change" in T_g during the weathering test gives significant information about the performance of the coating. The formulations which showed a lower increase in their T_g also have higher durability.

This study is based on the evaluation by means of this new technique of four commercial coatings well-established in the market and well-known in terms of their service life. The formulation of these coatings reflects their known durability, being properly balanced in terms of marketing strategies.

Experimental procedures

Materials and sample preparation

Four commercial water-borne coatings for wood for exterior use, supplied by the same manufacturer, were studied. Being commercial products, their behaviour in use is well known and the classification, in terms of durability, is reported in Table 1.

The preparation procedure of the free films was the same as employed in previous work. The films were prepared in CATAS laboratories, applying the coatings on glass by means of a film spreader, set in order to obtain a wet film thickness of 250~m.

Table 1: Products and their durability

Product	Durability
A	Good
B	Very high
C	Sufficient
D	High

When dried, films were detached from the substrates by means of water vapour at 40°C, and conditioned for a week at 20 ± 2°C and 65 ± 5% relative humidity (RH).

For natural weathering tests, the samples were set up following the guidelines reported in the standard EN 927-3.

Weathering

The artificial weathering trial was carried out using the system specified by EN 927-6 which allows the test conditions (temperature and irradiation) and their duration to be selected.

In this work, the cycle applied is the one described by the EN 927-6 standard. The weathering consists of a weekly cycle (168 h) composed of UV-A exposure, water condensation and a water spray phase, repeated 12 times for a duration of 2016 hours. The samples were analysed at 0, 1008 and 2016 hours.

The films were fitted in the sample holders without a stand on the back, in order to avoid possible adhesion problems and film breakages.

The natural weathering was carried out both following the standard methodology (EN 927-3: total test exposure of one year southward with slope of 45°) and with the introduction of a water trap, which is a blind hole in the middle of the wood panel. (see Figure 1 b).

DMA characterisation

The viscous-elastic properties of materials are tested by means of a Perkin Elmer DMA7 analyser, using a temperature scan test. This technique provides three parameters which characterise a polymer: the storage modulus (E'), the loss modulus (E'') and the loss factor (usually known as $\tan\delta$).

The loss factor can be calculated as the ratio of the loss versus the storage modulus:

$$\tan\delta = \frac{E''}{E'}$$

This $\tan\delta$ can be interpreted as an index of the viscous-elasticity of the material, being defined as the ratio between the viscous component and the elastic component of material. So a material with high value of $\tan\delta$ (low E'' , high E') has a more viscous behaviour than one with lower value of $\tan\delta$ (low E'' , high E').

In a typical thermogram of a polymer, the $\tan\delta$ curve has one or more peaks, commonly assumed to be the glass transition temperature (T_g) of the material.

The temperature scan test was chosen with a fixed frequency of 1Hz. The stretching stress was axial tensile with an amplitude of 10~m. The dimensions of the specimens were 10mm x 3mm; the thickness was assumed as the average value of four measurements, obtained with a digital micrometer, on the free films. Each sample was tested three times.

UV-Vis spectroscopy

UV-Vis transmission through the films was measured using a UV/visible spectrophotometer equipped with an integrating sphere of 50mm. The sphere allows the whole of the light passing through the film, including scattered rays, to be measured.

For each wavelength, the amount of transmitted light, in terms of a percentage (transmittance T), was measured. Low values

of T were expected in the UV range due to the presence of UV absorbers, whilst high values of T should, in theory, be found in the visible spectra if pigments are not present.

During weathering, an increase in T in the UV part of the spectrum was interpreted as a loss of the protection provided by the UV absorbers. The loss of protection in the UV range derived from the increase in transmittance of the weathered coatings, between 200 and 400nm. By contrast, a decrease in T in the visible range (400 to 800nm) can be associated with a loss of transparency of the film or with a colour change due to degradation processes. The result of the UV-VIS spectroscopy was represented by the spectra recorded after a weathering trial.

Results and discussion

In Figure 1 (a), a picture of the panels after one year of natural exposure is shown. After the trial, no visible changes among the samples were visible and it was impossible to differentiate between the high-quality product and the worst one.

More interesting are the results obtained from the same trial with the introduction of the water trap. From Figure 1 (b), it is clear that sample A had finished the trial without visible changes. However, samples C and D showed a number of deep cracks around the hole.

