
“Flexibilization of phenolic resin”

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Preface

This report presents the results of a Master Thesis carried out at the Department of Chemical Engineering at the University of Aveiro in Portugal under supervision of Professors João AP Coutinho and Ana Barros-Timmons. All the syntheses and work presented in this report were made at the University of Aveiro during the year 2004.

I would like to extend my heartfelt thanks to those who have assisted me in this work. Sincere gratitude is extended to Professors João AP Coutinho and Ana Barros-Timmons for accepting me into their group and serving as my research advisers. It was a pleasure and a privilege to be in their research group.

I am deeply grateful to Professor Georgios Kontogeorgis for arousing my interest in polymer materials during the last many years of my studies. I am also grateful for his inspiration, support, and comments on the report.

To engineers Maria Manuel M. Santos and António M. Seabre, thank you for sharing your research experience and for your technical assistance during my visits in “*Indasa*”; you have been an invaluable addition to the university research group. Also thanks to “*EuroResinas*” for giving me an opportunity to learn and synthesise phenolic resins.

I would like to thank the PATH Group as a whole for their support on a daily basis. Thank you all for your many conversations, fits of laughter, and research experience - you were great lab and office mates! To my family and friends in general, thank you for your love and support. I could not have done it without you!

6st December 2004, Lyngby

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Summary

Phenolic resin chemistry is an old branch of chemistry that started in the late 1800s. A lot of research work to gain understanding of phenolic resins has been done and reported in literature. However, most of the studies are based on phenol novolac resins. It was necessary to acquire more knowledge on phenol resole resins because sandpaper production has a great interest in resols being chemically modified.

The chemistry of the resole in question is unknown, and one of the major objectives of doing this work was to gain knowledge in this field. The chemical structures of the resin, its physical and mechanical properties and later performance are investigated using different analytical methods.

It was not possible to arrive at the complete chemical structure of the resole due to many impurities and the existence of different derivatives, but many functional groups had been assigned. However, carbonyl signal shifts on IR spectra showing that carboxylic acid is transformed into ester linkage when reacting with the phenolic resin during esterification.

The results showed that the phenolic resin could be modified with diacids, for example suberic acid, making it more flexible. Secondly, it was important to study and understand the effect of different reaction variables on the quality of the modified resin. The effect of diacid was investigated, where the flexibility was best achieved using 0,0014 moles of diacid for 1 g of resin. The effects of other reaction variables (e.g. solvent, reaction time and temperature) were also investigated. The reaction time had no visible effect on the resins' flexibility, while all the other variables showed a small effect on this parameter.

The results show that this approach provides a phenolic resin with significantly reduced brittleness and with better spreading properties than the original phenolic resin. The morphology of cured phenolic resin with diacids investigated by SEM suggests that there is no visible penetration, nor any interference of different coated films.

The mechanical properties of modified resole film are investigated by two tests, double folds and bursting strength. The experimentally measured results of double folds test are found to vary a lot. A detailed statistical analysis on these results shows the imprecision of the test. On

the other hand, the bursting test with its lower coefficients of variation can be used for evaluation of the properties of the coated films.

In addition, as part of the project, a detailed investigation on the finishing film disc P1500 is performed, where all obtained results are summarized in **Appendix R** at the end of the report.

Solving this chemical engineering problem in such a short period and fulfilling the need of the company, have proved that product engineering design is a new and faster approach to solving the problem.

Resumé

Fenolharpiks-kemi er en gammel gren af kemien som startede i slutningen af 1800-tallet. Forskningsarbejde for at få kendskab til fenolharpiks er blevet udført og refereret i litteraturen. De fleste studier er imidlertid baseret på fenol novolac harpiks. Det var nødvendigt at få mere viden om fenol resol harpiks fordi sandpapirproduktionen har stor interesse i at resoler bliver kemisk modificeret.

Den brugte resols kemi er ukendt, og et af hovedmålene for at udføre dette arbejde var at få større viden inden for dette felt. Harpiksens kemiske strukturer, dens fysiske og mekaniske egenskaber og senere ydelser udforskes med brug af forskellige analytiske metoder.

Det var ikke muligt at komme frem til resolens komplette kemiske struktur på grund af mange urenheder og forekomsten af forskellige derivater, men mange funktionelle grupper er blevet identificeret. Carbonyl-signalet flytter sig på IR spektrum, hvilket viser at carboxylsyre omformes til en esterforbindelse når den reagerer med fenolharpiks.

Resultaterne viste at fenolharpiks kunne modificeres med disyre, f. eks. octandisyre, som gør det mere bøjeligt. Dernæst var det vigtigt at studere og forstå effekten af forskellige reaktionsvariabler på kvaliteten af det modificerede harpiks. Effekten af disyre blev undersøgt, hvor den bedste bøjelighed blev opnået ved at bruge 0,0014 moler disyre til 1 g fenolharpiks. Effekten af andre reaktionsvariabler (f. eks. solvent, reaktionstid og temperatur) blev ligeledes undersøgt. Reaktionstid havde ingen synlig effekt på harpiks' bøjelighed, men alle de andre variabler viste en lille effekt på dette parameter.

Resultaterne viser at denne fremgangsmåde frembringer en fenolharpiks med væsentligt reduceret skørhed og med bedre spredning end den oprindelig fenolharpiks. Morfologien af hærdet fenolharpiks med disyre undersøgt ved SEM tyder på at der ikke er nogen synlige penetrationer eller vekselvirkning med forskelligt beklædte film.

De mekaniske egenskaber af modificeret resol film er undersøgt ved to tester; dobbelt fold og bristestyrke. De eksperimentalt målte resultater af dobbelt fold-testen viser sig at variere meget. En detaljeret statistisk analyse af disse resultater viser at testen er upræcis. Derimod

kan bristestyrke- testen med dens lavere variationskoefficienter bruges til evalueringen af de beklædte films egenskaber.

Som en del af projektet er der derudover udført en detaljeret undersøgelse af finpoleringsdisk P1500, hvor alle opnåede resultater opsummeres i **Appendiks R** i slutningen af rapporten.

Da dette kemitekniske problem er blevet løst på så kort tid, og firmaets behov er blevet opfyldt, er det bevist at produktdesign er en ny og hurtigere fremgangsmåde til at løse problemet.

Resumo

A química das resinas fenólicas data do final do sec. XIX. Desde então uma grande quantidade de trabalho tem sido desenvolvido e publicado com vista a uma melhor compreensão destas resinas. A maior parte dos estudos dirigem-se no entanto às resinas 'novolac'. Neste trabalho debruçamo-nos sobre resinas fenólicas do tipo 'resol' dada o seu interesse na indústria de abrasivos. Pretende-se aqui modificar quimicamente uma resina fenólica para alterar o seu comportamento mecânico, melhorando nomeadamente a sua flexibilidade.

A estrutura química da resina 'resol' em questão é mal conhecida e um dos principais objectivos deste trabalho prende-se com uma melhor caracterização da resina. As propriedades químicas, físicas e mecânicas da resina original e modificada são investigados usando uma série de métodos analíticos.

Não foi possível, nem era objectivo deste trabalho, resolver completamente a estrutura do 'resol' devido à presença de impurezas e à existência de diferentes derivados, no entanto muitos dos principais grupos funcionais foram identificados e caracterizados. Foi em particular possível por em evidência a formação de ligações éster na resina modificada através de desvios nos espectros de IR dos grupos carbonilo.

Os resultados mostram que a resina pode ser modificada com recurso a diácidos, como seja o ácido subérico, tornando-a mais flexível. Foi estudado ainda o efeito de vários parâmetros reaccionais na qualidade da resina modificada: O estudo da quantidade de diácido mostrou que se atingia os melhores resultados quanto à flexibilidade quando se usavam 0.0014 moles de diácido por grama de resina. Os efeitos de outras variáveis como o solvente usado e sua quantidade e tempo e temperatura de reacção são também descritos nesta monografia. Mostra-se que o tempo de reacção não afecta a flexibilidade da resina e que as outras variáveis tem um efeito marginal no comportamento mecânico desta.

Os resultados obtidos mostram que é possível obter uma resina fenólica de menos quebradiça e com propriedades de espalhamento superiores às da resina original. A morfologia da resina modificada após cura foi estudada com recurso à microscopia electrónica de varrimento

(SEM) que indica que não haverá penetração visível no suporte nem diferença significativas de comportamento a este nível entre a resina modificada e a original.

As propriedades mecânicas do ‘resol’ modificado foram investigadas através de dois testes: a dobração dupla e a tensão de rebentamento. Os resultados experimentais da dobração dupla variam imenso. Uma análise estatística deste mostra a imprecisão associada ao teste. Mostra-se no entanto que o teste de rebentamento tem baixos coeficientes de variação e pode ser usado para a caracterização das propriedades das resinas estudadas.

Além deste trabalho foi ainda analisado o lubrificante usado na preparação dos discos P1500. Os resultados obtidos que mostram ser o estearato de zinco o composto em causa são apresentados no **Apêndice R** desta monografia.

A resolução de este problema num curto período de tempo respondendo às solicitações e necessidades da empresa mostra como a Engenharia de Produto pode ser uma abordagem rápida e eficiente para utilização na indústria química.

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Flexibilization of phenolic resins

1. Problem formulation

The physical-mechanical characteristics of phenolic resins make them irreplaceable in various engineering fields and specific areas of daily life, being useful in a wide range of applications as for example the adhesive industry. Phenolic resins are the most commonly used resins, but the rigidity of the final product raises problems during its applications.

The objective of this work is to focus on the formulation and preparation of flexible phenolic resins for use in sandpaper production. The derivatization of the original phenolic resin is investigated to yield resins that are more flexible. Characterization of the nature of the structural changes of modified resin is performed by several analytical methods. The mechanical properties, such as bursting strength and double folds, are investigated and compared.

The following work is then divided into the following sections:

- In Section 2 is presented the first task in this project which is to find out what has been done until now by doing a thorough literature study on phenolic resins and what kind of modifications have been made so far.
- In Section 3 general theory, general properties of phenolic resins and paper, and manufacturing of sandpaper are included.
- In Section 4 experimental work is presented.
- In Section 5 the results from the first experimental work are given, as well as a discussion and the partial conclusion that are behind these results
- In Section 6 the summary is presented.

2. Introduction and background

The multidisciplinary nature of polymer science which from its earliest days has involved chemists, engineers, material scientists, and design engineers, is a feature that is often exhibited by other fields of natural science. Humans rely on polymers to keep them warm and dry (fibres); to preserve and protect their food, housing and transport (protective coatings) and to provide their entertainment (recording media) etc.

Phenolic resins are amongst the most popular condensation polymers. They are useful in a wide range of applications as thermal and sound isolation, moulding compounds, foundry resins and composite wood material. The economic importance of phenolic resins proves that they are irreplaceable in the various engineering fields and distinct areas of daily life. Their high temperature resistance, infusibility, and flame retardancy are the key properties which will contribute to a further market growth [1].

Phenolic resins are usually made from the condensation polymerization of phenol and formaldehyde, which gives them another name, phenol formaldehyde resins. However, they were not been known as a commercial product until a patent was granted to Leo H. Baekeland in 1909. After the publication of this patent, there followed during the next few years further papers and patents disclosing the basic principles on which the industry has developed [2].

Since phenolic resins have a wide range of application, a lot of researchers pay attention to how to affect preparation conditions on resin's properties. Being the oldest thermosetting polymers, the influence of many synthesis parameters has already been studied. The molecular structure and properties of the resin depend on many factors, related to prepolymer formation and curing reactions, such as type and amount of catalyst, pH and temperature [3] and formaldehyde/phenol (F/P) ratio [4]. Thus, all research focuses on the determination of optimum preparation conditions to obtain phenolic resins with the desired properties.

In general, phenolic resin is rigid in structure due to its bulky benzene rings, and brittle because of the gaps existing between the benzene rings. Consequently, the phenolic resins used in the manufacturing of sandpaper have limited use in applications where the sandpaper

needs to be very flexible. Recently, thermoset resins have been modified with flexible elastomers [5] or thermoplastic modifier [6], poly(ether)sulfone, to made them less brittle, but most of these focus on epoxy resins because a versatile amine modifier and the high reactive epoxy ring are able to modify epoxy resins easily. The results have shown that the toughness is lowered due to the reduced crosslink density of the cured resin, which is due to the distance between amino groups on the thermoplastic modifiers and to the phase separation of the thermoplastic to give a particular morphology [6].

Phenolic resin exists in two types: resol and novolac type of resin. The novolac type is almost unable to crosslink without a curing agent. An approach by Ma *et al.* [7] has been proposed to improve the toughness of novolac resin by blending it with poly(adipic ester), such as poly(ethylene adipate) (PEA), poly(butylene adipate) (PBA), poly(hexamethylene adipate) (PHA), poly(octamethylene adipate)(POA), and poly(decamethylene adipate) (PDA).

The work has demonstrated that a set of equilibrium constants describing self association and inter association, obtained from the results of Fourier transform infrared spectroscopy of low molecular weight analogues in dilute solution using Painter-Coleman association model (PCAM), are used to predict the thermodynamic properties of phenolic and polyester polymer blends such as phase diagrams, miscibility windows, the degree of hydrogen bonding, and maps of polymer blend systems involving specific interactions. The main equation used in this model is based on the classical Flory-Huggins relation [7].

The miscibility of phenolic resin and poly (adipic ester) in this case occurs at the molecular level, and the blend exhibits true compositional homogeneity. The hydroxyl group of the phenolic resin interacts whenever possible with another modifier that contains a hydrogen-bonding functional group, and the effects of chain connectivity and stiffness are minimized in the phenolic blend system. The obtained results suggest that the nature of hydrogen bonding in phenolic resin is satisfactorily predicted by PCAM, and it is to be expected that the characters of phenolic resin, such as the high hydroxyl group density and low molecular weight, compensate the effect of compositional heterogeneity in the phenolic blend, and thus minimize the chain connectivity and rotational freedom making the phenolic resin more flexible [7].

In the invention presented in US patent [8] the phenolic resin is toughened by the poly (alkylene oxide) due to hydrogen bonds formed between the ether groups of poly (alkylene

oxide) and the hydroxyl groups of the phenolic resin, and a reduced free volume which gives a more compact structure by filling the gaps with long flexible chains of the poly (alkylene oxide). The long flexible chains of the poly (alkylene oxide) are able to increase the amount of energy absorbed and extend the path of breakdown when an external force is applied to the modified phenolic resin.

Resol resins have many reactive hydroxyl groups, which help modify these types of resins by chemical reaction with polyurethane or nitrile rubber. There are some studies performed on combining phenolic resin and rubber, because each possesses unique properties individually, and by finding their suitable combinations, some very characteristic properties can be utilized, such as flexibility.

These rubber modifications may be carried out by mixing the powdered resin and rubber together, and then fluxing on hot rollers with a vulcanising agent; but this gives an expensive product owing to the cost of obtaining the materials in powdered form. A second method is to add the rubber to the unreacted or partially condensed resin mixture. The rubber may be added as latex in a solvent, or as a swelling agent, and it may be vulcanised after the resin has been formed; but the inhibiting action of the resin on the vulcanisation results in a rather poor product. For these reasons, there has been no extensive production of products of this type [9]. The mechanism of the reaction of resols and rubber on heating together occurs at the unsaturated positions of the rubber chain, where a phenolic resole is changed to an *o*-methylene quinone intermediate by dehydration at high temperatures. This intermediate reacts with the double bonds of olefins and forms chroman structures by a 1,4-cycloaddition [10].

US Patent [11] discusses the modification of phenolic resin by incorporating some silicone-based rubber components in the phenolic resin composition, which according to them obtains excellent flexibility and fast curing properties.

Achary and Ramaswamy [12] have studied reactive compatibilization of a nitrile rubber blend and phenolic resin and its effect on adhesive and composite properties. Incorporation of *p*-cresol formaldehyde is done to obtain better dispersed phase that provides useful improvements in adhesive and mechanical properties.

