

# USE OF FT-NIR SPECTROSCOPY FOR ON-LINE MONITORING OF FORMALDEHYDE-BASED RESIN SYNTHESIS.

Eugenia Dessipri, Elpida Minopoulou

*A.C.M. Woodchemicals plc.*

Georgios D Chryssikos, Vassilis Gionis, Alkiviadis Paipetis

*Theoretical & Physical Chemistry Institute, National Hellenic Research Foundation*

## SUMMARY

A new method is being developed for the fast and reliable assessment of the pathway(s) followed during formaldehyde-based resin synthesis at both laboratory and industrial scale. The method is based on FT-NIR chemometrics. No sample manipulation is necessary and the complete evaluation can be performed on- or off-line in less than one minute. FT-NIR chemometrics were found to be valuable in providing a fast and consistent way of monitoring directly the effects of a change of resin formulation when evaluating new procedures at laboratory scale. Similarly, during industrial production, NIR will soon become a standard tool for ensuring reproducibility and improving overall quality. Measurements are performed on-line and deviations from the standard synthesis pathway can be detected early, allowing the necessary steps to be taken in order to return to the desired pathway. Furthermore, NIR methodologies have been developed to identify and check the conformity of raw materials and final products from urea and UFC solutions to laminating paper produced by impregnation with formaldehyde-based resins. This can prove particularly useful in applications (such as in laminating paper production) where the reproducibility of production and the effects of storage are both questionable and difficult to assess.

## INTRODUCTION

Formaldehyde-based resins have been known for many years. However, new formulations for their synthesis are still being based, mostly, on trial and error experiments, mainly for two reasons. First, there are many different factors that affect, in subtle ways, the synthetic pathway, which are sometimes difficult to control and accurately reproduce. Second, even with the most elaborate equipment, there are difficulties associated with the accurate analysis of the intermediate and final products. This is due to the "living" nature of the system and the destructive nature of the sample manipulations (dilution, drying, etc.) necessary for most analyses. Furthermore, these analyses are labor intensive, time consuming and, therefore, rather expensive.

A new method is being developed for the fast and reliable assessment of the pathway(s) followed during formaldehyde-based resin synthesis at both laboratory and industrial scale. The method is based on FT-NIR chemometrics. No sample manipulation is necessary and the complete evaluation can be performed on- or off-line in less than one minute.

The use of NIR spectroscopy to monitor various processes has been developed systematically during recent years and, in the Fourier transform mode, is known to yield high signal-to-noise spectra in a matter of seconds. The use of optical fibres has allowed for remote and non-destructive operation. Parallel advances in computing hardware have enabled the coupling of NIR with chemometrics, the discipline concerned with the application of statistical and mathematical logical methods to large sets of data (for a recent review, see Brown et. al., 1996). NIR chemometrics have been applied to various industries such as the oil industry, pharmaceuticals, the food industry, for control of fermentation, and in the manufacture of

certain polymers. NIR monitoring has been used either on-line or for end point determinations and reaction co-ordination for both homogeneous and heterogeneous reactions. The analysis has been carried out on liquid and vapour phase process streams. In-line process monitoring on polymer systems by NIR spectroscopy is discussed by D. Fischer (1997) and J. Dunkers (1998). Monitoring of raw wood quality by NIR for use in particleboard (composite board) manufacturing has been advanced by B. Engstrom (1999).

For this work FT-NIR chemometrics have been utilised in order to evaluate new procedures for laboratory scale resin synthesis. They have been found to provide a fast and consistent way of monitoring directly the effects of a change in resin formulation. Similarly, during industrial production, NIR will soon become a standard tool to ensure reproducibility and improve overall quality. Measurements are performed on-line and deviations from the standard pathway of synthesis can be detected early, allowing for the necessary steps in order to return to the desired pathway.

Furthermore, NIR methodologies have been identified with which to identify and check the conformity of raw materials and final products, from urea and UFC solutions, to laminating paper produced by impregnation with formaldehyde based resins. More specifically, NIR algorithms have been developed to evaluate quantitatively the concentration of urea and formaldehyde in aqueous solutions and concentrates (UFC). Algorithms have also been developed for the determination of the quality of laminated paper. These depend on both the quality of the resins used in production and on the conditions under which the paper ages, which, in turn, are a complex function of formulation, natural age, conditions of transport and storage environment. Knowledge of the aging status and the general quality of the laminating paper can, on one hand protect manufacturers from the use of non-conforming paper and, on the other, prevent the waste of well-preserved paper.

The examples that follow highlight applications of NIR chemometrics which relate to the manufacture of wood-based panels, the efficient use of raw material, a decrease in the time needed for analysis and quality control, and the reassurance of reproducibly high-quality products.