Concerning the artificial weathering test, the process cycle adopted can be considered quite hard for the free coating

films: products of lower quality were not able to withstand the test, as in the case of sample C. During the last part of the weathering trial, this coating film became progressively more brittle until it was not able to resist the mechanical stress caused sample C at this weathering stage, and this explains the absence of the data at 2016 h as shown in Figure 2

and Table 2, where T_g values versus time of weathering are reported. Figure 2 clearly shows that the T_g increases during weathering and that the higher the quality of the coating, the less the increase.

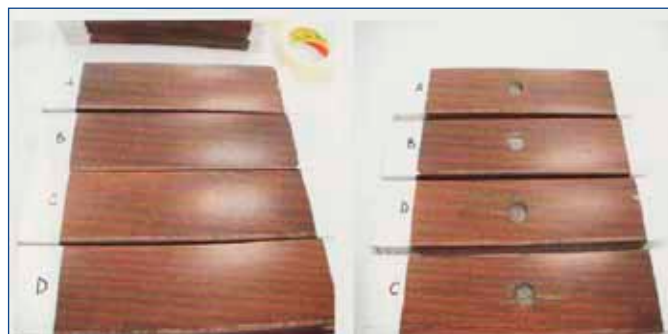


Figure 1: Samples after one year of natural exposure: (a) standard trial EN-927-3; (b) trial with water trap

In order to study the durability of a coating when applied to wood, mechanical and humidity, wood is subjected to dimensional changes which induce stress at the interface with the coating film. That means that an important feature for a coating is its ability to follow the movements of wood in order to avoid the formation of high stresses at the interface that could lead to detachment of the coating itself.

Table 2: Visco-elastic parameters before and after the weathering test

Sample	E' [MPa]	E'' [MPa]	tanδ
A	354	91	0.269
	486	96	0.198
B	206	55	0.267
	237	66	0.279
C	93	23	0.250

IMCD New Zealand Ltd is a leading supplier of specialty and commodity chemicals into the New Zealand Coatings, Inks, Construction, Adhesive and related markets.

Some of our key agencies include...

Dow Chemicals - Glycols, Epoxy resins, Glycol Ethers, Amines, PEGs, Surfactants and Water Treatment systems.

Troy - Wet/Dry film Biocides and Additives.

AkzoNobel - Organic Peroxides.

Sasol - Surfactants and Olefins.

DuPont - Capstone Fluoro-Additives and Micro Powders.

Wacker - EVA Polymer Emulsions and Powders, Silicones, Silanes, Siloxanes and Fumed Silica.

New Supplier: Eagle Chemicals - Solvent based resins (Alkyds, Polyester and Acrylics).



Our contact details:

Paul Armistead and Warren Strickett • 09 582 0250 • imcdcs@imcd.co.nz • www.imcd.co.nz



Value through expertise

	-	-	-
D	235	60	0.253
	415	106	0.253

Table 2: Visco-elastic parameters before and after the weathering test

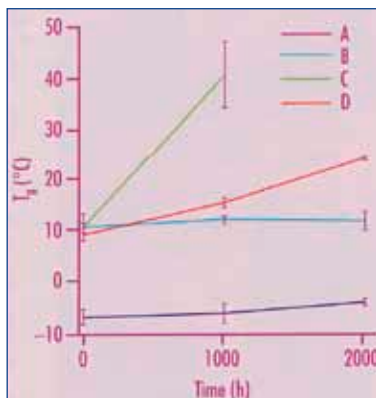


Figure 2: Variation in T_g during weathering trial

The data reported in Table 2 show that sample B had a good combination of viscous-elastic properties: a low value of the E' modulus and a high value of $\tan\delta$. This means that inter-facial stress due to wood deformation will be low and easily relaxed by the viscous movements of the coating.

Furthermore, sample A was stated to be more prone to blocking problems. By the analysis of its viscous properties value (see Table 2), it was evident that it had the highest value of E'' and, as a consequence, a high tendency to a viscous behaviour. This evidence could be related to the stated blocking problems.

Coatings are complex systems composed of a number of substances mixed together in order to give the final formulation its proper features. In particular, one of the more important of these additives is the UV absorber which protects the binder against the harmful UV radiation of the solar spectrum.