Unsaturated phenols are of interest because they provide further crosslinking by addition polymerization. Most important are those presented in using cashew nutshell liquid (CNSL). This has given the idea of modifying the phenolic resins by using this CNSL, which is a natural product.

The main constituents are a mixture of different phenolic compounds, anacardic acid, cardol and cardanol shown in **Figure 1**. Due to its dual functionality in resin-forming reactions, possessing the hydrophilic hydroxyl group and the hydrophobic aliphatic side chain, CNSL derived products can therefore be condensed with formaldehyde through the phenolic nuclei, and polymerised through the unsaturated side-chains.

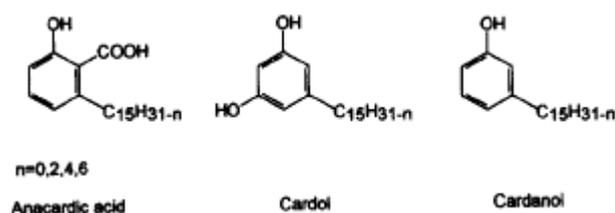


Figure 1. Constituents of crude CNSL.

Mahanwar and Kale [13] have investigated the effect of process conditions and characteristics of CNSL on properties of resins prepared from a mixture of CNSL and phenol with formaldehyde. The addition of CNSL into phenol seems to increase reaction times for the preparation of novolak and resole type resins from 4 hours to 6 hours after the first addition of CNSL. The reaction times become almost double as more and more of the phenol is replaced by CNSL. This increase in reaction time can be due to the low reactivity of the CNSL, arising from the steric hindrance caused by the side chain.

Other properties are also influenced after the addition of CNSL. The following results are obtained:

Table 1. Properties of CNSL based resole.

Phenol:CNSL [w:w]	Tensile Strength [Kg/cm ³]	Charpy Impact [J/mm ²]	Breakdown Voltage [V/mm]	Hardness [Shore D]
100:00	319.49	0.969	1674	85
75:25	216.69	2.430	2283	90

All these changes are due to CNSL having a long side chain, which induces a plasticizing action and changes the properties of the resin [13].

Alternatively, the resin may be introduced into rubber to obtain better heat- and solvent-resistance and surface gloss. Menon *et al.* in 2002 [14] have published a scientific study where natural rubber (NR) has been modified with cashew nut-shell liquid-formaldehyde (CNSLF) in order to improve the mixing and curing of the NR, and with that improve the physicommechanical properties of the final product, such as tensile strength, elongation at break, etc. The presented results have shown that tensile strength increases from 9 MPa for unmodified NR to 13 MPa, and elongation at break increases from 990% for unmodified NR to 1060%.

Aniline can react with formaldehyde in one of two ways to form a white solid anhydroformaldehydeaniline or a low-melting thermoplastic resin. When phenol is introduced into the reaction as a third component, the links between the phenolic nuclei of the resulting resinous product can either take form (a) as presented in **Figure 2**, which occurs when phenol is added after the aniline and formaldehyde have reacted, or form (b) in **Figure 2**, which occurs when aniline reacts with methylphenols.

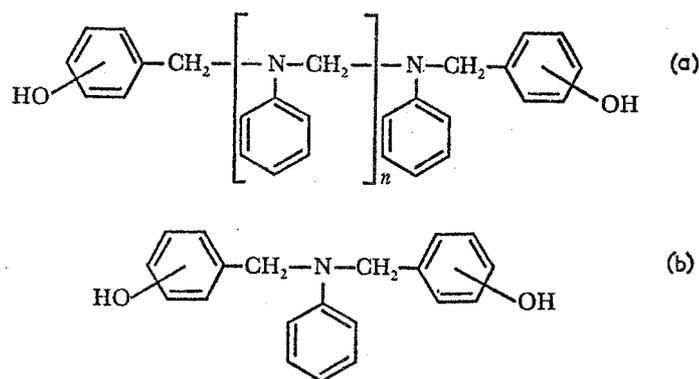


Figure 2. Phenol- aniline – formaldehyde resin units

These types of resins are more flexible when cured than straight phenolic resins, because the density of crosslinking is lower [2]. However, it has been reported that the reason why these types of modified resin have no technical importance is due to difficulties in processing, low flow and hazards which are connected with the use of aniline [1].

Choi *et al.* [15] have tried to modify the resol type phenolic resin with a lower molecular weight flexible diacid, such as adipic, suberic, sebacic or dodecanedioic acid, by inducing a chemical reaction between acid groups of diacids and methylol groups of phenolic resin to form an ester linkage during the cure of phenolic resin as in **Figure 3**.

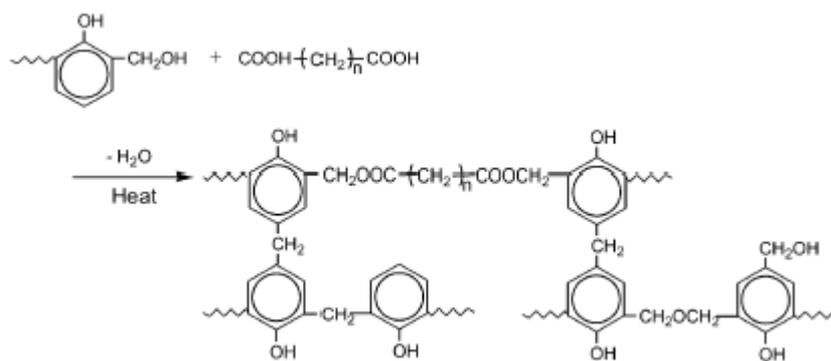


Figure 3. The reaction of phenolic resin with diacids.

Their results when measuring toughness and elongation at break of modified phenolic resins are presented in **Figure 4** showing that the brittleness of the phenolic resin is reduced by the incorporation of these diacids.

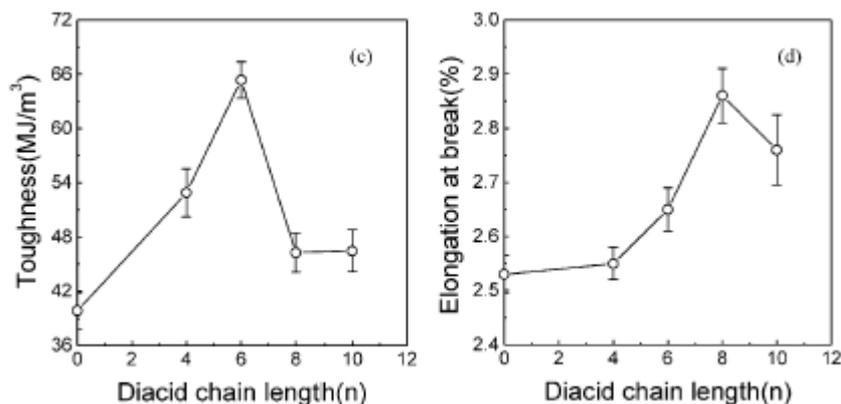


Figure 4. Tensile properties of modified phenolic resins as a function of diacid chain length. The suffix (*n*) indicates the number of methylene units for each diacid.

Preparation and characterisation of the carbonised material of phenol-formaldehyde resin have been studied by Horikawa *et al.* [16]. They have synthesised a resin with addition of various organic substances having straight chain formulas, such as ethylene glycol (EG), 1,6-hexanediol, and polyethylene glycol (PEG).

The results of these reactions have been studied by using thermo-gravimetric analysis, Fourier transform infrared spectra (FT-IR), etc. The signal at 1035 cm^{-1} observed on their FT-IR results presented in **Figure 5b** is assigned to the acetal formation after the reaction between EG and formaldehyde. This signal not being present in **Figure 5a** and **Figure 5c** indicates that only EG has reacted with formaldehyde during the synthesis of the resin, and has formed cross-linking bonds in the phenolic resin.

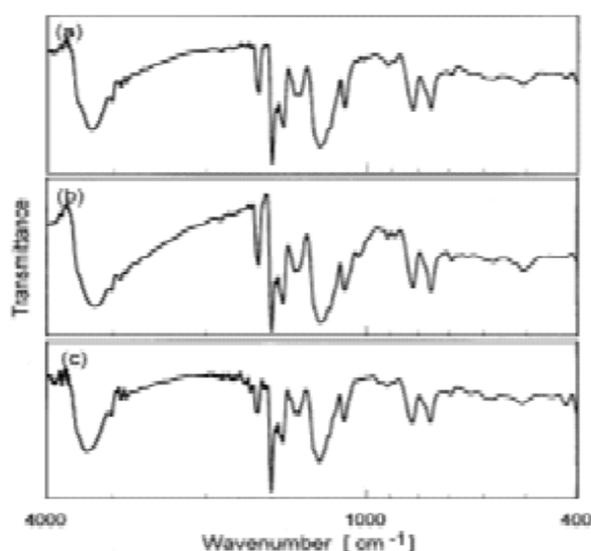


Figure 5. FT-IR spectra of phenolic resin. a) Pure resin, b) with 5% EG, and c) with 5% PEG.

Many researchers have tried to use some other resins as modifying agents for phenolic resins. When for example urea resin is mixed with phenolic resin, the results have usually been very disappointing. The urea resins do not make satisfactory polymers when cured under alkaline conditions, as the pH is usually low enough to cause almost immediate gelation, and there is the question of incompatibility. However, a patent has been granted on a novel urea-phenolic glue [17], which claims mixture of phenolic resins or mixture of urea resins with other amine aldehyde condensation products, where such mixtures are used with or without further reaction and cured with known catalysts, preferably acids, at room temperature.

Table 2 gives an overview of what has previously been done about chemical modification of phenolic resin.

*Table 2. Literature investigations on modification of phenolic resins.
The numbers in references refer to the comments given above.*

Reference	Used method
Ma <i>et al.</i> [17]	Mixing with poly(adipic ester)
US 5,959,671 [8]	Mixing with poly(alkylene oxide)
US 6,664,343 [11]	Mixing with rubber
Achary and Ramaswamy [12], Mahanwar and Kale [13]	Mixing with CNSL
Whitehouse <i>et al.</i> [2]	Mixing with aniline
Choi <i>et al.</i> [15]	Mixing with diacids
Horikawa <i>et al.</i> [16]	Addition of EG, 1,6-hexanediol, PEG
FR 845,399 [17]	Mixing with urea resin

Besides finding a way to chemically modify rigid phenolic resin, a few other things need to be looked into.

Historically, phenolic resins have only been available in organic solvent based formulation. When developing a new modified phenolic resin, one of the concerns is that the new resin should have a low amount of solvents used. This is due to the fact that environmental concern has become increasingly important in recent years. This concern extends not only to

preservation of the environment for its own sake, but also to safety for the public as to both living and working conditions.

One way to make phenolic resin more hydrophilic and with that to substitute organic solvents with water is by making a stable phenolic dispersion of hydrophilic phenolic resin polymer. According to a US patent [18], incorporation of a small portion of an etherified bisphenol-A resin into an aqueous solution of phenolic resin is done to maintain the desired crosslink density and to serve as a more hydrophobic component that, along with the protective colloid, such as polyvinyl alcohol, forms a stable dispersion with low volatile organic solvent content. The results show that the obtained dispersion exhibits good stability, good film forming properties, and coatings that are chemically resistant like those made from hydrophilic resins. However, using more water in these adhesive compositions will lengthen the drying times of films of these coating compositions, which is an unwanted property.

Additionally, it is known that the properties of the coats used for production of sandpapers are influenced by the properties of the separate constituents from which they are made up. The polymer used is only one part of the formulation, but is often the first part to start with. The type, the form, and the relative amount of the resin have a pronounced effect on almost all aspects of the behaviour of the finished product. Similarly, the nature and amount of fillers have an equally important bearing. Lastly, the presence of any other modifiers such as catalysers, colouring matter, etc., will have a pronounced influence on the properties of the final product. This is the reason why the properties of the coat are not simply the sum of the properties of constituencies, but have to be taken into consideration when developing and modifying the coating formulation [19].

3. General theory

The subject matter in this chapter is confined to the general theory behind this work. Section 3.1 is devoted to the study of the chemical mechanisms which take part in the formulation of phenolic resins, covers the manufacturing procedure and the plant, and gives an overview of the general physical properties of phenolic resins. Section 3.2 covers some important aspects of the chemistry of paper, while section 3.3 presents a detailed description of the manufacturing of sandpaper.

In the adhesive field, a phenol formaldehyde resin commonly called a phenolic glue or more simply a “PF” glue, means a condensation product of formaldehyde and a phenol including phenol itself, cresols, etc.

The term “adhesion” has several meanings depending on the area where it is used. In physical chemistry, it means the attraction between a solid surface and a second phase, which can be a liquid or a solid. In adhesion technology, only the interaction between a solid surface and a second liquid phase or solid phase is termed adhesion, while the same term is possibly used differently in some other branches of science [20].

3.1 Phenolic resin chemistry

The phenolic resin normally used for coated adhesives is a resin produced by subjecting a phenol and an aldehyde to polycondensation. Examples of the phenols for use in producing phenolic resin include phenol, cresol, xylenol, ethylphenol, propylphenol, catechol, resorcin, hydroquinone, bisphenol-A, bisphenol-F and the like. These phenols may be used individually or in any combination of two or more. Examples of aldehydes include formaldehyde, paraformaldehyde, benzaldehyde and the like, which may be used individually or again in any combination of two or more [11].

One important parameter for the synthesis of resins is the choice of catalyst used. A catalyst to be used at the time of reaction of the phenol and the aldehyde, is a metallic salt such as zinc acetate and an acid such as oxalic acid, hydrochloric acid, sulphuric acid, diethyl sulphate, or paratoluene sulphonic acid, which can be used either individually or in any combination of

two or more. Besides alkali and alkaline earth hydroxides, ammonia is used in a few instances. Alkali hydroxide catalysts produce a low free monomer content, good durability in water, high reactivity, and rapid initial drying [1]. Most phenolic resins that are made using phenol and formaldehyde are divided into two groups depending on pH, and according to their structures and curing processes.

3.1.1 Resoles chemistry

Resoles are types of products where formaldehyde is used in molar excess, where the molar ratio of formaldehyde to phenol ranges from about 1:1 to 3:1, under alkaline conditions. The temperature should not go higher than 120°C to avoid self-hardening. The viscous resin, resol, is obtained. Since resol contains reactive methylol groups in its molecule, it can be cured by being heated to 150°C. The "crosslinked" resin is a hard yellow solid, which is insoluble in any common solvents [20].

In an aqueous alkaline medium, phenol and formaldehyde are present in the form of phenolate and methylene glycole respectively. **Figure 6** shows both equilibrium reactions. At the same time, phenol is considered with three reactive positions, having a potential functionality of 3, namely 1(*ortho*) and 2 (*para*) and is presented by E_1 . Formaldehyde is considered with two reactive positions, having a potential functionality of two, and is presented by E_2 [21].