## EXPERIMENTAL

### Spectroscopic techniques

Near-Infrared spectra were acquired using a FT-NIR spectrometer (Bruker Vector 22N) in fibre-optic data acquisition mode. Typically, spectra were collected at  $8\text{ cm}^{-1}$  optical resolution and represent averages of ca. 100 scans. In this average case, acquisition time was 1 min. A quartz single fibre optical cable with a transmission probe (quartz, 1 mm optical path length) was used for liquid samples. The total length of the fibre was between 4 and 40 m, depending on the application. Solids, including laminating papers, were measured in the diffuse reflectance mode via a suitable fibre optic bundle probe. Data treatment and chemometric multivariate analysis was based on subroutines available in the Bruker-OPUS software.

Off-line data acquisition for raw material characterisation was performed after conditioning the samples at constant temperature. On-line data acquisition (at laboratory or industrial scale) was performed by immersing the transmission probe directly in the reactor.

### Synthesis of DMU

Urea (30 g, 0.5 mol) was dissolved in 50 g H<sub>2</sub>O. 10g of a 10% solution of Na<sub>2</sub>HPO<sub>4</sub> was added (pH 7.6, 25°C). Spectra were acquired every 120 sec. Formol (21 g of 37% sln; 0.25 mol) was added dropwise (pH 7.3, 25°C). The reaction mix was stirred for 30 minutes. Formol (21 g of 37% sln; 0.25 mol) was added dropwise (pH 7.0, 27°C). pH was adjusted to 7.3 by addition of 2 drops of 16% NaOH and the reaction mix was stirred for 30 min. Formol (42 g of 37% sln; 0.5 mol) was added dropwise. pH was again adjusted to 7.3. The final amount of formol (21 g of 37% sln; 0.25 mol) was added dropwise 30 minutes later. Final pH was 7.1; this was not adjusted

### Laboratory Resin Synthesis – Monitoring with NIR

A typical procedure for the laboratory synthesis of a UF resin is as follows.

A 6l, 4-neck round bottom flask, equipped with a mechanical stirrer; a thermometer, a pH meter and a NIR probe, is charged with formurea solution and water. The temperature is controlled by a heating mantle connected to the thermometer which is immersed in the solution. The pH of the solution is adjusted and urea is added to the desired molar ratio for the polymerisation. The solution is heated up to the desired temperature, and the pH is adjusted again by addition of acid. After a certain amount of time, or when the viscosity has reached a certain value, polymerisation is terminated by the addition of a base. A second amount of urea is added to achieve the desired final molar ratio.

## RESULTS AND DISCUSSION

### Raw material characterisation

Figure 1 shows 7 pairs of room temperature spectra of urea solutions with concentrations 20 to 40% w/w. The spectra exhibit a strong dependence on urea concentration. This can be seen best in the 4970 - 4250 cm<sup>-1</sup> range, which includes the strong combination doublet of the -NH<sub>2</sub> group and is free from water vibrations.

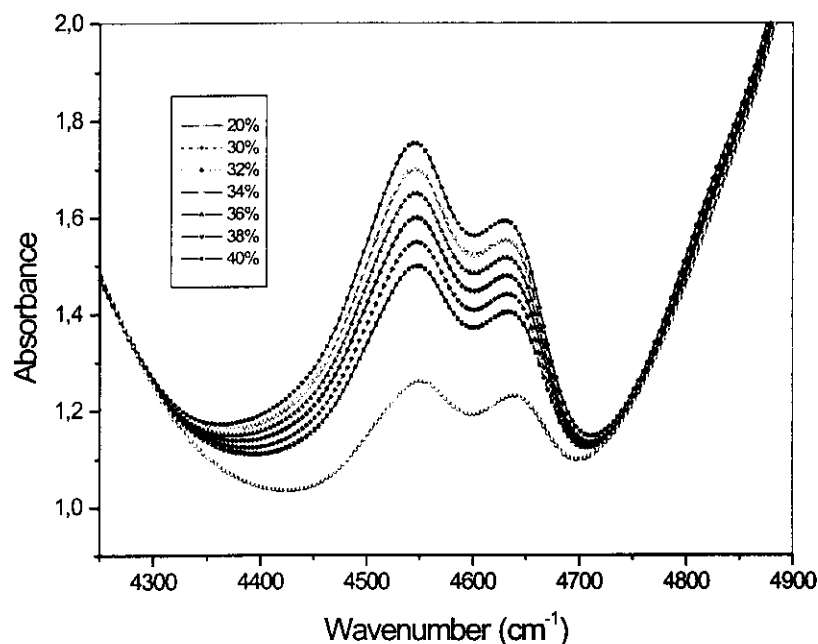


Figure 1: Spectra of urea solutions of concentrations 20% to 40% w/w. The dependence of the spectra on the urea concentration can be seen best in the 4970 - 4250 cm<sup>-1</sup> range.