However, when clear or semi-transparent coatings are used, the

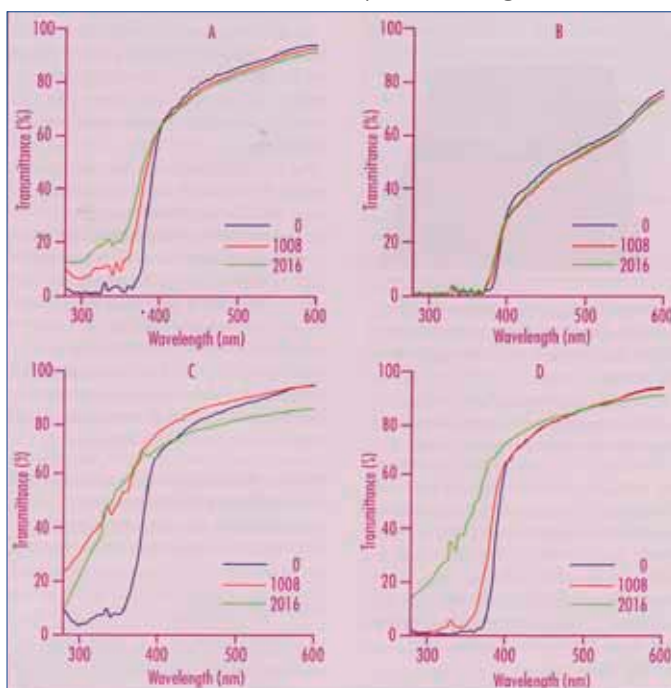


Figure 3: UV-Vis transmission spectra of coating samples at different stages in the weathering test

UV absorber acts like a shield against the UV radiation, and also of course protects the wood below. Without this protection, UV rays can easily degrade wood, one consequence of which is also a loss of coating adhesion.

For these reasons, as highlighted in the previous research, an

important feature for the UV absorber is its stability, which depends on the chemical nature of the absorber as well on the interaction with the binder.

The results of the UV spectroscopy are reported in Figure 3. The spectra clearly show that samples A and B, which represented the top quality coatings, also had a lower transmittance in the UV region (280 to 400nm) during the whole weathering trial. In particular, sample B showed the best performance with only faint changes in the spectra during weathering. This could be related to the presence of a higher pigment loading in this formulation than in the others, which was evident in terms of a low transmittance in the visible region (above 400nm). In this region, non-visible changes occurred during weathering except for sample C which showed a decrease in transmittance due to chalking phenomena.

Conclusions

Four commercial water-borne coatings for wood for exterior use were studied during an artificial weathering trial by means of DMA and UV-Vis spectroscopy.

It was confirmed that a correlation exists between the stability of the T_g and the resistance to weathering of coatings, as well as with their mechanical properties (such as the E' and E'' modulus and their ratio, $\tan\delta$), as initially tested in previous works.

The UV absorber played an important role on the coating durability in two ways: protecting the polymer against the UV radiation and preventing the UV rays from reaching the substrate. As a consequence, the stability of the UV absorber during outdoor exposure was an important feature of the coatings which directly affected film properties. not strictly related to their weathering resistance (for example, blocking problems), but nevertheless useful for producers in order to help them to improve their products.

The proposed approach provided important objective information about the behaviour of the coatings film during an ageing trial. The results obtained were objective measurements and not 'visual evaluations', being especially useful to coating formulators in order to improve their products. their durability. The results obtained in this research, as well as in the previous studies, highlighted also the beneficial effect of a high pigment loading which acts like a shield against solar radiation, supporting and complementing the activity of UV absorbers.

The analyses carried out in order to characterise the coatings were also capable of providing other information about the film properties. not strictly related to their weathering resistance (for example, blocking problems), but nevertheless useful for producers in order to help them to improve their products.

The proposed approach provided important objective information about the behaviour of the coatings film during an ageing trial. The results obtained were objective measurements and not 'visual evaluations', being especially useful to coating formulators in order to improve their products.

References available from - Surface Coatings International 2011/5



CONNELL BROS COMPANY AUSTRALASIA LIMITED

(formerly Wilbur-Ellis Connell Bros)

3rd Floor, 19 Great South Road, Newmarket, Auckland

PO Box 9956, Newmarket, Auckland

☎ +64 9 984 4700 📠 +64 9 921 3391

www.connellbros.com



Rohm and Haas New Zealand Ltd

- Paraloid® Thermoplastic/Thermosetting Acrylics
- Primal® Acrylic Copolymers
- Acrysol®, Orotan®, Kathon®, Ropaque®, Skane®, Rocima®, Additives
- Acumer®, Acusol® Dispersants/Detergent Polymers

Rhodia

- Rhodoline® Defoamers, Dispersants, Wetting Agents
- Abex®, Alkamuls®, Antarox®, Geropon®, Igepal®, Rhodasurf®, Soprophor® Surfactants

Aditya Birla Chemicals

- Epotec® Epoxy Resins, Reactive Diluents & Curatives

Columbian Chemicals Company

- Raven® Carbon Black Pigments

Dynasol

- Calprene® and Solprene® Elastomers

Huber Engineered Materials

- Calcium carbonate, Silica/silicate, Kaolin clay, Alumina trihydrate, Barium sulphate, Engineered composites