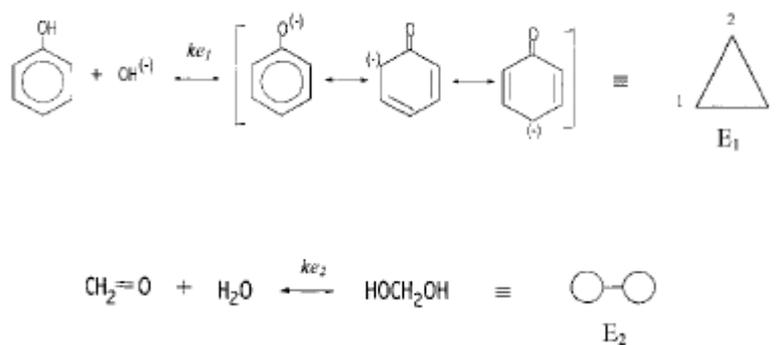


Figure 6. Formation of reactive compounds from phenol and formaldehyde

The overview of the reaction between phenol and formaldehyde in the alkaline conditions to form resol, which is based on two types of reactions, is the following:

1. Addition of hydroxymethyl groups to the ortho and para free positions of phenol (shown in **Figure 7**).

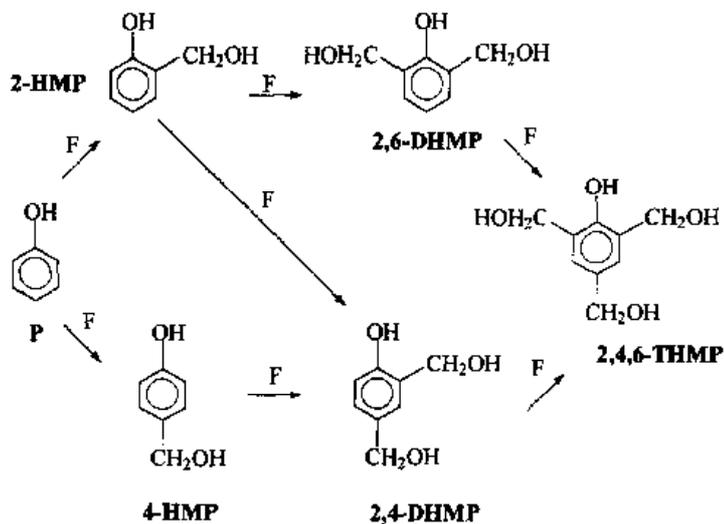


Figure 7. Reaction mechanism for addition of formaldehyde to the phenolic rings. *F* stands for formaldehyde, and all the other names are assigned according to the position of the methyl groups.

2. Condensation reactions between one hydroxymethyl group and one free position in phenol gives rise to methylene bridges or two hydroxymethyl groups forming methylene ether bonds (shown in **Figure 8**).

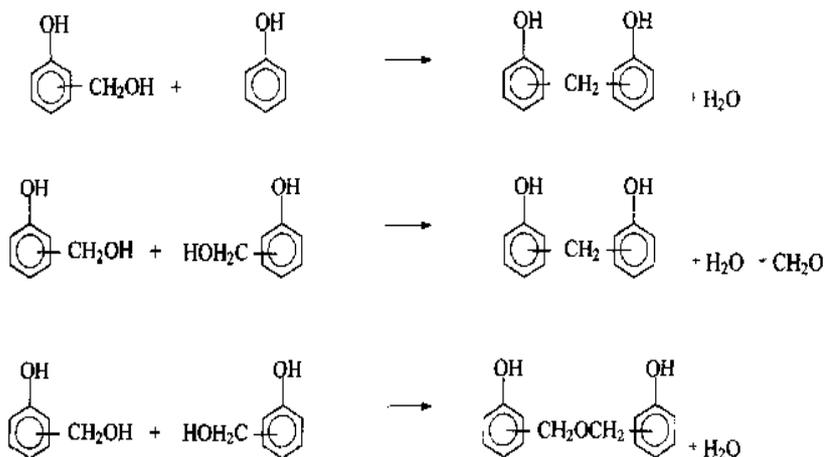


Figure 8. Reaction mechanisms for condensation.

From this figure, it can be seen that as a result of condensation reactions mostly water and formaldehyde are released.

3.1.2 Novolacs chemistry

Novolacs are types of products where phenol is used in molar excess, where the molar ratio of formaldehyde to phenol ranges from about 0.6-1:1, under acidic conditions produced via the electrophilic aromatic substitution of phenol with formaldehyde. The colourless viscous mixture, novolac, is obtained. Three reactive sites are available for electrophilic substitution on phenol, which gives rise to three different aromatic linkages: ortho-ortho, ortho-para, and para-para. A novolac resin of ten phenolic monomer units may give rise to 13,203 possible isomers [20].

This resin cannot be cured by itself. A curing agent such as hexamethylene is needed along with heating up to 110° C for 10 minutes in the curing process. The “cured” resin from novolac is similar to that from resol [20].

When reacting with sufficient additional formaldehyde under alkaline conditions, it is possible to convert a novolac into a resol. The basic difference between resoles and novolacs is that the latter contain no hydroxymethyl groups and thus cannot convert to network high polymer simply by heating [20].

The resols and novolacs resins are low molecular weight products often referred to as A-stage resins. On hardening, these resins pass through a rubbery stage in which they are swollen, but not dissolved, by a variety of solvents. This is referred to as B-stage. Further reaction leads to rigid, insoluble, infusible, hard products known as C-stage. When prepared from resols, the B-stage is known as a *resitol* and the C-stage product a *resit* [20].

3.1.3 Manufacturing plant and procedure

The manufacturing of the phenolic resin is presented briefly in this subsection. **Appendix A** provides a detailed description of the process used in “EuroResinas” for the production of the phenolic resin.

A continuous process can carry out the manufacturing, but in practice, nearly all phenolic resin production is carried out by a batch process. For this latter, the main plant requirements are a large reaction vessel, and all other necessary equipment, such as different valves, condenser, distillate tank, vacuum pump, etc. For detailed description of the reaction vessel refer to the sketch presented in **Appendix B**, while **Appendix C** briefly presents the company “EuroResinas”.

3.1.4 General properties

Novolaks are normally pale yellow or light brown, but if made from pure materials they are almost colourless. It is the addition of an amine that makes the resin yellow, which is the characteristic colour of the resin synthesised under an acidic medium. On the contrary, resols are always darker in colour, being usually red, orange, or brownish, even when made from pure raw materials. It is the presence of hydroxyl ions that give the resols resin a red colour [2].

Phenolic resins are relatively stable up to about 200°C. Above this temperature, they begin to char slowly, and at higher temperatures, charring is more rapid. Above about 400°C decomposition is rapid, yielding the original (and other) phenols, and aldehydes, and leaving a coke-like residue [2].

The mechanical and chemical properties of the resins are considerably influenced by their moisture content, and this applies to plastics made from the resins by incorporating fillers, plasticizers, and other ingredients. Data presented in different tables stated in the book by Whitehouse *et al.* [2], show that the properties are largely dependent on the type and orientation of the filler.

A summary of the important physical properties measured in phenolic resin is given in **Table 3**. This table also includes comments on how the reaction variables influence some of the properties and the interrelationship between the properties.

Table 3. Physical properties for testing phenolic resins.

Physical properties	Analytical method	Comments
Viscosity	Falling ball viscometer	Estimates degree of condensation and increase in molecular weight
Molecular weight (Mw)	GPC	Dependent on F/P ration, type of catalyst, reaction time and temperature.
Molecular weight distribution	GLC, GPC, TLC	Increasing with increasing reaction time, as well as with wt% of catalyst
Molecular structure	NMR, IR, HPLC	Dependent on activity of catalyst
Free formaldehyde content	Hydroxylamine hydrochloride method	Varies little with increasing reaction time
Free phenol content	Koppeschaar method, GC	Decreases with increasing reaction time or with increasing F/P ration
Water content	Karl Fischer, Gravimetric method	Decreasing the melting point and viscosity

3.2 The chemistry of paper

Paper can be defined as a sheet material made up of a network of natural fibers, whose chemical composition depends greatly upon the chemical treatment during paper-making. Mechanical, optical and other properties of papers are highly dependent upon the nature of this network [22].

Paper is mainly composed of cellulose, hemicellulose, lignin, non-cell-wall material, and relatively small amounts of organic extractives and traces of inorganic materials. The chemistry of each individual group of components is considered briefly in the following.

Cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1,4- β -bonded anhydroglucose units that contains alcoholic hydroxyl groups and is used by plants to produce cell walls. These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and intermolecular hydrogen bonds among other cellulose macromolecules as well as with hydroxyl groups from water in the air [23].

Another cellulose derivative is hydroxyethylcellulose. It differs from regular cellulose in that some or all of the hydroxyl groups (shown in red) of the glucose repeat unit have been replaced with hydroxyethyl ether groups (shown in blue).

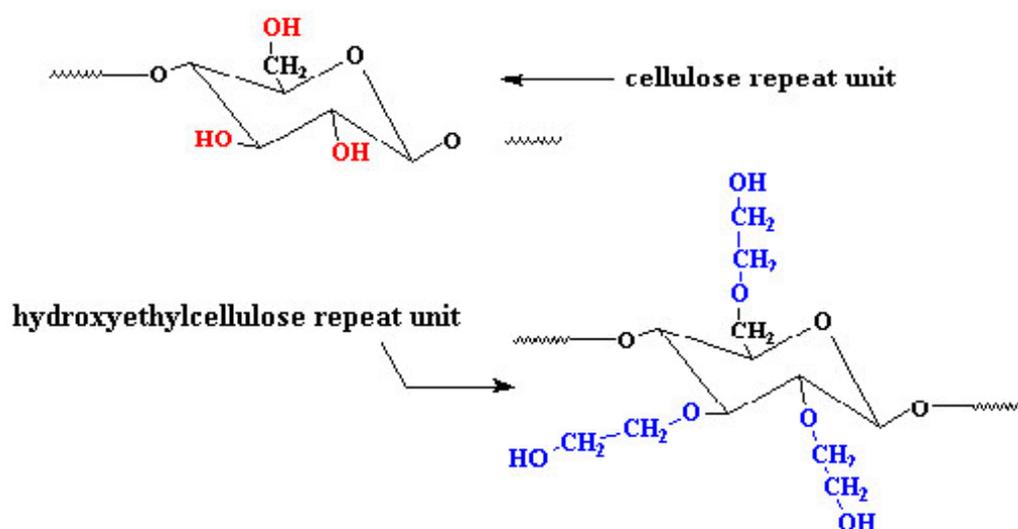


Figure 9. Cellulose- and hydroxyethylcellulose repeat unit.

Hemicellulose is any of a group of complex carbohydrates that, with other carbohydrates (e.g., pectins), surround the cellulose fibres of plant cells. The most common hemicelluloses contain xylans (many molecules of the five-carbon sugar xylose linked together), a uronic acid (*i.e.*, sugar acid), and arabinose (another five-carbon sugar). It is known that the hemicellulose provides more polar groups to attach water. Hemicelluloses have no chemical relationship to cellulose. However, it is widely recognised that hemicelluloses are beneficial to paper properties and that the tensile strength of paper correlates positively with hemicellulose content [23].

Lignins are biochemical phenolic polymeric materials that function as a structural support material in plants. Lignins are formed from phenolic precursors such as p-hydroxycinnamyl alcohols, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol through a metabolic pathway. Lignin is characterized by its associated hydroxyl and methoxy groups. During synthesis of plant cell walls, polysaccharides such as cellulose and hemicellulose are laid down first, and then lignin fills the spaces between the polysaccharide fibres, cementing them together. This lignification process causes a stiffening of cell walls that protect the carbohydrate from any chemical and/or physical damage. The lignin, being polyfunctional, exists in combination with more than one neighbouring chain molecule of cellulose and hemicellulose, making a cross-linked structure [23]. A small section of an extremely complex lignin polymer presented in **Figure 10** illustrates some typical chemical linkages seen in lignin.

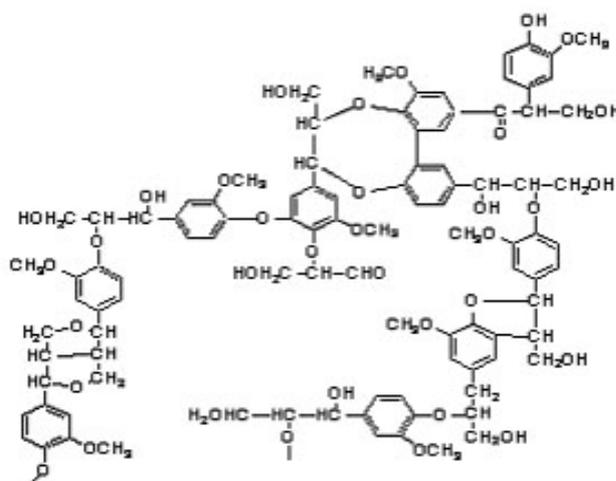


Figure 10. Chemical linkages in lignin.

The chemical composition and structural parameters of a paper vary considerably, depending on the origin, age, retting (mode of extraction of fibres from the source) process adopted, etc [22].

Plant matter that has been processed to create a solution consisting of cellulose filaments suspended in water can be made into paper. A screen is passed through the solution so that the filaments can collect on it and thus form a layer. This layer of cellulose fibers is then pressed and dried to produce a usable sheet of paper. The source of the cellulose fibers, and the degree to which that source is refined, determine the nature and quality of the paper produced [22].

The two most important factors that affect the quality of paper are the presence of impurities and an acidic pH. Finished papers may contain natural impurities, such as lignins that have not been removed during processing, synthetic impurities, such as residual chemicals, like sulphites, not washed out during final processing, or such chemicals as alum that have been added during the final processing.

Lignins are undesirable in a finished paper product. They age poorly, turn brown, become acidic over time, are waterproof, and resist the natural bonding of cellulose fibers to each other. If lignins are not removed and are left in contact with the surrounding cellulose fibers in paper, their acidity will break down the cellulose and the paper will become brittle as a result of photochemically catalysed oxidation processes [22].

The chemistry of paper is a very complex study, and it is beyond the scope of this work to discuss it in detail, nor is there a need to present the detailed mechanics of the paper formation process. However, one thing that should be considered more is the existence of possible functional groups on the surface of the paper that can influence the spreading properties of the film.

3.3 Manufacturing of sandpaper

This sub section gives a short overview of the production steps used for making the sandpapers at the sandpaper company “Indasa”. General information about “Indasa” is presented in **Appendix D**. Before discussing the manufacturing process and the phenolic resins which I have been familiarised with from many visits to the company, the following comments on the other raw materials needed for manufacturing these products are discussed.

Coated abrasive articles generally contain an abrasive material, typically in the form of abrasive grains, bonded to a backing via one or more adhesive layers. Such articles usually take the form of sheets, discs, belts, bands, and the like, which can be adapted to be mounted on pads, wheels or drums. Abrasive articles can be used for sanding, grinding or polishing various surfaces of, for example, steel and other metals, wood, wood-like laminates, plastic, fibreglass, leather or ceramics. Depending on their area of application, there are many different kinds of sandpaper.

Materials used as backing in sheet form are paper, cloth based on cotton and polyester, vulcanized fibers or, in rare cases, polyester film. The papers are tear-resistant special papers, which are classified according to their weight where A is very light and E is very heavy. For waterproof abrasive papers, the paper is impregnated with synthetic resin dispersions, so-called latex paper. This often requires higher flexibility as well as water resistance. The cloths are differentiated by their finish and by their weight where X is heavy and J is light. They are given a preliminary coat on the grain side. This prevents penetration of the primer coat (which causes embrittlement) and improves its adhesion. Vulcanised fibre is a laminate made of parchmented paper. Abrasive products based on papers and cloths are marketed primarily as belts, sheets or rolls, whereas vulcanised fibres are used only as disks.

Binders for the purpose of adhering the abrasive granules to the backing include the traditional phenolic resins, urea-formaldehyde resins, hide glue, varnish, epoxy resins, and polyurethane resins, or more recently a class of radiation cured crosslinked acrylate binders.

3.3.1 The primer coat

The first part of the production is the primer coat process. The primer coat typically includes a tough, resilient polymer binder that makes the abrasive particles adhere to the backing. In the primer coat process, the backing is printed on the reverse (logo etc.), the primer coat is applied by roller, and the grain is distributed in the electric field. The electrostatic scatter takes place against gravitational force, and so the scatter can be controlled by the grain size distributed in the field and by the field strength. The elongated abrasive grains align themselves in the electric field. The material then passes through a drying tunnel. The primer coat is thereby bonded so that the grain cannot be displaced by the nip rolls when the sizer coat is applied.

There are some requirements that the primer coats need to meet. The primer coat needs to have a certain flexibility to ensure a good bond between the highly flexible backing and the very rigid sizer coat, as well as to wet the grain and dry rapidly.

3.3.2 The sizer coat

The second part of the process is the sizer coat process. The sizer coat which also typically includes a tough resilient polymer binder that may be the same as or different from the primer coat binder, is applied over the primer coat and abrasive particles to further reinforce the particles. The purpose of the sizer coat is to assist the abrasive grains in performing their task during grinding.