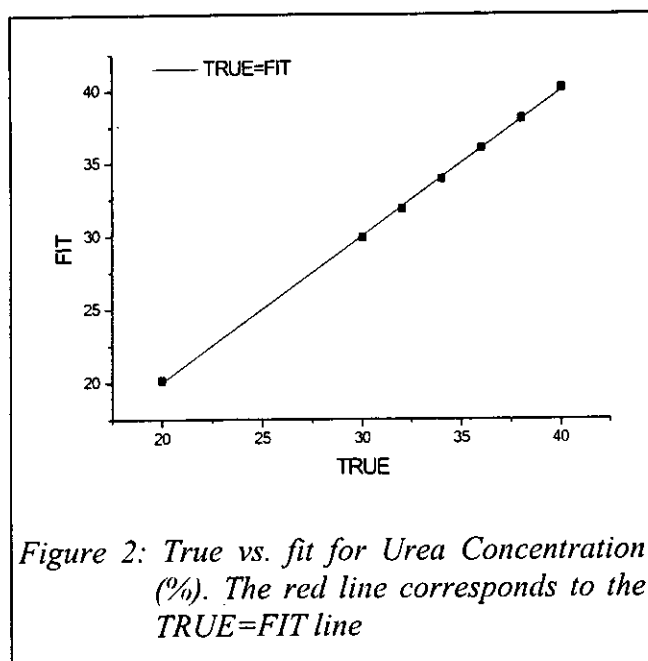


Figure 2: True vs. fit for Urea Concentration (%). The red line corresponds to the TRUE=FIT line

Frequency range 4970 – 4250 has been employed in the 2<sup>nd</sup> derivative formalism to construct a Partial Least Square methodology for the determination of the concentration of aqueous urea solutions. Figure 2 allows for the comparison of the true vs. predicted (fit) concentration values.

The method is valid with an overall prediction accuracy of 99.6%. Note that in this particular concentration range, and due to the judicious selection of the frequency range and data pre-treatment, only one rank (eigenvector) was sufficient to correlate the analytical and spectroscopic data. In industrial applications this method can be used on-

line to predict the concentration of urea in the aqueous solutions used for the production of UFC, provided that its' calibration is adapted to the desired measurement temperature.

More vectors (and more reference samples/spectra) are necessary to quantify complex multicomponent systems. For example, a similar PLS methodology developed to predict the total concentration of urea and formaldehyde species in UFCs (not shown) was based on 72 reference samples and found to require 6 ranks in order to reproduce the accuracy of the independent calibration data.

### Reactions between urea and formaldehyde

Chemical reactions are multi-component systems, where the concentration of reactants, intermediates, products (and by-products) are time-dependent. At the same time pH and temperature may also vary. It is quite simple to tune NIR to record spectra with sufficient sampling frequency. However, the independent analytical data which are necessary for a chemometric calibration are seldom available. Different strategies need to be employed, and some of them are presented here.

The first approach involves the study of model reactions, and is used to provide band assignments and a series of reference spectra. Figure 3 shows parts of the 2<sup>nd</sup> derivative NIR data corresponding to successive additions of formaldehyde to urea solution. As such, the spectra represent "snapshots" from the synthesis of N, N' dimethylol urea (the latter being verified by <sup>1</sup>H NMR). The spectra are dominated by the monotonic decrease of the -NH<sub>2</sub> combination bands (at ca. 4550- and 4650 cm<sup>-1</sup>), and the appearance of a new feature at ca. 4450 cm<sup>-1</sup>, which is attributed to the CH<sub>2</sub> combination band of the methylol group.