General Chemicals

- Glycols, Coalescents, D-Limonene, EDTA, Iron Oxides, Surfactants, Hot Polymerised SBR Rubbers, Various Commodities

AArbor International Corporation

- Silverking® Aluminium Pigment Pastes

Alberdingk Boley GmbH

- Refined Linseed Oils

Sherwin Williams Chemicals

- Moly-White® Corrosion Inhibitors



LANXESS

Energizing Chemistry

Bayer New Zealand Ltd

PO Box 2825

Auckland

Phone 64 9 441 8595

www.lanxess.com



"TECHNOLOGY AND COLOURS FOR COATINGS"

- Organic /Inorganic Pigments (DIC, Sudarshan, Sun E.C. Pigments)
- Fiesta Fluorescent Colours (Swada, NovaGlo, Glowbug)
- Ultramarine Pigments
- Gasil Matting Silicas, Silica gels, Freeflow (PQ Corp)
- Pigment Dispersions (DIC Group)
- Coating & Composite Resins (Reichhold & DIC Group)
- Epoxy Curing Agents/Resins (Reichhold & DIC Group)
- Polyisocyanates/Polyurethanes (Reichhold & DIC Group)
- Aluminium Pastes/Powder (Benda Lutz)
- Solvent Dyes (Rathi)

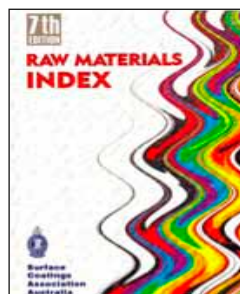
DIC New Zealand

PO Box 12-748, Penrose, Auckland 1642

Telephone 09 636 2947 • Fax 09 636 5522

email: penny.meads@dic.co.nz • website: www.dic.co.nz

CLEARANCE SALE - WHILE STOCKS LAST!



LIMITED STOCKS OF THE 7TH EDITION OF THE SCAA RAW MATERIAL INDEX ARE AVAILABLE

\$10 + \$5 P&P



LIMITED STOCKS OF SCANZ VESTS ARE AVAILABLE

5 – XXL, 8 – XL and 1 – L

Note that these sizes are large for their rating

\$10 + \$5 P&P

Contact: Marina Parshikova • marina@apconz.co.nz
With your details to arrange payment and delivery

nuplex®

**Proud
Supporters
of SCANZ**

Manufacturers & Suppliers of:

- Alkyd Resins
- Polyester Polyols
- Solution Acrylics
- Polyester Gelcoats
- Aqueous Polymer Dispersions
- Polyurethane Dispersions
- M/C Urethanes
- Waterborne Alkyds
- Acrylic/Alkyd Hybrid Resins
- Speciality Resins
- Acrylic Polyols



Building the Future Together



Cooks Composites & Polymers



P O Box 12-841, Penrose, Auckland. Phone: 0-9-579 2029. Fax: 0-9-571 0542. Toll Free: 0800 803 000

Proud supporter of SCANZ



CRISTAL
Global

Millennium
Inorganic Chemicals
A Cristal Company

PO Box 5175
Rotorua West, Rotorua 3044
Toll Free NZ only:
0800 4 TIONA (0800 484 662)
Phone +64 7 346 2225
Fax +64 7 346 2224
Mobile: 021 643 192
www.cristalglobal.com

Supplier of TIONA® brand Titanium Dioxide

**Wish that you could buy
from stock?**

**Looking for a company
committed to supporting
your business?**

Think...



Proud supporters of SCANZ

**Contact one of our team, and we will
make it happen!**

Phone: (09) 486 6637

Fax: (09) 486 6286

sales@rebain.co.nz

www.rebain.co.nz



Responsible Care®
Good Chemistry at Work



Bayer MaterialScience

Bayer: Science for a Better Life
Raw materials for superior coating performance

Aliphatic and aromatic polyisocyanates – Desmodur®
Water reducible polyisocyanates – Bayhydur®
Polyurethane dispersions – Bayhydrol®
Water reducible polyols – Bayhydrol®
Polyether/polyester/polyacrylate polyols – Desmophen®
Radiation curable resins – Desmolux®
Unsaturated polyester resins – Roskydal® UP
Raw materials for powder coatings – Crelan® & Rucote®

For more information contact:

Melbourne +61 (0)3 9263 2293

Sydney +61 (0)2 9391 6000

Auckland +64 (0)9 443 3093

www.bayercoatings.com