After application of the sizer coat the abrasive passes through another tunnel. Here the resin is either cured or, as in most cases (e.g. with phenolic resins), bonded sufficiently to go through post curing in rolls. Depending on the plant design, the drying tunnels are classified into suspension dryers and tensionless dryers. In suspension dryers the abrasive is suspended in long loops and passed through a large-volume drying tunnel. In tensionless drying the abrasive is transported flat, and hot air from nozzles is directed onto it. Both designs have advantages and disadvantages depending upon the plant.

The next part of the process is producing the supersizer coat, which includes one or more antiload ingredients or perhaps grinding aids, which may then be applied over the size coat if desired.

3.3.3 Curing

When using phenolic resin in the manufacturing of sandpaper, it needs to be cured. This post-curing of phenolic resins happening in a jumbo roll, which is several hundred meters of abrasive rolled on a hollow mandrel, is done for 20-50 h at 80-125°C, depending on the application. At these temperatures, the backing material fibres are dehydrated and consequently embrittled. The embrittlement can be very largely eliminated by reconditioning (storage for a long period in a damp atmosphere). After conditioning, the abrasive is flexed. In flexing, the back of the rigid abrasive is drawn at a sharp angle over a steel blade (old method) or flexed in special flexing machines. The flexibility of the abrasive is adjusted according to the type of flexing operation (at right angles, crosswise, diagonally, etc.).

At the end, in a typical manufacturing process, a coated abrasive article is made in a continuous roll form and then converted into a desired construction, such as a sheet, disc, belt, or the like.

A brief description of the whole manufacturing process is given in **Figure 11**.

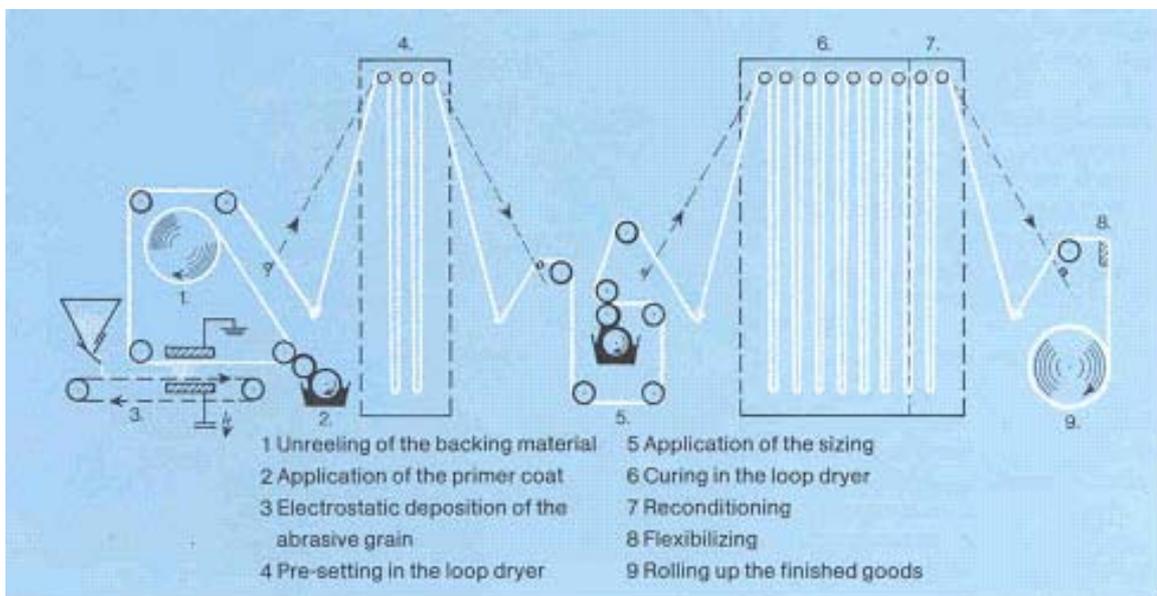


Figure 11. A description of the manufacturing process for sandpaper

4. Experimental work

This chapter deals with the first approach towards solving the problem and the experimental part of the work performed on characterizing unmodified resin and performing chemical modifications.

The original or unmodified phenolic resin referred to in the report is the resin that “Indasa” uses presently, and which needs to be modified to improve its characteristics. The commercial resin **VPR 1740** is a new phenolic resin offered to “Indasa” by another company, that gives different characteristics when used as a primer coat in sandpaper.

Having a produced phenolic resin which needs to be modified, but not being aware of its structure, makes it of primary importance to investigate the unknown structure of a polymer chain and to relate the structure to the performance properties of the polymer in end use. If a polymer chain in phenolic resin is completely characterized and the structural basis of its properties is known, the later modification can be optimised and controlled to produce the best possible properties for the chemical system.

Whatever type of polymer is being dealt with, generally the first question concerns the origin of the material. Is it what it is believed to be? Does it have the desired and required properties? All these questions come under characterization.

Thus, this early investigation is divided into four main stages:

- The chemical product design strategy
- Preliminary observations of general physical characteristics of the resin.
- Identification of the elements and key functional groups present within the structure.
- Tentative proposal of candidate structures based on the results from the first two stages and confirmation of identity by further reactions to furnish recognisable structure.

4.1 Strategy

The problem formulation of this work is something that almost every product designer can expect to do at some point in their work. In this work, the idea is to use a method described in the book “Chemical Product Design” by E. L. Cussler and G. D. Moggridge [24] for inspiration, to obtain the best results in a given time. The described product design takes place in four sequential steps. Needs have to be identified; then ideas that will fill these needs are generated; third, the best ideas are selected; and last, procedure will be considered.

As every product is unique, this individual work will not slavishly follow this method but will be a template, a starting point from which to proceed. To be able to improve the product that will appeal to “Indasa”, it is necessary to know what they need. After properly defining these needs and the specifications for the new product, it is necessary to come up with some good ideas that meet those needs. The best and most promising idea is to be defined and further considered in the development process. Finally, if there is enough time left, it is to be decided what the product should be like and how it should be manufactured in commercial quantities.

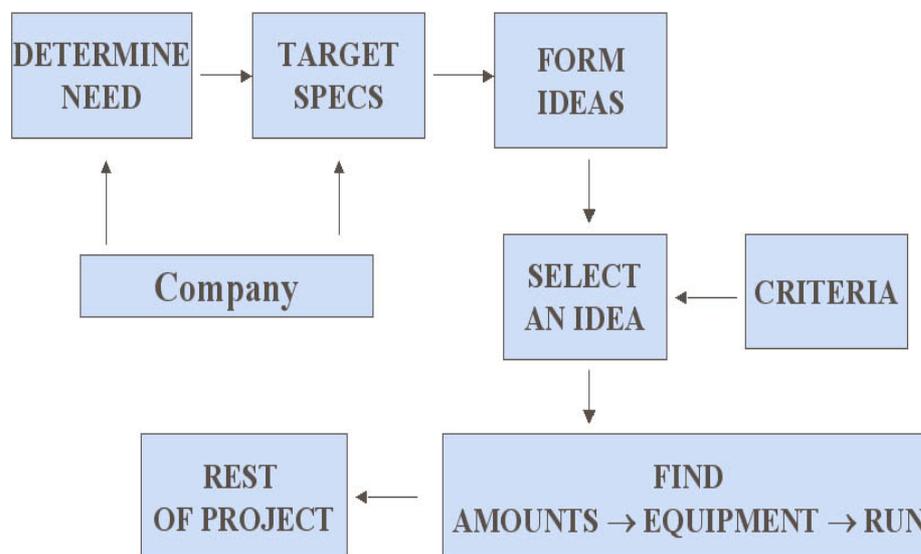


Figure 12. Products engineering steps

At this point, the chosen benchmark, which is a standard for comparison, is an existing unmodified phenolic resin that needs to be analysed before doing anything else.

4.2 Analysis

Different experimental techniques have been used in this project to characterise the structure of resin that is subjected to chemical modification, as well as to analyse the results during the modification. The following subsections therefore specify apparatus, analysis amounts and measuring areas of each.

4.2.1 Infrared spectroscopy (IR)

Solid IR-spectra are performed on a “Bruker IR” spectrometer. Before taking an IR-spectrum, a background scanning is done first, after which a sample is placed on a diamond lens, and 128 scans in the area from 650 cm^{-1} are performed.

Liquid IR-spectra are performed on a “Mattson 700” Fourier transform IR spectrometer using a 2.0 cm^{-1} resolution and 64 or 128 scans depending on the noise to peak ratio.

4.2.2 Nuclear magnetic resonance spectroscopy (NMR)

Samples have first been dissolved in 99-atom percentage deuterated dimethyl sulfoxide (DMSO- d_6), an agent to obtain a deuterium lock and an internal chemical shift standard.

^{13}C chemical shift is measured with a Bruker spectrophotometer.



A “Bruker Advance 500” spectrometer (**Figure 13**) is used to obtain solid-state ^{13}C NMR spectra of the cured resins. The samples are packed into a zirconia’s rotor sealed with Kel-FTM caps and spun at a rate of 5 kHz. The high power dipolar decoupling and magic angle sample spinning (MAS) methods are used during the analysis. Hexamethyl-benzene is the standard for the chemical shift calculations. The acquisition parameters are as follows: 90° pulse width $4\ \mu\text{s}$, contact time 8 ms, dead time delay 60 s.

Figure 13. “Bruker Advance 500” spectrometer.

The solvents containing aromatic groups cannot be used because of a possible overlap in the aromatic region and possible reaction with samples, while the other more used organic solvents do not dissolve the resin completely.

4.2.3 Scanning electron microscopy (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image and is designed for direct studying of the surfaces of solid objects providing information on the topography of a specimen.

SEM micrographs of the fractured surface of the tension test specimens are obtained using a “Hitachi S4100” SEM (**Figure 14**) instrument, where the specimen is cut and mounted on an aluminium stub and is sputter coated with a thin layer of carbon before being viewed by a SEM.



There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field allowing a large amount of the sample to be in focus at one time, and it also produces images of high resolution, which means that closely spaced features can be examined at a high magnification.

Figure 14. “Hitachi S4100” SEM instrument.

The regular SEM requires a conductive sample. All metals are conductive and require no preparation to be viewed using an SEM. In order to view non-conductive samples such as plastics, the samples must be covered with a thin layer of a conductive material by using a small device called a sputter coater.

They work in the following way: The primary electron beam strikes the specimen, secondary electrons are emitted and sensed by a detector. The electrons are then converted to light energy, which is converted into electrical current. This signal culminates in a cathode ray tube, which produces a picture much like that of a television. The resulting image can be photographed or viewed on a computer for analysis. The obtained image appears three-dimensionally. The aforementioned secondary electrons in combination with backscattered

electrons, which are electrons from the specimen that are boosted to a higher energy level by the electron beam and subsequently absorbed by the detector, are responsible for the 3-D quality picture. The number of electrons detected varies with the topography of the specific area of the specimen being scanned.

4.2.4 Elementary analysis

A “LECO's CHNS-932” instrument (**Figure 15**) is used to analyse nitrogen, carbon and oxygen contents in homogenous microsamples (2 milligrams) of the unmodified phenolic resin. The sample is burned at a temperature of 1000°C in flowing oxygen for C, H, N and O analysis in the analyser.



The CO₂, H₂O, and NO_x combustion gases are passed through a reduction tube with helium as the carrier gas for converting the NO_x nitrogen oxides into N₂ and binding the free oxygen. Selective IR detectors measure the CO₂ and H₂O combustion gases. After corresponding absorption of these gases, the content of the remaining nitrogen is determined by thermal conductivity detection.

Figure 15. “LECO's CHNS-932” analyser.

For oxygen, a separate sample is decomposed in a pyrolysis furnace at 1300°C. The oxygen set free reacts with activated charcoal forming CO. The gas is passed through an oxidation tube with the helium carrier gas and is oxidized forming CO₂. The amount of CO₂ gas is measured as above by an IR detector.

4.2.5 The Brookfield viscosity

Level the viscometer (Brookfield viscosity meter Model DV II) using the level of bubble on the device and adjust the feet of the support. The sample should be stabilized to the temperature of assay (normally 25 ± 2°C). Always dive the spindle and the scaffolding of the viscometer in the sample, using an elevator, and verifying that there is no formation of air

bubbles. Bind the engine of the viscometer and select the speed of adjusted rotation. When the display value is constant, register it.

4.2.6 Hydroxyl group analysis

The quantitative determination of the “available” hydroxyl group in phenolic resin is important when trying to optimise the synthesis. It is helpful to know how many hydroxyl groups have reacted with diacids or monoacids and how many can react at all to give the best results [25].

Although hydroxyl groups show very strong absorptions in the infrared region, general quantitative procedures based on the direct infrared measurements are often hampered by the tendency of the groups to form hydrogen bonds among themselves and with other polar groups. The intensity of the absorptions normally depends on the degree of association in the system, which can be controlled by the procedures specifying conditions [25].

Another way to determine hydroxyl groups is acetylation by acetic anhydride in pyridine. The uncatalysed reaction proceeds at 100°C for 3 hours, whereas the reaction catalysed by sulphuric acid proceeds within 1.5 hours.

It is known that acetylation technique possesses a number of disadvantages and limitations. The reaction is relatively slow, and the volatility of the anhydride requires that some precautions against losses be taken, whereas work with pyridine presents some difficulties.

However, acetylation can be modified in order to be more acceptable. Maleic anhydride is one of the most reactive reagents with respect to alcohol hydroxyl groups, and it can be used as a reagent for the determination of hydroxyl groups [25].

Pyridine will not catalyse this reaction, because its basicity ($pK_a=5.20$) is insufficient to bind the carbonyl group. Therefore, triethylamine ($pK_a=10.85$) can be used as a catalyst. The nucleophilic interaction of ternary amine (II) with the carbon atom of the carbonyl group of maleic anhydride (I) is taking place in accordance with the commonly accepted mechanism of the formation of zwitterionic intermediate (III). Zwitterionic intermediate readily reacts with the functional groups containing mobile hydrogen atoms (IV), which in this case are the hydroxyl groups of alcohol, resulting in the regeneration of the catalyst. The latter favours the binding of the resulting acid (V) (**Figure 16**).

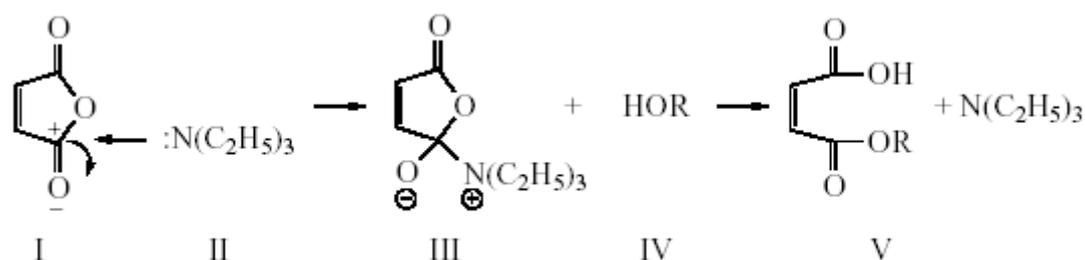


Figure 16. The scheme of the acetylation technique.

The advantages of this procedure are a significant reduction in the duration of the analysis, the elimination of volatile acetic anhydride and pyridine, and the possibility to determinate hydroxyl groups in even low molecular phenolic resin, which contains less than 1% hydroxyl group [25].

The procedure to perform acetylation is the following:

1 g resin is dissolved in 10 mL of maleic anhydride, and 1 mL of a triethylamine solution is added (if the solution becomes turbid, 2 mL of methylsulfoxide is added). The solution is held at 70°C for 20 min. It is then cooled slowly, 30 mL of water is added to hydrolyse the excess of anhydride, and the solution is titrated with a 0.1 KOH solution within 5 min, as the rose hue of the solution starts disappearing. The blank experiment is carried out simultaneously with no resin added.