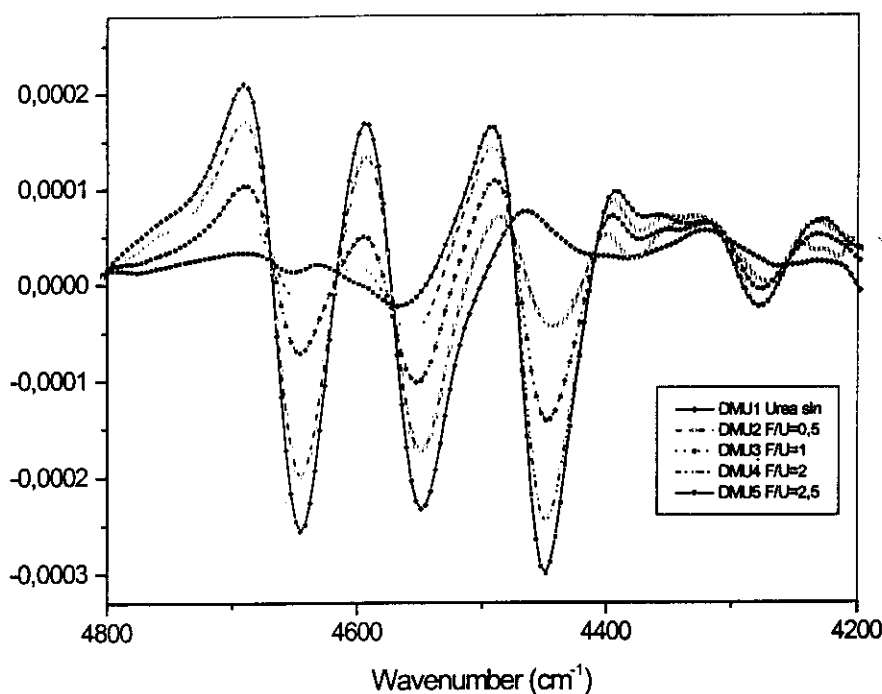


Figure 3: FT-NIR spectra ( $2^{nd}$  derivatives) acquired on-line during the laboratory synthesis of DMU. Progressive additions of formaldehyde to a urea solution lead to consumption of urea.

The acquisition of such assignments has allowed the construction of an algorithm to monitor the kinetics of spectral changes during reactions between urea and formaldehyde. The algorithm yields the reaction progress by interpolating between two reference states, which in this case are defined as the beginning and end of the reaction, respectively. Figure 4 shows the time evolution of such progress scores (normalized from 0 to 100), in 2 min steps, for methylation reactions between urea and formaldehyde at 75°C and pH 7.5 or 8.5.

The traces in Figure 4 demonstrate clearly that methylation at pH 8.5 occurs much faster than at pH 7.5 which is in agreement with the literature (Pizzi A, 1994). Similar experiments have been performed at various temperatures and levels of pH.

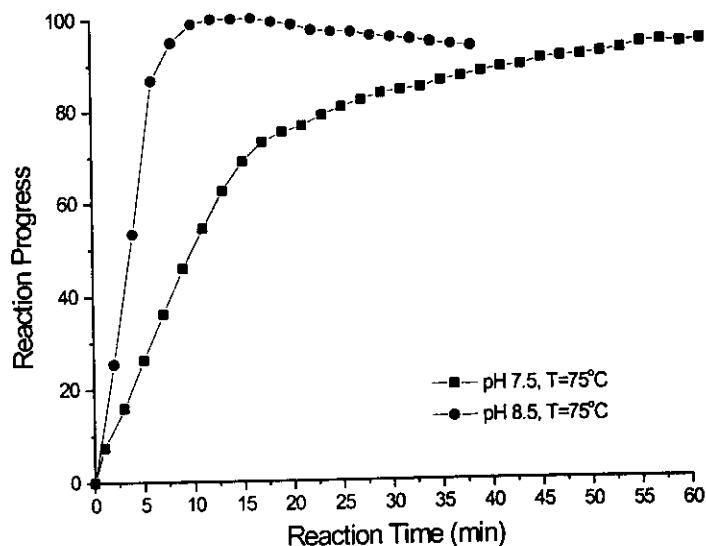


Figure 4: Methylation at molar ratio  $F/U=2.0$ . Reaction monitoring on-line with NIR using special algorithms. As expected from the literature, methylation is faster at pH 8.5 than at pH 7.5.

### Resin synthesis

By extending this approach to real reactions, the number of reference states can be increased to include intermediate phases. These reference states now define a phenomenological reaction pathway that accurately describes the synthesis. NIR can be used to a) check whether this is followed by an unknown reaction and b) to establish how fast the reaction moves from one reference state to the next.

The trace outlined by the black squares in Figure 5 represents the standard pathway for synthesis steps in a known resin reaction. The score, (calculated automatically from the NIR spectra as the reaction proceeds) monitors the approach to a state (where score=0, observed at  $t=50$  min) when the synthesis requires an external change of reaction conditions. The trace outlined by red triangles demonstrates the reaction pathway after an incorrect application of the same synthesis. In this latter case, the reaction is seen to start much faster and deviates from the desired reference state. NIR can be used to provide an early warning for this deviation, and, in this case, allows the operator to apply corrective actions and save the reaction (blue circles).