The difference between the titration volumes in the two experiments is equivalent to the number of hydroxyl groups in the phenolic resin!

4.2.7 Physical properties

Solubility in distilled water is very often an indication that the component either has a low molecular weight (particularly if a liquid) or possesses hydrophilic groups such as CO_2H , NH_2 , or OH . The solubility is performed by adding a drop of phenolic resin to 1 mL distilled water in a small test tube [26].

The same solubility test is done using saturated sodium bicarbonate solution and 2 M sodium hydroxide to confirm the presence of phenols. Testing the solubility of the resin in the most common organic solvents is carried out in the same manner, to obtain its likely polarity. This information is very useful in deciding on the choice of solvent for preparation of any samples for the structural analysis, such as NMR [26]. The appropriate solvent is chosen by another fundamental requirement, which is high volatility for easy elimination when necessary. For example, when performing IR analysis using the KBr disks, it is important that the selected solvent provides easy elimination from the KBr disk and must not dissolve the KBr disk [26].

Elementary analysis of the resin is performed to detect any other elements present in the sample except the usual elements of carbon, hydrogen and oxygen.

4.2.8 Standard chemicals

All the standard chemicals used during this work are listed in **Table 4**, where the purity and the suppliers of those chemicals are given as well:

Table 4. List of standard chemicals, their purity and supplier.

Chemical	Purity	Supplier
Acetone	Not given	
Adipic acid	99%	Sigma-Aldrich
Butanol	Not given	
Chloroform	Merck	
Dimethyl amino ethanol (DMEA)	Sigma-Aldrich	
Dimethyl sulfoxide	99%	Aldrich Chem.
Ethanol	Not given	
Ethyl acetate	Lab-scan	
Lauric acid	96 wt%	Riedel-de Haën
Maleic anhydrite		Sigma-Aldrich
Malonic acid	98%	Sigma-Aldrich
Methanol	HPLC grade	Riedel-de Haën
n-Caproic acid	99 wt %	Sigma-Aldrich
Oleic acid	95 wt %	Sigma-Aldrich
Polyethyl glycol 600	Fluka	
Stearic acid		Sigma-Aldrich
Suberic acid	98%	Sigma-Aldrich
Tetrahydrofuran	Riedel	
Toluene	Panreac	
Triethylamine	Sigma-Aldrich	

All other commercial products such as Abrakoll, Araldite, K54 and different fillers (for example TiO₂) are used as obtained from “Indasa” without any further purification.

The structures of the used chemicals are presented in **Appendix E**.

4.3 Preparation of the resin films

The objective of this subsection of the experimental part is to make a phenolic film and an epoxy film on backing paper and to use these films for further comparison after and before modification. The aim is to determine the flexibility and hardness of the films and to use the values of these properties as references for future work.

A piece of backing paper is cut into 18×20 cm. Resins with different compositions are prepared and spread on the paper by means of an applicator having the same thickness of 120 micron. The curing of the film is done using the same time and temperature interval as previously determined for sandpaper production. For phenolic resins film this curing is performed in an oven at 90°C for one hour, then at 95°C for one hour, followed by curing at 105°C for one hour and 125°C for one hour to obtain the properly dried and cured film. The film of epoxy resin is dried in an oven at 105°C for one hour.

Table 5. The coating films studied in this work.

Sample nr.	Base resin	Components		Ratio
1	Epoxy	Araldite	Resin	3:1
		Abrakoll	Crosslinker	
2	Epoxy	Araldite GZ	Resin	10:1
		Abrakoll	Crosslinker	
3	Phenolic	Unmodified resin		100
4	Phenolic	Unmodified resin		1:0.02
		K54	Curing agent	

To obtain consistent and desired properties, it is desirable to react the epoxy resin with Abrakoll, as an available commercial product, which acts as a crosslinker. They are mixed just before being applied at approximately stoichiometric quantities depending on desired end use properties. In general, it is recommended by “Indasa” to use the given ratio, which in this case gives the best performance trends of the systems. K54 is another commercial product that functions as a curing agent when used with phenolic resin.

4.4 Chemical modifications

The major need of “Indasa” is thus for a phenolic resin that has to be given a more flexible primer coat on a backing paper when producing sandpaper. There are many ways to obtain such a product, meaning that there exist many ideas that can meet this need as described in Section 2, but there are other product characteristics that need to be taken into consideration when choosing the best solution, among which are:

- Not interfering with any existing patents.
- Keeping the product as little toxic and carcinogenic as possible, by not increasing solvent content, nor adding hazardous components.
- The drying time of a primer coat should not be prolonged.
- Avoiding extreme temperatures as high temperatures can affect some chemicals, while low temperatures can be extremely expensive.
- Not increase the price of the final product by for example introducing some expensive and inaccessible reagents
- Keeping the original rheology properties of the product
- Unmodified phenolic resin is made in a big reactor in “EuroResinas” which is not dedicated to this product but useful for different products, and therefore there should not be big changes in the original manufacturing of the phenolic resin. Therefore the key is not only to optimise one new product, but to schedule and not effect other of their products.
- Easy to identify any expected improvements and to state how large these improvements can be.
- As few risks as possible.
- Speed to reach the marketplace

A careful search for ideas has produced many interesting alternatives, including many different chemical modifications. After careful analysis, it has been decided that the best choice is modifying an already existing resin by a chemical reaction with a component that will decrease the gaps existing between the benzene rings. Introducing some longer chains in its original resin structure can do this.

If the purpose is to make modified resin by making the phenolic resin from scratch, it will need a much longer time than the time given for this product development, and due to this the idea is not considered further.

4.4.1 Phenolic resin and diacids

The first attempt to chemically modify phenolic resins is by using diacids as described in an already published work [15]. This modification is theoretically based on a chemical reaction between the phenolic resin and low molecular weight flexible diacid forming an ester linkage during the cure of phenolic resin. Normally when doing esterification to produce larger esters, there is a tendency for these to be formed more slowly than smaller esters. In these cases, the reaction mixture is heated under reflux for some time to produce an equilibrium mixture. However, for the esterification of phenolic resins, this heating up will cause some further crosslinking of the resin. Therefore, the idea is to mechanically mix phenolic resins with diacids and if necessary, warm the solution up to 70°C, that is under the boiling point of ethanol (the used solvent).

According to the earlier work by Choi *et al.* [15], the optimum diacid content is determined to be 0.0014 moles applicable to all the diacids for each gram of phenolic resin. Using this optimum amount, the phenolic resin is modified with the following diacids: malonic (C₃H₄O₄), adipic (C₆H₁₀O₄) and suberic (C₈H₁₄O₄) acid.

0.0014 moles of diacid are placed in a reaction flask previously equipped with a magnetic stirring bar, and 3 mL ethanol is added under constant stirring and slowly increasing the temperature. More ethanol is added if necessary to completely dissolve the diacid. After dissolving the diacid, 1 g of phenolic resin is added under constant stirring until a homogeneous reaction mixture is obtained. Subsequently, the temperature is allowed to stay at around 55°C, and the reaction is stirred for another 3 hours. The excess of ethanol in the reaction mixture is removed by passing nitrogen gas in the mixture. The final mixture is spread on a previously cut backing paper and cured at 140°C for 1 h followed by curing at 160°C for 1 h.

The procedure that is schematically presented in **Figure 17** is followed when working with diacids that are in solid state. When using diacids in liquid state no ethanol is used or only in very small quantities to obtain a homogeneous mixture.

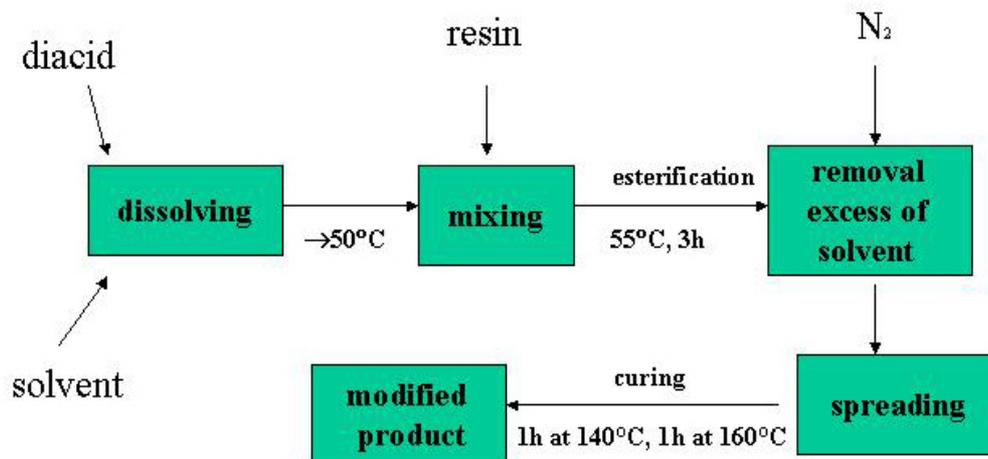


Figure 17. Process diagram

4.4.2 Phenolic resin and monoacids

The same procedure as in section 4.4.1 is used when performing modifications with the following monoacids: caproic ($C_6H_{12}O_2$), lauric ($C_{12}H_{24}O_2$), stearic ($C_{18}H_{36}O_2$) acids, and as well as unsaturated oleic ($C_{18}H_{34}O_2$) acid.

At this point, it should be noted that even though the number of OH groups possible to react with phenolic resin is decreased by half when using a monoacid, the optimum content of monoacids is kept to 0.0028 moles per one gram of phenolic resin to be sure that there is an excess of monoacid in the reaction mixture.

4.4.3 Phenolic resin and DMEA

Dimethylethanol amine (DMEA) is used in the preparation of water-reducible coating formulations. Often the resins used in coating formulations are not water soluble, but can be made so by reacting them with this amine.

As some small traces of DMEA are present in the phenolic resin VPR 1740, which gives better spreading characteristics than original phenolic resin, the aim of this modification is to check the effect of DMEA after being mechanically mixed with unmodified phenolic resin. The same procedure is followed as in section 4.4.1, where the same ratio of the components is kept through this modification. In this case, no solvent is used due to fast-achieved miscibility of these components, and the curing is performed at the same conditions as in section 4.4.1.

4.4.4 Phenolic resin and PEG 600

According to Horikawa *et al.* [16], the usage of organic substances, such as polyethyl glycol (PEG) when preparing carbonised materials with phenolic resin, gives the results that indicate that PEG has reacted and formed cross-linking bonds in the resin. To see if it is possible to obtain any promising results in the case of using such organic additives, chemical modification is performed with PEG with average molecular weight 600.

The first attempt is performed by using the same conditions which are used in section 4.4.1. If this attempt does not give any results, then the second attempt is to use 50 weight percent of the organic additive which is the starting amount used in the work of Horikawa *et al.* [16].

4.5 Mechanical tests

The intention of the present tests is to investigate mechanical properties of the chemically modified phenolic resin that is used as paper coating material. The results of the properties before and after the modification are then compared and analysed.

Bursting strength (defined in ISO 2758:2001(E)) is determined by the Burst-o-Matic tester as described in **Appendix F**, constructed so as to record the pressure per square inch which may be exerted before rupturing the paper.

The greater the stretch of the paper, the greater the bulge of the sheet before it bursts. The pressure required to effect a burst is approximately inversely proportional to the spherical radius of the bulge, so that with papers having equal tensile strength, the greater the stretch, the higher the bursting strength. Usually this test closely follows its tensile strength [27].

Folding endurance (double folds) (defined in ISO 5626:1993(E)) is determined with the Kohler-Molin Folding Endurance Tester as described in **Appendix G**, which folds a strip (15 mm width and 100 mm length) of paper back and forth in a slot, the strip being clamped at either end to a spring device which maintains a uniform tension. Those strips are previously cut with a double-knife cutter. The number of double folds which the strip withstands, is automatically registered. This property is of importance in all papers subjected to repeated folding, especially for folds that occur in the same place each time.

The strip has to be well inspected before attaching it in the instrument to make sure that the line of fold to take place has the same translucency as the rest of the strip, and also that it does not include any other defect. It has been previously reported that the number of folds is directly proportional to the basis weight of the sheet, as well as that the increase in tensile strength closely follows that of the logarithm of the number of folds. For this reason, it is necessary to use the logarithm rather than the actual number of folds when plotting test results [27].

Folding endurance is greatly dependant upon the nature of the instrument used. The test is very sensitive, and there are many things that can affect the test, such as the tension applied, the strip's moisture content, curliness of the fibres in the specimen, fibre length and coarseness, etc. [27].

5. Results and discussion

This section is divided into sections 5.1 and 5.2 that cover results of tests performed on different phenolic resins, unmodified phenolic resin and VPR 1740 respectively. Section 5.3 presents the results after testing coated papers, while section 5.4 shows the results from the chemical modifications of phenolic resin. This section also includes some discussions and indications of the future work that may be performed on resins.

5.1 Tests performed on unmodified phenolic resin

5.1.1 Physical-mechanical characteristics

Insolubility in saturated sodium bicarbonate solution, which is a weakly basic reagent, and solubility in 2 M sodium hydroxide is evidence of a phenol present. An intensification of colour on dissolution in the base is an indication that the resin is aromatic as expected, while a brown coloration in a resin sample when kept at room temperature is normally an indication that some degradation occurs [26].

Each test is carried out in a test tube using a drop of resin in 1 mL of solvent, and solubility in both cold and warm solvent is examined. The dissolution of the resin is followed for 15 days.

Table 6. The results of testing solubility of the original phenolic resin

Solvent	Results
Toluene	Not soluble
Chloroform	Not soluble
Acetone	Not soluble
Tetrahydrofurane	Solubility achieved after longer time
Methyl sulfoxide	Soluble
Water	Insoluble

From the results in **Table 6**, dimethyl sulfoxide is chosen as the most efficient solvent for dissolving the resin and is used for the preparation of an NMR sample as well.

The solubility of the resin in mineral acids is also tested in the same manner. The resin is slightly soluble in concentrated nitric (HNO₃) acid and sulphuric (H₂SO₄) acid, but insoluble in concentrated hydrochloric (HCl) acid.

The rheological properties of coatings are of prime importance in their preparation, storage, and application. In fluids, such as coatings, the key factor in rheology is the viscosity of the fluid. In some cases the viscous properties of the combination of the polymer, pigments, and solvent are sufficient to provide the correct viscosity for the coating.

Unmodified phenolic resin is kept at constant temperature in a slightly covered beaker. The reactivity of phenolic resols during storage is a known problem, where prepolymers increase in viscosity and change in colour.

The results of measuring resol viscosity as a function of time is presented in **Figure 18**.

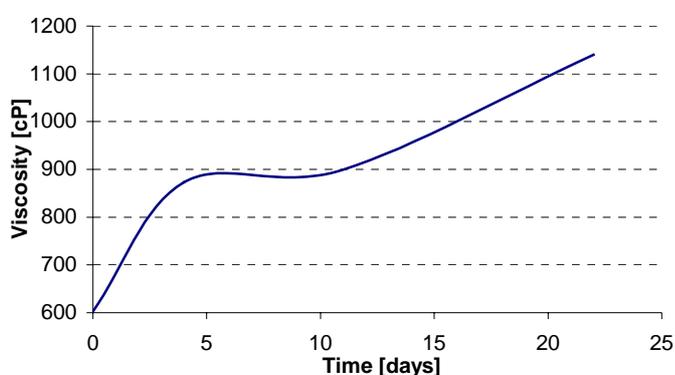


Figure 18. Time dependency of the viscosity of phenolic resin

Those results show the classical increase of the viscosity of the phenolic resol when stored for long periods of time, particularly at room temperature, known as rheopectic behaviour. Since polymers do not display strict Newtonian behaviour, this kind of rheopectic behaviour is observed.

This can be due to the setting up of chemical links between the molecular chains of a resin to form a three-dimensional network polymer system or to some degradation, as well as free phenol and formaldehyde are consumed, as the beaker is not sealed. In addition, there is the possibility of simple mechanical tangling of those long molecules present in the resin sample, which can cause considerable “thickening” of the sample. Due to all these transformations, storage of resols becomes a problematic task which will need further study in the future.

The observed results are very important when working with the same sample of the resin during prolonged periods of time as it is very possible that this property can have an effect on some other results during the work.

After performing the last physical characterisation of unmodified phenolic resin, the next step is to obtain and study spectroscopic data (IR, NMR) to be able to determine the actual candidate structure.

5.1.2 IR-tests

Unmodified phenolic resin is expected to be highly branched multifunctional hydroxymethyl phenol, and a large distribution of its isomers will make it very difficult to characterize.

Results from the IR spectrum performed on the phenolic resin are presented in **Table 7**, where despite the complexity that the IR spectrum presents in the fingerprint region, it is possible to approximately assign some of their stronger bonds using the literature [29] when necessary:

Table 7. The results from the IR spectrum of unmodified resin.

Wavenumbers [cm^{-1}]	Assignment of the peaks
3373	OH stretchings of phenolic ring and methylol group
2950 and 2889	CH stretching of the phenolic ring
2750	aliphatic methylene (-CH ₂ -)
2626	dimethyl ether (-CH ₂ -O-CH ₂ -) bridges
1613 and 1595	two aromatic ethylene bond (-C=C-) of phenolic ring
1235	C-O stretchings of phenolic ring, dimethylene ether bridge
1024	the C-O stretching
1482 and 757	ortho and para substitution
888, 827 and 693	CH stretching (out of plane)

The following figure presents the IR spectrum of the unmodified phenolic resin:

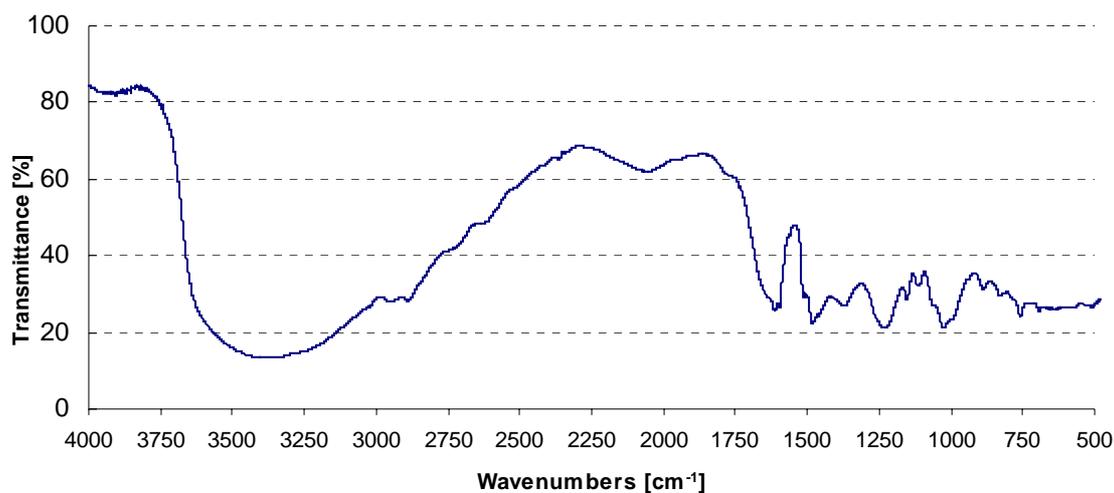


Figure 19. IR spectrum of unmodified phenolic resin.

Although FT-IR spectroscopy is a powerful tool for the identification of functional groups, it is limited in its capabilities in determining structural detail. FT-Raman spectroscopy, based on polarization changes during the vibrational motions can also be explored for the qualitative characterization of phenolic resins. FT-Raman spectroscopy has previously been proved advantageous over FT-IR. The interference resulting from presence of the hydroxyl functionality is not usually observed in Raman spectroscopy. In the analysis of phenolic resins, the areas of interest in Raman spectroscopy include $2800 - 4000 \text{ cm}^{-1}$ where phenyl C–H stretching and methylene bridges are observed, and between 400 and 1800 cm^{-1} where bands due to elongation of aromatic bonds (C=C) and methylene were discernible. Within the $2800 - 4000 \text{ cm}^{-1}$ range, two strong bands are characteristic of phenolic resins, a band at 3060 cm^{-1} due to C–H of the phenyl ring and 2940 cm^{-1} due to C–H of the methylene bridges [28]. However, it has not been possible to take FT-Raman spectrum of unmodified resin.

5.1.3 NMR-tests

NMR spectroscopy can be utilized for obtaining several microstructural details and is exceptionally important for determining the nature and degree of substitution patterns on different ring carbons in phenolic resin. However, it is important to keep in mind that the NMR absorption pattern for methylene carbons of phenolic resins is sensitive to the positional isomerism.

Results from the ^{13}C spectrum (**Appendix H**) performed on phenolic resin are presented in **Table 8**:

Table 8. ^{13}C NMR assignment of the peaks for unmodified resin.

Peak [ppm]	Assignment of the carbons
150-157	Phenoxy carbons
132.26-132.73	Substituted para carbon atoms
124,54-129.00	Meta carbon atom, substituted ortho and para carbons
118.68-118.87	Unsubstituted para carbon atoms
114.51-115.26	Unsubstituted ortho carbon atom
81.9	Oxymethylene
88.1, 63.05	Phenolic hemiformals
59.36-62.81	Para methylol
58.24-58.29	Ortho methylol
38.67-40.34	DMSO- d_6 solvent
25.18	Methylene ether bridges

In the DMSO solvent, the presence of oxymethylene (81- 82 ppm) and phenol hemiformals (65-70 ppm, 86-88.6 ppm) are detected as expected corresponding to the additional products. Those hemiformal molecules in the resole are a potential source of free formaldehyde. In the presence of a high amount of water, the oxymethylene units bonded to the ring will cleave and react with other phenolic rings giving rise to hemiformal species of the type $\phi\text{-CH}_2\text{O}(\text{CH}_2\text{O})_x\text{CH}_2\text{OH}$, where ϕ represents the phenolic ring. Due to the continuous presence of free formaldehyde in the mixture, addition reaction can occur simultaneously with condensation reactions, while hydroxymethyl groups will be available in the solution for addition to free phenol or free phenolic positions during further chemical processes [30].

It is expected that every methylene bridge which has a different chemical environment, has a different chemical shift. Theoretically, there is the possibility that different structures next to *ortho-para* methylene bridges are larger than those of *para-para* methylene bridges. However, those signals are not easy to distinguish in the highfield regions, due to the poor separation of the signals in that area.

The phenoxy carbon region is important from an analytical standpoint as the amount of free phenol, the concentration, and types of end groups can be determined by means of these signals. The spectrum shows the phenoxy carbon region, where phenol appears at 150 ppm - 157 ppm, monoalkylated phenols at 156.20 ppm, and two different dialkylated phenols at 152.97 ppm and 151.8 ppm as presented in **Figure 20** [31].

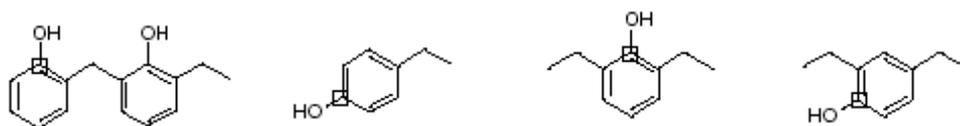


Figure 20. Structures of substituted phenols.

Results from the ^1H NMR spectrum (**Appendix I**) performed on the phenolic resin are presented in **Table 9**:

Table 9. ^1H assignment of the peaks for unmodified resin.

Peak [ppm]	Assigned groups
8.48	Benzylic protons
7.25 and 6.6	Aromatic protons
4.50	$-\text{CH}_2-\text{O}-\text{CH}_2-$
2.5	R-OH
1.75	Methylene $-\text{CH}_2-$

The chemical shift of the aliphatic OH group present from the unreacted alcohol is variable, as its position depending on concentration, solvent, temperature, and presence of water or of acidic and basic impurities. That is why the peak can be found anywhere in the range of 0.5 to 5 ppm. It is the same with aromatic protons that can be in the range of 4 to 9 ppm [32].

The NMR spectrum not only shows how many different types of protons a molecular of the original phenolic resin has, but also reveals how many of each type are contained within the molecule. The given area under each peak is proportional to the number of hydrogens generating the peak. The height of the integral does not give the absolute number of hydrogens, but the relative number of each type of hydrogens. So for those obtained integrals to be of any use, there must be a second integral to which it may be referred. Not to forget that

the concentration of each detected component affects the size of the integrated peak. When looking at the obtained spectrum, the variety of those integrals makes the whole assignment even more difficult.

For example, it is expected to find some signals that will be assigned to the following ether bridge $-\text{CH}_2\text{-O-CH}_2-$. The hydrogens attached on the carbon next to oxygen are deshielded due to the electronegativity of the attached oxygen, so they should appear as two sharp singlets with intensity of two hydrogens, but there are none like those.

The influence of catalyst type in addition reactions between phenol and formaldehyde has been already reported [4]. It is found that the used barium hydroxide for the synthesis of the phenolic resin [**Appendix A**] has the *para* directing characteristics, and therefore the addition of formaldehyde onto *para* is much more favoured than onto *ortho* position. These higher amounts of free *ortho* positions can result in an increase of the reaction rate in the thermal cure reaction of the prepolymers, since crosslinks in *ortho* positions are favoured over *para* positions. These facts can be used if more detailed analysis is required for future work.

It has not been possible to predict the final structure of this resin, because the obtained IR spectrum does not give enough information, while the NMR spectra show too pure separation of some peaks. The resole is in fact a mixture of many other components, such as free phenol and free formaldehyde, as well as many hydroxymethyl derivatives of phenol that are in equilibrium with respective hemiformals. Due to this fact, the repeating unit of the resole is extremely difficult to assign. To obtain a fully quantitative NMR spectrum of unmodified phenolic resin, several NMR factors need to be optimised and taken into consideration: the NOE-effect, the signal /noise ratio, and the relaxation time.

In addition, it would be a big help to have a gas chromatogram of resole that would determine the resole composition, or to run a thin layer chromatography to obtain even more quantitative analyses of the resole.

But when combining the assigned groups together where some of them are based on the former studies on resoles, the following structure can be proposed:

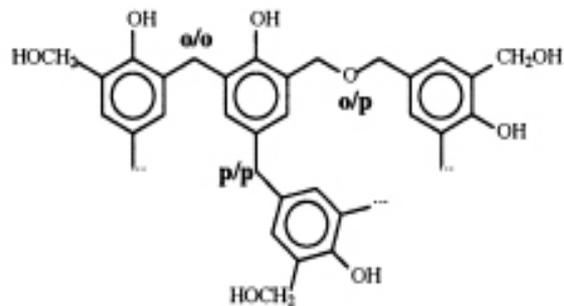


Figure 21. Chemical structure of resole resins

5.2 Tests performed on VPR 1740

5.2.1 Physical-mechanical characterisations

When observing the appearance of this resin, it looks like a milky watery dispersion, as stated in the technical paper of the resin. A sample of the resin is analysed under the microscope using both dark and light field and 50 times and 100 times magnifiers, and it has been possible to observe the presence of polymer micelles that are extremely small, smaller than 1 μm , which is very close to the area of the microscopic limit. The sample has not been diluted, and therefore micelles are very concentrated. The micelles are all the same spherical shape. Compared to some other oil/water emulsion, this emulsion seems very similar. From these results, it is possible to confirm that this resin is an oil/water emulsion.

Table 10. The results of testing solubility for VPR 1740.

Solvent	Results
Toluene	Not soluble
Ethanol	Phase separation
Butanol	Phase separation
Acetone	Phase separation
Tetrahydrofurane	Not soluble
Methyl sulfoxide	Not soluble
Water	Diluted
Ethyl acetate	Not soluble

The solubility of VPR 1740 in the most common organic solvents is examined as for the original phenolic resin in section 5.1.1 in order to obtain an impression of its polarity.

Each test is carried out using a drop of resin in 1mL of solvent, and solubility in both cold and warm solvent is examined. The dissolution of the resin is followed for 15 days.

5.2.2 Elementary analysis

The elementary analysis is performed after the solvent has been evaporated on the rotary evaporator at room temperature, and the last traces of solvent have been removed using high vacuum.

The results of the elementary analysis show that there is 65.1 % carbon, 6.6 % hydrogen and 4.7 % nitrogen, which shows the existence of nitrogen in the resin.

5.2.3 IR-tests

Results from the IR spectrum performed on VPR 1740 are presented in **Table 11**, showing the most distinguishable peaks:

Table 11. The results of the IR spectra of VPR 1740.

Wavenumbers [cm^{-1}]	Assignment of the peaks
3415	OH stretchings of phenolic ring and methylol group
1613 and 1510	two aromatic ethylene bonds (-C=C-) of phenolic ring
1221	C-O stretchings of phenolic ring, dimethylene ether bridge
1054	the C-OH stretching

The exemplary IR spectrum of resin VPR 1740 is the following:

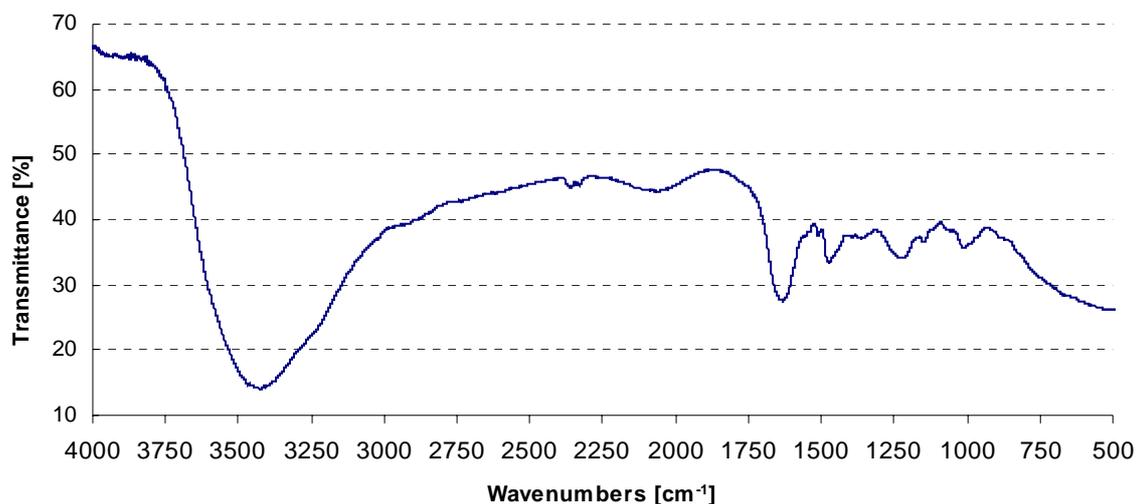


Figure 22. IR spectrum of the phenolic resin VPR1740.

Different analytical tests performed at “EuroResinas” show that VPR 1740 has some nitrogen present, and it is confirmed by the results from the elementary analysis. However, if there is any nitrogen trace present which has been chemically reacted with the resin, IR should show some N-H stretching vibrations or the C-N absorptions. The N-H vibrations occur in the range of 3500 cm^{-1} to 3300 cm^{-1} which are much weaker and sharper than the OH vibrations. These N-H stretchings are not visible on the IR spectra obtained from this resin [32].

The C-N stretching occurs in the range 1350 cm^{-1} to 1000 cm^{-1} . Aliphatic absorbs from 1250 cm^{-1} to 1000 cm^{-1} , while aromatic absorbs 1350 cm^{-1} to 1250 cm^{-1} which occurs at a higher

frequency due to the fact that the resonance in aromatic increases the double-bond character between the ring and the attached nitrogen atom. These C-N stretchings are not visible on the IR spectra either [32].

The presence of the nitrogen detected in “EuroResinas” and confirmed by elementary analysis can be due to the presence of 2-(Dimethylamino) ethanol, which is possibly used for pH adjustments or as a curing agent, and is not directly bonded to the basic structure. In the actual technical data sheet of this resin, it is stated that the amount of 2-(Dimethylamino) ethanol is 4%.