A subtler situation is shown in Figure 6. Here, the indicator is chosen to magnify the spectral changes occurring during the polycondensation stage of production of a UF resin. The onset of this stage, (score = 100 at  $t \approx 70$  min), is marked by the arrow on the standard pathway (red squares). Polycondensation rate is strongly dependent on pH. A difference in pH of less than 0.1 is difficult to measure reliably in real conditions and yet results in a considerably faster polycondensation (blue trace). NIR monitoring provides a clear warning of this situation and prompts the operator to initiate viscosity measurements much earlier.

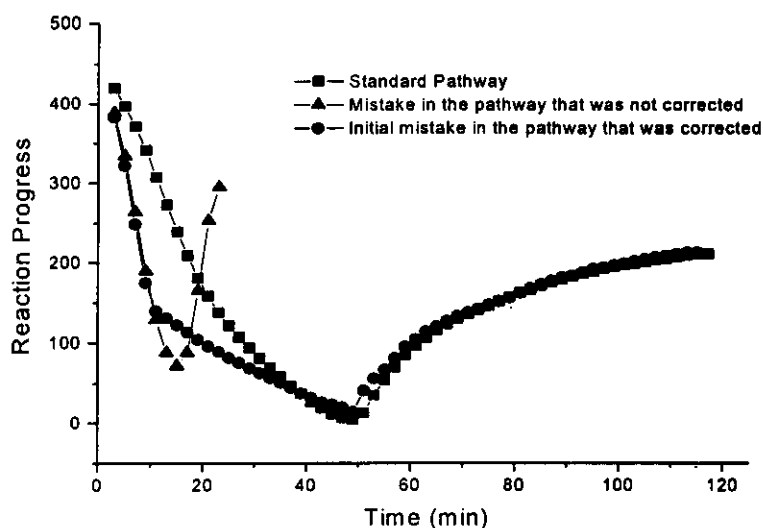


Figure 5: Monitoring resin synthesis. Deviations from the standard pathway can be detected and corrected.

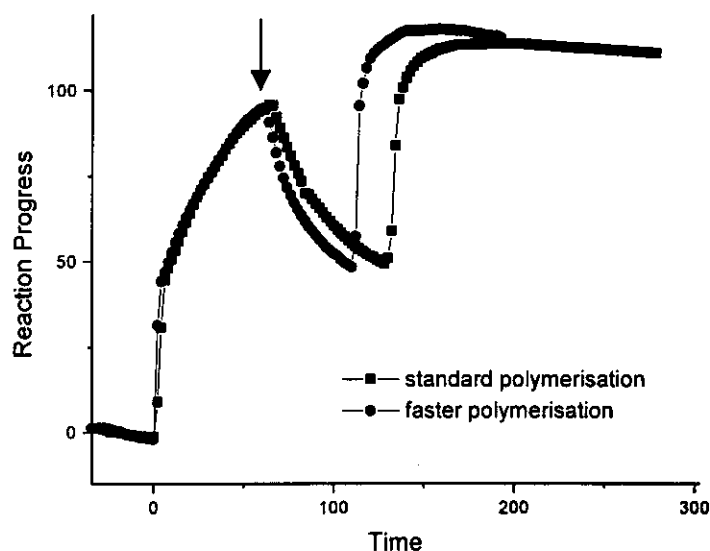


Figure 6: Monitoring polymerisation with NIR. Fast reaction rate can be detected from the beginning of the polymerisation providing early warning of a short reaction time.

#### Time independent pathways for monitoring

The methodologies described above deal with the use of the evolution of NIR indicators with time for the evaluation of the reaction progress. However, there are parts of the UF synthesis where reasonable deviations in the kinetics, due for example to small variations in the heating rate, do not affect the quality of the final product. In order to take account of these situations it is also desirable to have NIR time-independent reaction trajectories. These describe the relative concentration of species present in the reaction mixture and are independent of the rate of the reaction.

Examples of such pathways for two methods of resin preparation are given in Figure 7. The axes correspond to the intensity of NIR absorption in frequencies where  $-\text{NH}_2$  and  $-\text{NH}-$  vibrations are active. Since 2<sup>nd</sup> derivative spectra are employed (to eliminate broad background effects), the more negative the spectral intensities are, the higher the concentration of the respective chemical species. Indeed, these intensities are proportional to concentration by some (species-dependent and unknown) extinction coefficient, which is assumed to be constant throughout the reaction.