5.2.4 Solid NMR-tests

Resin is further characterized by taking a solid NMR. This technique is ideal in this application because sample preparation, i.e. solubility, is not an issue.

Results from the ^{13}C NMR spectrum performed on the phenolic resin PVR1740 are presented in the following table, where some of the peak assignments are based on literature references:

Table 12. ^{13}C chemical shifts of PVR 1740.

Peak [ppm]	Assignment of the carbons
152.16	Phenoxy carbons
129.27	Meta carbon, substituted para and ortho carbons
116.13	Unsubstituted carbon atoms
60.68	Dimethylene ether bridges
34.60	Ortho-ortho methylene bridge

Figure 23 shows the ^{13}C spectrum of VPR 1740:

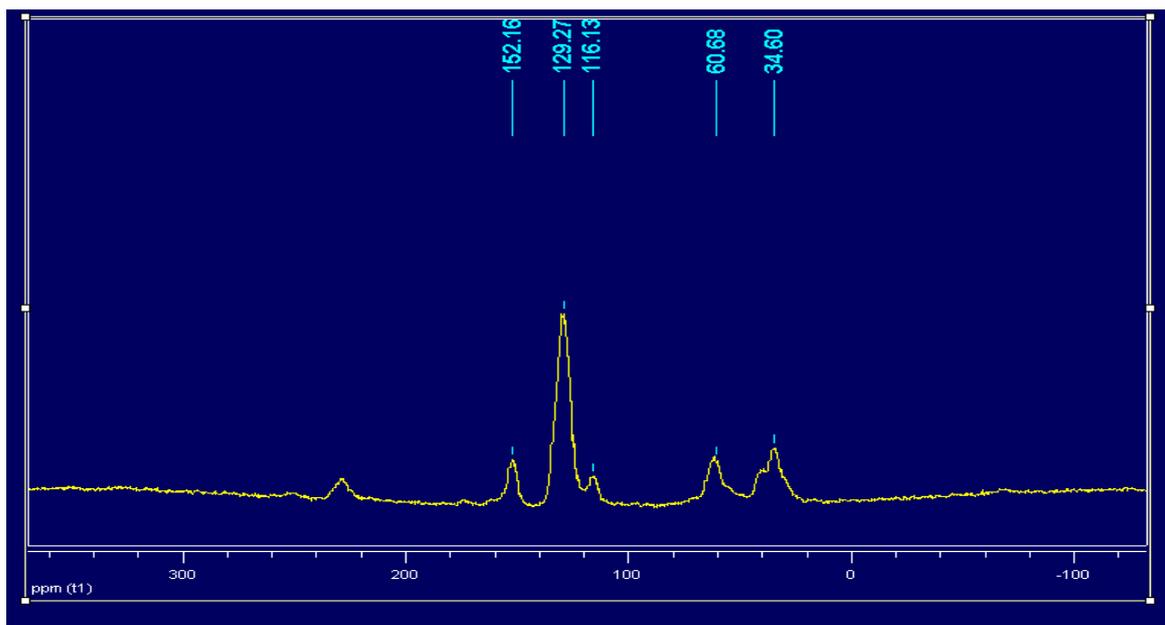


Figure 23. ^{13}C NMR spectrum of VPR 1740.

The results from this spectrum and the spectrum taken of unmodified resin show no significant structural difference in those two resins that can give better properties to the resin.

Due to lack of time it is decided to concentrate more on the original phenolic resin, so there will not be any further work performed on the resin VPR 1740.

5.3 Preparation of the coating film

5.3.1 Addition of the fillers

A film of pure phenolic made on the previously chosen backing paper, cannot be used for testing the mechanical properties of the resins, due to the formation of the so-called “fisheyes” which are patterns of small surface depressions or craters in the film normally caused by surface contamination such as oil or silicone materials or surface tension problems. In this case, a possible explanation to these problems can be due to the presence of a special top layer of the backing paper. This waterproof backing paper system is designed for traditional wet sanding applications such as automotive repair, general metal sanding, and oil sanding of wood. The paper is engineered to provide flexibility, durability and toughness - properties that ensure that the backing paper lasts even after prolonged periods of immersion in water [33]. As the layer makes the backing paper water resistant, it is very possible that the layer has some silicone component or something similar to make the paper water repellent, which makes it difficult for the resin to be evenly dispersed when directly applied. The specific physical properties of the backing paper are presented in **Appendix J**.

In addition to wet durability, backing paper has specially designed barrier coatings for superior holdout and adhesion to primer and size coatings. Barrier coatings are formulated to be compatible with water or solvent-based primer coatings. Because many primer and size coatings actually involve highly complex chemistries, custom barrier coating formulations present on backing paper are designed to enhance the barrier coating’s interaction with the present systems [33].

Other tests are performed to see if the problems with dispersity will be solved when another kind of backing paper is used, which will not have any water repellent layer, or adding some fillers, such as TiO₂ that is used in the primer coat formulation and some glycol to obtain a better miscibility. The conditions under which those tests are performed are stated in the following tables:

Table 13. The amount of agents used for the phenolic film formulation.

Phenolic film	Resin [g]	K54 [g]	Glycol [g]	TiO ₂ [g]
1	50.0	1.0	1.5	-
2	50.0	1.0	1.5	3.7
3	50.0	1.0	1.5	7.4

Table 14. The amount of agents used for the epoxy film formulation

Epoxy film	Araldite GZ [g]	Abrakoll [g]	Glycol [g]	TiO ₂ [g]
1	50.0	16.7	2.1	-
2	50.0	16.7	2.1	3.75
3	50.0	16.7	2.1	7.50

The observations on the films' formulations after the curing are presented in **Table 15**. The photos of those films are made using a digital camera and are in **Appendix K**.

Table 15. The observations after curing the films.

Sample nr.	Formulation	Observations after curing
1	Resin + K54 + Glycol	Transparent film with fisheyes
2	Resin + K54 + Glycol + 10% TiO ₂	White film with small fisheyes
3	Resin + K54 + Glycol + 20%TiO ₂	White film with small fisheyes
4	Araldite GZ + Abrakoll + Glycol	Transparent, nicely dispersed, very flexible film
5	Araldite GZ + Abrakoll +Glycol + 10% TiO ₂	White film with miscibility problems
6	Araldite GZ + Abrakoll +Glycol + 20% TiO ₂	White film with miscibility problems

Observations:

From those results, it is possible to conclude the following:

- There are only very slight improvements of the film even when using both phenolic and epoxy resins.
- The addition of 20% TiO₂ seems not to make the phenolic film better dispersed, and it is hard to see any visible changes of the properties.

- The addition of only 10% TiO₂ makes the film very brittle and not properly attached to the backing paper.
- The addition of TiO₂ has not made any improvement in the film formation, and there are still the same problems with the formation of the so-called fish-eyes. After this addition, both phenolic films with and without the filler are still brittle.
- The fisheyes' size increases with increasing amount of the filler.

5.3.2 Production formulation

The aim of the next tests is to make exactly the same formulation with the same amount of each component that is present in the production formulation, and to test these films in the same way. Removing of components one by one from this formulation can give an idea which of the components is responsible for the removal of “fisheyes”.

At the same time, it is investigated if the addition of some other fillers in small quantities, such as calcium carbonate, gives any improvements, and if the addition of extra solvent, such as methanol, influences the film dispersity.

The right amount of start components are weighed out and added in a specified order under continuous stirring to obtain complete miscibility. In the final mixing, the rest of different binders and additives are added, where the viscosity is adjusted with a small amount of solvent, and the colour is determined and adjusted by a specific pigment.

The production of primer coat which largely consists in mechanically mixing raw materials, is not as simple as it may seem, because it needs to ensure all the necessary requirements. There is only one recipe existing for the production of one single base phenolic coating that ensures that the right raw materials are used, and added in the right amounts in the correct order.

The results obtained by this test indicate that the nicely dispersed film is formed only when all the components have been mixed together and in the exact right amounts. It has not been possible to determine which of the components is responsible for removing the earlier obtained “fisheyes”. Addition of a small quantity of calcium carbonate has no effect on the film dispersity, nor has the addition of extra solvent.

5.4 Results from chemical modifications

To investigate the nature of the structural changes of modified resin produced by chemical modification, several tests are performed.

Solid FT-IR results: A sample for solid FT-IR is prepared by first putting a few drops of the reaction mixture in a Petri dish and further curing in an oven at 140°C for one hour, followed by curing for one hour at 160°C. Secondly, the sample is ground in a mini mill to obtain a homogeneous sample. This technique is ideal even in this application because sample preparation, i.e. solubility, is not an issue.

In all spectra taken by using a diamond lens, a broad peak centred at $\sim 3330\text{ cm}^{-1}$ is the characteristic of the O-H stretchings of phenolic ring, methylol group of phenolic ring, and diacid. When comparing all spectra in **Appendix L**, it can be seen that this peak is relatively weaker in case of modified resin. This small decrease in intensity corroborates the chemical reactions that the methylol groups of phenolic resin participate in directly or indirectly. It is expected that the chemical modification of phenolic with the diacids will take place at the site of methylol, with the methylol peak intensity decreasing consequently. Still the methylol peak for the phenolic resin is weaker than for the other unmodified resin, but not as much as expected. This may be due to the fact that only a very small percentage of the available methylol groups has reacted. An attempt to determine hydroxyl groups of the phenolic resin before and after the chemical modifications is presented in section 5.4.2.

Theoretically, the carbonyl signal shifts to a higher frequency with the curing reaction, which eventually indicates that diacid acid is transformed into ester linkage when reacting with a methylol group of phenolic resin. However, attempts to analyse the modified phenolic resin by FT-IR have not always been so successful, because the ester group signal is indistinguishable with this method from acid group signal (see the arrow in **Figure 24**). Another problem is that it is extremely difficult to obtain a sample in a nice powder form that will not interfere with the apparatus, as the crystals are very hard and very difficult to grind properly after the curing.

A new attempt to obtain spectra that are more distinguishable is to analyse the modified phenolic resin by taking a “surface” FT-IR on the diamond plate of the film that is spread on a backing paper and cured in an oven. A small piece of this backing paper with the cured film is analysed, and the following results are obtained:

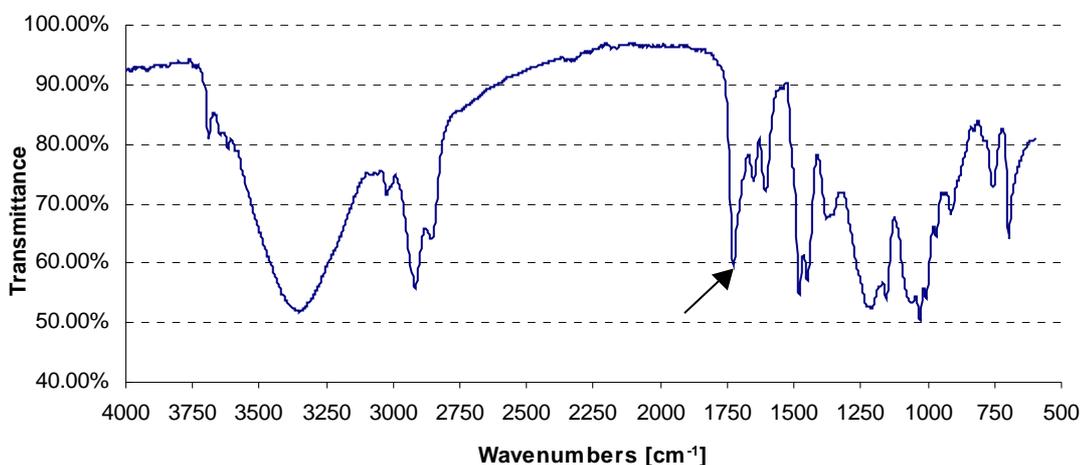


Figure 24. FT-IR spectrum of modified resin with suberic acid after curing.

It has not been possible to obtain a good spectrum of unmodified phenolic resin cured in the same way, because the intensities of the peaks were very low and the spectra could not be reproduced. This is most probably due to the existing fish eyes on the cured film.

Taking IR spectrum by using carefully prepared KBr pellets are the ones that normally give excellent results. Therefore, the next attempt to record IR spectra of samples in the solid state is in the form of a KBr pellet. However, there are two notes of warning. Since KBr is hygroscopic, the spectra often show an extra OH absorption, and this is due to the absorbed water in the pellets. Secondly, the pellets may give different spectra from those taken on the diamond plate, and it is not possible to have a direct comparison of solid spectra taken by those two techniques [26].

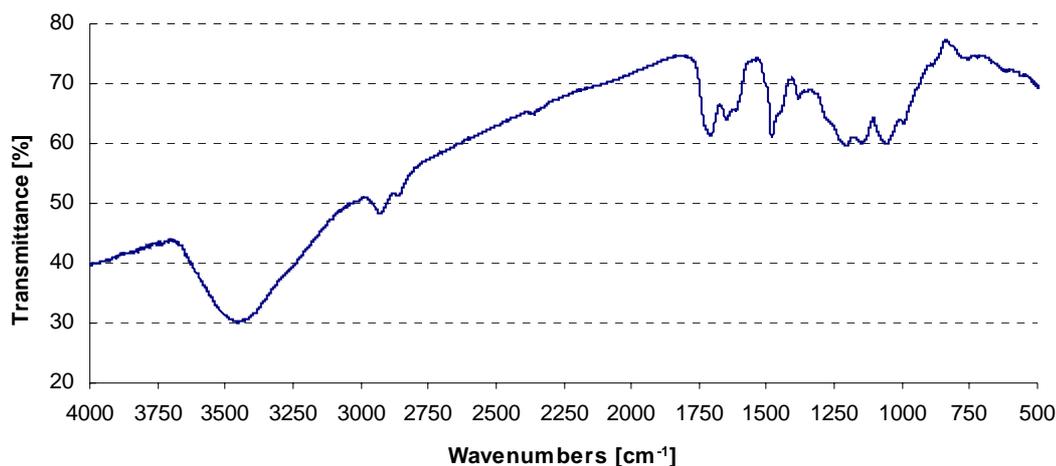


Figure 25. IR spectrum of modified resin with suberic acid using KBr pellets.

To distinguish if the peak at around 1720 cm⁻¹ is due to diacid or ester, the solid sample of the phenolic resin modified with suberic acid is extracted with ethanol by using a Soxhlet apparatus. The small solid sample is packed into a special “thimble” made of thick filter paper. This thimble is placed in the apparatus, and the whole Soxhlet extractor is placed on top of a round-bottomed flask containing ethanol being connected with a reflux condenser. Ethanol is used as a solvent because suberic acid is dissolved in ethanol, while modified resin is not. In this way, the rests of diacid will slowly leak out of the solid into the hot ethanol, leaving the solid to be dried properly and tested by taking a new IR spectrum (**Figure 26**).

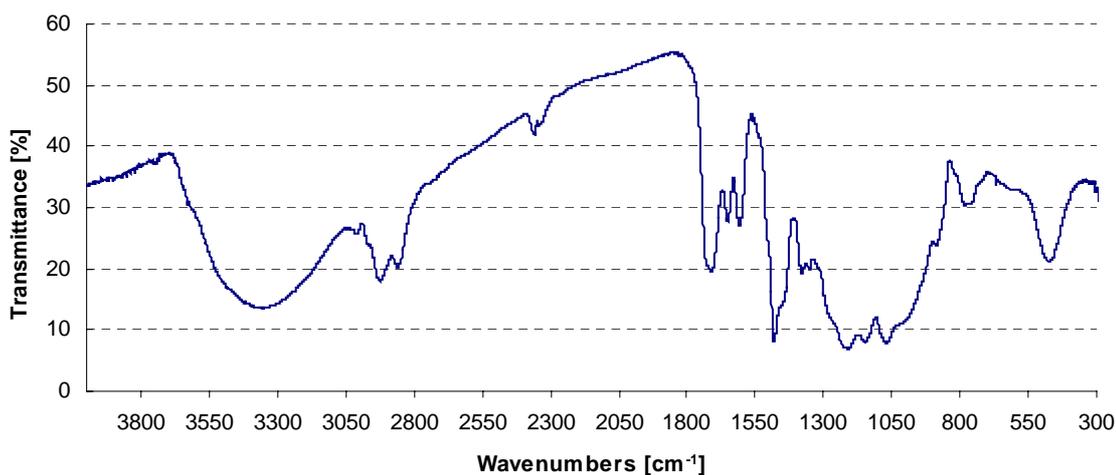


Figure 26. IR spectrum of modified resin with suberic acid after extraction.