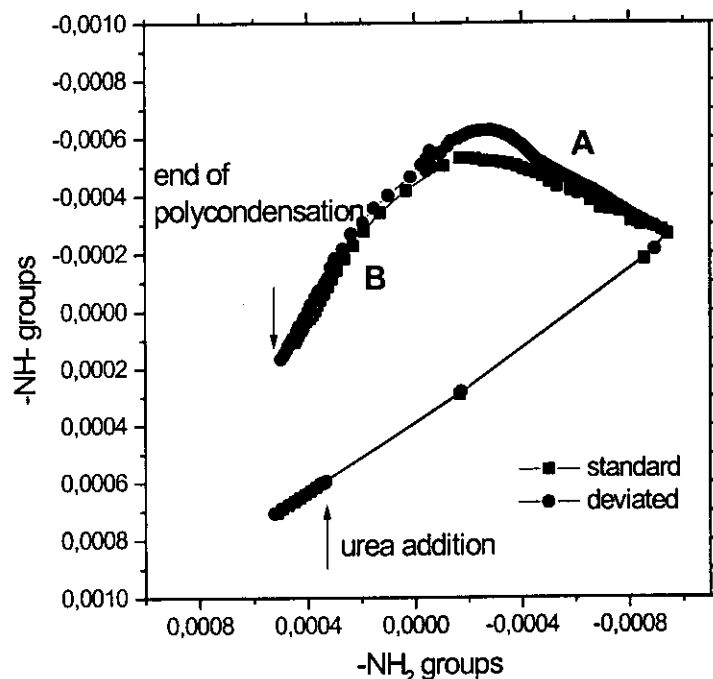


Figure 7: Time-independent pathways describe a synthesis as the change in relative concentration of functional groups and allow monitoring not just of the rate of resin synthesis but also of the effect of the rate on the relative concentrations of the species produced.

As such, a trajectory in Figure 7 corresponds to a periodical monitoring of a quantity proportional to the relative concentration of  $-\text{NH}_2$  and  $-\text{NH}-$  groups in the reaction mixture. Overall, this trajectory represents a very large and continuous set of reference states (in the sense described in section 3), with no information on kinetics except for the variable spacing between points.

Two ranges can be observed in a standard reaction (A, and B in red trajectory). During the first range (A), which corresponds to methylation, the concentration of  $-\text{NH}_2$  decreases while that of  $-\text{NH}-$  increases. Obviously, the slope of segment A will depend on whether the formation of N, N-, or N, N'-dimethylol urea is prevailing during methylation. The second range (B) corresponds to polycondensation, where the concentrations of both primary and secondary amides are decreasing.

The blue trace in Figure 7 depicts the trajectory of a deviated reaction. This yielded a final product with approximately 20% lower performance in laboratory particleboard production. The attribution of this particular deviation to differences in the relative concentration of products, based on the previously described time-dependent indicators (ie those in Figures 5

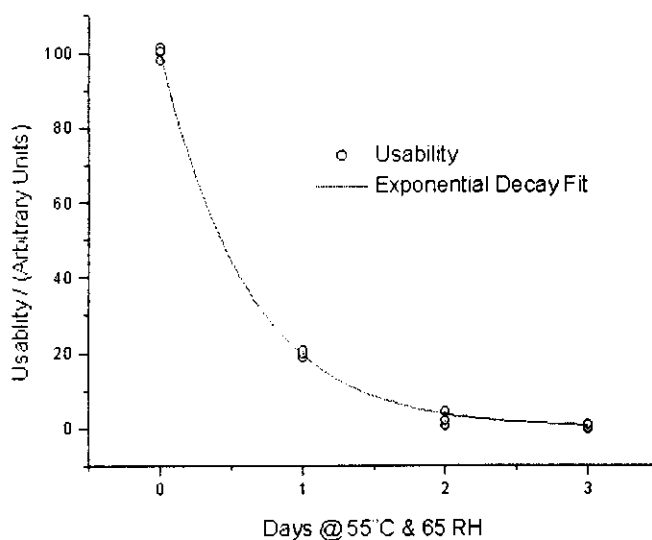


and 6) would have been particularly tedious. Only the simultaneous inspection of more than one indicator would reveal that these reach their characteristic extrema in a non-synchronised manner.

### End Products – Laminating Paper

While reaction monitoring by NIR chemometrics is a valuable laboratory and industrial tool, the evaluation of finished products is, per se, an interesting and useful application. It can be used to provide a quick and reliable conformity test, especially when ageing and storage conditions affect the quality of the product. The following example concerns the usability of laminating papers and is of paramount importance because alternative non-destructive techniques are not available.

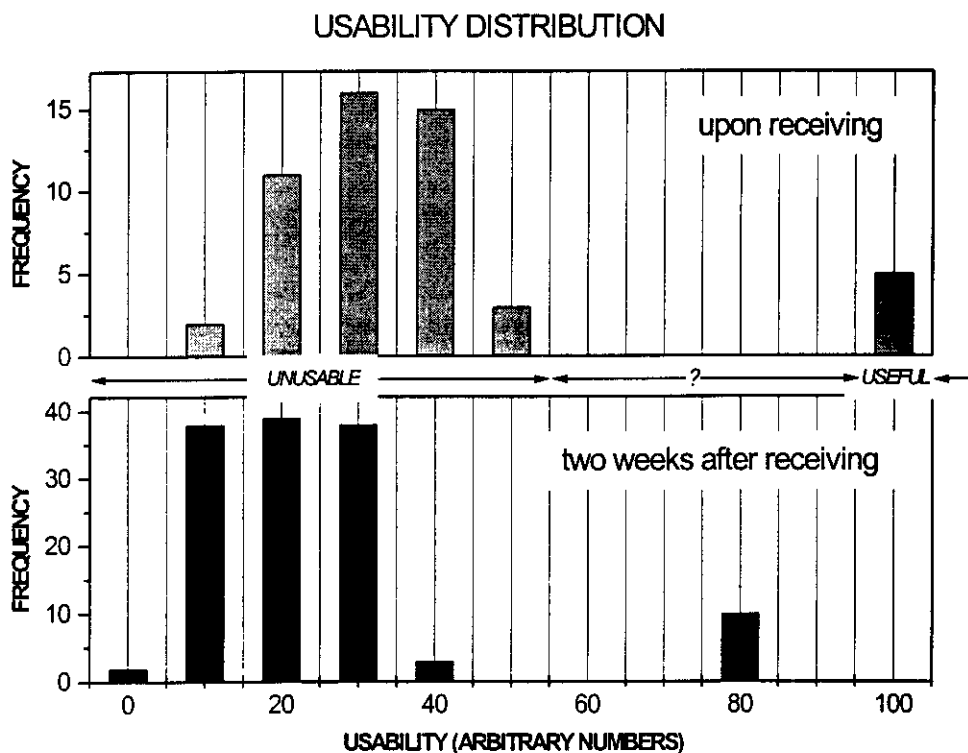
Spectra from melamine paper samples can easily be obtained in the diffuse reflectance mode. Comparison of such spectra taken from fresh samples with spectra taken from samples which had been subjected to accelerated ageing suggests that ageing induces major spectral changes. These are attributed to both the concentration of terminal resin groups and water. Chemometrics have been employed to translate these changes into an empirical usability index, varying between the values of 100 (fresh paper) and 0 (representing the spectrum of the “worst” sample observed). Figure 8 demonstrates the variation of this usability index as a function of time upon ageing at 55 °C and 65% relative humidity.



*Figure 8: Drop in usability index of paper subjected to extreme environmental conditions. The exponential fit allows us to estimate the useful remaining lifetime.*

The spectroscopically defined usability index is found to decrease monotonically with time in a manner that can be fitted quite successfully by a single exponential decay function. Deterioration of fresh samples can be quite rapid under improper storage conditions, but aged samples deteriorate more slowly. Independent laboratory evaluations of paper usability indicated that the paper became unusable after the first day of treatment.

The spectroscopic usability index has been employed in order to evaluate and classify a large number of industrial samples of varying age. The distribution of NIR usability indexes is depicted in the upper histogram of Figure 9. The cluster with index values ranging between 15 and 50 had been classified as unusable. After two weeks of ageing at ambient laboratory conditions, the usability index of the same samples was re-evaluated (lower histogram in Figure 10). The usability of the fresh sample was found to be reduced by some 20 units, while the aged specimens suffered less severe deterioration and the centre of distribution had fallen by ca. 10 units. This trend is in agreement with the previously deduced exponential law of ageing.



*Figure 9: Distribution of usability indexes for two days of monitoring. The difference between the two histograms demonstrates the deterioration of the usability index due to room temperature ageing. The large difference in usability indexes between the acceptable and problematic pallets verifies the adequacy of the methodology.*

In Figure 10 the useful and unusable ranges are clearly defined and separated by 50 usability units. On-line calibration would be necessary in order to accurately define the zone where the melamine papers may safely be used for production and to dictate appropriate pressing conditions.

The deterioration of the quality of laminating paper is associated with inappropriate storage conditions. Board manufacturers have to assume that the papers coming from one pallet are all of the same quality. However, the possibility of differential deterioration of melamine paper within a pallet is demonstrated in Figure 10, where the usability of samples from different positions on the same pallet is shown. It is apparent that sample deterioration commences at the bottom of the pallet. This may be attributed to factors such as moisture

absorption, and clearly indicates that local environmental changes may affect paper quality. In addition, deterioration of paper at the top left side is apparent throughout the height of the pallet. The data collected from the top left side exhibits a wide spread. This may be explained by the fact that there is damage nucleation extending radially on the surface of the paper.

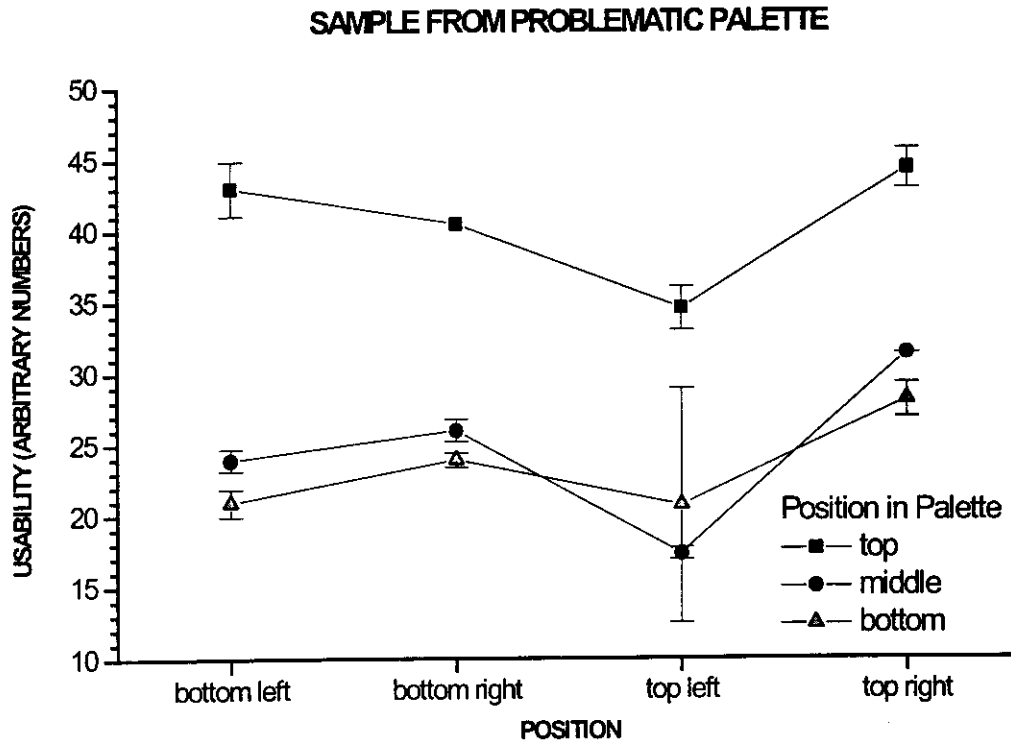


Figure 10: Spatial distribution of usability for a problematic pallet. The assumption often made that the quality of paper is the same within a pallet is not correct.

### CONCLUSIONS

FT-NIR chemometrics can be used for a fast and reliable assessment of the pathway(s) followed during formaldehyde-based resin synthesis at both laboratory and industrial scale. No sample manipulation is necessary and the complete evaluation can be performed on or off-line in less than one minute. The methodologies developed can be valuable in providing a fast and consistent way of monitoring directly the effects of a change in formulation when evaluating new protocols at laboratory scale. Similarly, during industrial production, NIR will soon become a standard tool to ensure reproducibility and improve overall quality. Measurements are performed on-line and deviations from the standard synthesis pathway can be detected early, allowing for the necessary steps to be taken in order to allow a return to the desirable pathway. Furthermore, NIR methodologies have been developed to identify and check the conformity of raw materials and final products from urea and UFC solutions, to laminating paper produced by impregnation with formaldehyde based resins. The methodologies will find applications during board production as well as in laminating paper production or use.

### ACKNOWLEDGEMENT

The research was partially funded by the Hellenic GSRT under the project PAVE 99BE 422. Laboratory scale resin synthesis and measurements were performed at A.R.I. Ltd., Thessaloniki, Greece (research facilities of ACM Wood Chemicals plc.). Measurements during industrial resin production were performed at Hadjiloukas S.A., Komotini, Greece. The contribution of Mr D Loukoumis is greatly appreciated.

### REFERENCES

- BROWN SD, SUM ST and DESPAGNE F (1996): Anal. Chem. 68: 21R-61R
- DUNKERS J, FLYNN K, HUANG M and McDONOUGH W (1998): Fourier Transform – NIR monitoring of Reacting Resins Using an Evanescent Wave High Index Fiber Optic Sensor: Applied Spectroscopy 52 (4): 552-556.
- ENGSTROM B and HEDQVIST M (1999): Prediction of the Properties of board by using a spectroscopic method combined with multivariate calibration: US-A-5,965,888.
- FISCHER D, BAYER T, EICHHORN K and OTTO M (1997): Fresenius J. Anal. Chemistry 359: 74-77
- PIZZI A (1994): Advanced Wood Adhesive Technology: Marcel Dekker Inc., New York-Basel-Hong Kong.