The peak at 1720 cm⁻¹ is present after the extraction, which confirms the fact that this is the peak of ester bond formed after the modification and not due to the presence of diacid.

IR spectra taken for all the other modified resins with other modified diacids are presented in **Appendix M**. An overview of all distinguishable peaks from the IR spectra that show phenolic resin modified with DA4, DA6, MA12 and DMEA are shown in **Table 16**.

Table 16. The peaks from IR spectra using KBr pallets.

Resin	VPR 1740	DA4_PR	DA6_PR	MA12_PR	DMEA-PR
3373	3419	3417	3438	3443	3373
2950 + 2889	2912	2950 + 2889	2935 + 2856	2922 + 2850	3011 + 2908
1613 + 1595	1643	1646 + 1613	1648 + 1617	1647 + 1610	1640 + 1609
1235	1232	1210	1207	-	1213
1024	1014	1054	1061	1054	1052
1480 + 757	1477	1482 + 753	1482 + 754	1482 + 779	1479 + 755

The peaks' positions are compared to the peaks for unmodified phenolic resin as well as VPR1740. A brief look at those peaks indicates that there are no big changes in the basic structure of the resins. As the IR bonds of polymers are inherently broad and weak, it is very difficult to detect minor chemical changes occurring on the polymer chain, and it is therefore often necessary to account for the interfering absorptions of the unreacted portions of the polymer in the observed spectrum.

Solid NMR results: The same solid samples that are prepared for the solid FT-IR are used in this analysis as well.

The summary of the results from the ^{13}C NMR spectrum of the phenolic resin modified with suberic acid (**Figure 27**) are presented in the following table:

Table 17. ^{13}C chemical shifts of modified resin with suberic acid.

Peak [ppm]	Assignment of the carbons
200.44	Spinning sideband
175.10	Carbonyl groups of diacids acid and esters
150.63	Phenoxy carbons
129.99	Meta carbon atom and substituted ortho carbons
114.97	Unsubstituted para carbon atoms
62.08	Dimethylene ether bridges

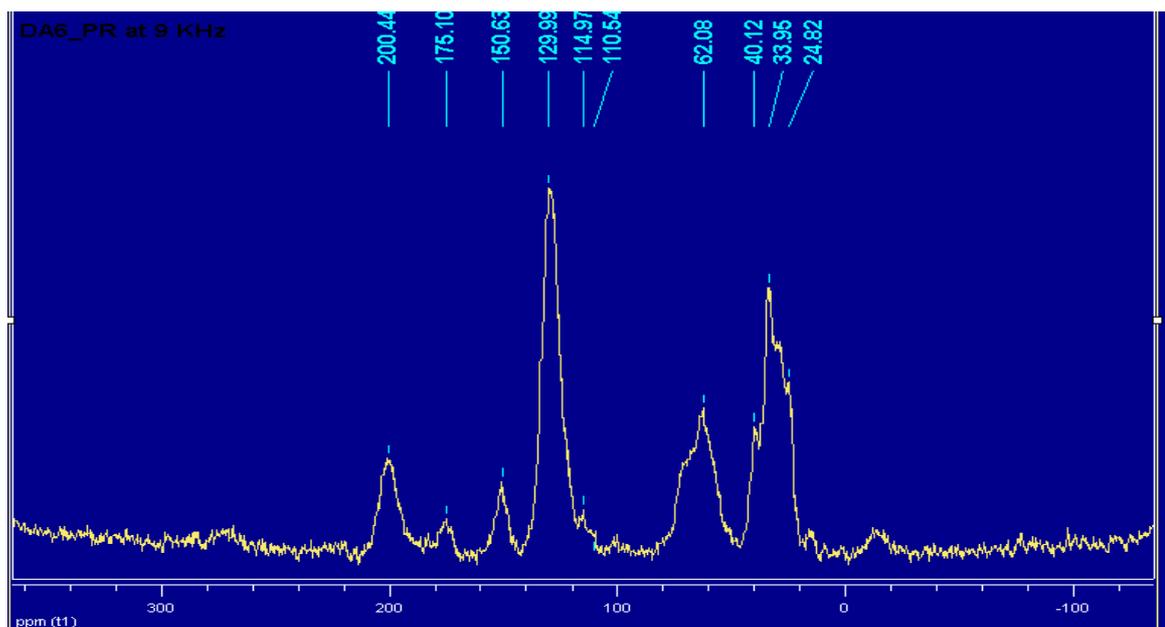


Figure 27. ^{13}C NMR spectrum of modified resin with suberic acid.

All the peaks of the spectra of the phenolic resin modified with DA4, MA12 and DMEA (Appendix N) have the similar chemical shift trends as are shown in Table 18. The peaks' positions are compared to the peaks for unmodified phenolic resin and VPR1740, where it should be mentioned that the peak at around 200 ppm is not included as it only represents the rotational bands of the main signals.

Table 18. ^{13}C chemical shifts of original and modified resins.

Resin	Peaks [cm^{-1}]				
	VPR 1740	DA4_PR	DA6_PR	MA12_DR	DMEA-PR
157.3	152.2	151.8	150.6	152.6	151.9
129.0	129.3	129.2	129.9	129.2	128.9
114.9	116.1	116.7	114.9	116.4	116.2
79.2	-	-	-	-	-
59.5	61.6	70.1	62.1	71.8	71.9
39.5	39.7	39.6	40.1	39.4	39.2
-	34.6	33.1	33.9	33.7	34.3
25.18	-	24.2	24.8	29.7	-
-	-	-	-	14.4	18.0

From these results, it is possible to say that there has been no chemical change in the structure of the basic repeating unit of the resin when reacting with those chemicals.

In other words, as these spectra are almost the same as for the unmodified phenolic resin, the existing small changes that are observed prove that the chemical reaction has taken place.

5.4.1 Optimisation of the reaction with diacids

So far, the studies have mainly been focused on the combination of phenolic resin with different components in order to reach its specific properties. Although there is much work done in the field of synthesis of modified phenolic resin, some aspects of the reaction mechanisms remain unanswered. The effect of decreasing the amount of solvent (ethanol), optimising the amount of diacid, and the temperature and time influence on the performance of the modified film is to be analysed.

One thing to keep in mind is that there is no reliable laboratory test for evaluating new resins for coated abrasive products. Modified resin can only be evaluated by making a coated abrasive product right on a manufacturer's production line or on a scaled down pilot reactor. Only by running performance tests on the finished coated abrasive product, can the manufacturer determine the utility of modified resin. That is why each time quantitative optimisations are performed, it has been necessary to make coating films, cure them, and visually analyse their performance.

In order to study the optimisation of the solvent and diacid on the properties of coating film, different mixtures are synthesised according to the procedure stated in section 4.4.1 with variable amounts of individual components as presented in **Table 19**:

Table 19. Amounts of components during the optimisation process.

	[w(resin):w(diacid)]	Phenolic resin [g]	Suberic acid [g]	Ethanol [g]	Observations
Solvent optimisation	4:1	17.11	4.17	19.75	Acceptable
	4:1	17.11	4.17	15.80	Not good
	4:1	17.11	4.17	11.89	Not good
Diacid optimisation	6:1	5.97	1.04	3.16	Rigid, thick
	7:1	7.19	1.04	3.16	Rigid, thick
	8:1	8.43	1.04	3.16	Rigid, thick

The first observed influence of the amount of solvent is reflected on the density of the mixture. Higher density immediately gives thicker films on the backing paper that after curing gives very brittle films and reformation of "fish-eyes". At the same time, when decreasing the amount of solvent, it takes longer time to dissolve diacid and needs higher temperatures.

A similar effect is observed when the amount of diacid is decreased. The results follow trends similar to the results obtained when decreasing the amount of solvent.

The temperature has to be kept below 55°C to avoid earlier crosslinking of the resin, and due to this, the temperature has no effect on the reaction. The reaction time of three hours gives the best results. Increasing the reaction time to 5 hours gives no noticeable changes in the adhesive properties.

5.4.2 Determination of hydroxyl groups

This experimental part has not been successfully performed when following the procedure given by Evtushenko *et al.* [25]. There is no change of colour when doing the titration with an aqueous solution. The attempts to change the concentration of the reagent and titrant give no positive results. If the process is followed as stated in the above-mentioned paper, it cannot be determined reliably, and the measurements based on the change in colour are difficult to determine.

IR spectroscopy may be a convenient method for the determination of hydroxyl groups in phenolic resin, as the resin is insoluble in common solvents used for other methods such as acetylation technique in pyridine. It is expected that the accuracy of this spectral method is significantly higher than by the chemical method. Even though the direct IR measurements often are hampered by the tendency of the groups to form hydrogen bonds among themselves and with other polar groups, in this case, it may be the only way to determine hydroxyl group in the resin in future work.

5.4.3 Mechanical tests

All kinds of papers are hygroscopic and can absorb from, or lose appreciable quantities of absorbed water to, the surrounding atmosphere. This moisture affects both the performance of paper product and test results. Thus Young's modulus and the tensile strength of both paper and fibres decrease with increasing moisture, and their extensibility and especially their folding qualities increase [27]. This is the reason why all specimens that are to be tested need to be placed in an atmosphere with a relative humidity of around 42 % and a temperature of 23° to be conditioned. However, it is assumed that the coated backing paper used in this case will not absorb any significant amount of water, being waterproofed, and due to this are used for tests on the same day.

All data, particularly numerical, are subject to error for a variety of reasons, but because decisions will be made on the basis of analytical data, it is important that this error is quantified in some way.

Obtained data for a variable will include one or more values that appear unusually large or small and out of place when compared with the other data values. These values, known as outliers, are included in the data set. This is because these outliers come automatically and are products of test uncertainties, and there will not be taken any steps to identify outliers nor to review each one.

At the same time, the coefficient of variance (CV) is calculated. It is the degree to which a set of data points varies and is often called the relative standard deviation, since it takes into account the mean (average). The CV is typically displayed as a percentage. The lower the CV percentage, the better the precision between replicates, which can give an idea how reproducible the tests are.

The complete statistical analysis of the results of these mechanical tests is presented in **Appendix O** and **Appendix P** showing all relevant graphs and different tests performed on the values.

Double folds:*Table 20. Results from the double folds tests*

Samples	Mean value of Double folds [nr. of folds]	Standard deviation	Coefficient of variation [%]
Unheated backing paper	2151	452	21.0
Heated backing paper	1574	479	30.4
Epoxy resin - pure	446	171	38.2
Epoxy resin production	1633	448	27.2
Phenolic resin - pure	505	385	76.2
Phenolic resin - production	45.7	54.7	121
Modified phenolic resin with suberic acid	50.7	38.3	76.7

Observations:

When observing the crack propagation while performing the double folds test, it is noticeable that the cracks of the films on the backing paper initiate further cracks that propagate continuously through fibres of the backing paper.

If double folds test is favourably regarded as an indicator of durability, then the results in **Table 20** indicate the following:

- Heating uncoated backing paper up to 160° decreases double fold numbers by half.
- Results give the idea that pure epoxy and unmodified phenolic resins have the same properties. However, due to the existence of the “fisheyes” on this type of phenolic film, it is not possible to give more confident evaluation.
- Addition of fillers in both phenolic and epoxy film, which is the case with production formulation, increases double folds numbers.
- The thickness of the coated film of the backing paper influences the results of double folds test.
- The statistical analysis performed on the results (**Table 20**) calculates very high values of the coefficient of variations, which express the reproducibility of the test. The results show that the test is not the best way to evaluate these coated films.

Bursting strength:*Table 21. Results from the bursting strength tests*

Samples	Mean value of Bursting strength [kPa]	Standard deviation	Coefficient of variation [%]
Unheated backing paper	320	32.2	10.1
Heated backing paper	190	13.7	7.21
Epoxy resin - pure	691	93.9	13.6
Epoxy resin - production	326	24.2	7.42
Phenolic resin - pure	294	59.3	20.2
Phenolic resin - production	244	42.7	17.5
Modified phenolic resin	188	21.2	11.3

Observations:

The test that measures the bursting strength of paper has given the results presented in **Table 21**. The results give the following indications:

- Heating the backing paper up to 160°C decreases bursting strength of the paper by almost half.
- Addition of fillers in the coating films for phenolic and resin coating decreases the pressure exerted on the test sample before rupturing it.
- The bursting strength of modified resin film is the lowest of all tested films,. The value is very close to the value of heated uncoated backing paper.
- The statistical analysis performed on the results (**Table 21**) calculates the values of the coefficient of variations which are not as high as for the double folds test. Therefore, it can be concluded that bursting strength test has better reproducibility, but is still very difficult to draw any conclusions from the obtained experimental results.

Besides those results, the next attempt is to explain the behaviour of the films during those mechanical tests by looking closely at the chemistry of paper, as well as looking at some of the more important facts of surface chemistry aspects of the paper-resin film. A possible penetration of the applied layer of testing resin into backing paper when performing the curing of the film in an oven can influence the results of the mechanical tests. This possible absorption of resin by backing paper can be considered as a combination of both surface

wetting and capillary pore penetration. The forces of adhesion between the paper and the resin are smaller than the forces of cohesion of the resin. This is observed when the pure phenolic resin is placed on a smooth surface of backing paper, it will not spread and not wet the surface.

Additionally, when applying the coating on the backing paper, the earlier applied coating barrier gives a relatively dense layer of material on the surface of the sheet through which the test resin will have to stick, and it will most probably behave differently to each coating.

The specific interactions are postulated to be Lewis acid–base type interactions or electron acceptor - donor interactions. A thermosetting phenolic resin has acidic functional groups whereas fibres possess both acidic and basic functional groups. It is expected that the type of fibre–resin interactions (i.e., strong or weak) will depend on the percentage of those functional groups present on the carbon fibre surface, and this is expected to influence the properties of the spreading.

In general, instability in instruments contributes a lot to obtaining such results from the latest mechanical tests. That is why it is essential in order to minimize the danger of obtaining such systematic errors in the results that great care is to be exercised in the choice and use of analytical instruments. If necessary one must to find another way to evaluate the obtained results.

To be able to prove and look more closely at any of these above mentioned postulates, a few microscopic investigations will be performed.

5.4.4 SEM-analysis

SEM-analyses are performed in order to have a more detailed look at the morphology of the coatings, and at the same time to obtain information about the coating thickness and the interaction of the coating with the fibre and the waterproof coating on the backing paper.

The coating on the backing paper and the interfaces developed after the curing between different coatings are observed by SEM (**Appendix Q**) where the cross-sectional samples of size 1.5·0.1 cm are cut by a pair of scissors and are fixed with carbon paste on the sample holder of the SEM.

In SEM, finer surface structure images can generally be obtained with lower accelerating voltages. At higher accelerating voltages, the beam penetration and diffusion area become larger, resulting in unnecessary signals (e.g., backscattered electrons) being generated from within the specimen. These signals reduce the image contrast and veil fine surface structures. It is especially desirable to use low accelerating voltage for observation of low-concentration substances. In this case, the voltage of 20 kV is used.

Image quality depends a lot on tilt angle. Normally, secondary electron images contain some backscattered electron signals. Therefore, if the tilt direction of the specimen surface and the position of the secondary electron detector are geometrically in agreement with each other, more backscattered electrons from the tilted portions are mixed, causing them to be seen more brightly due to synergism. In this case, most of the specimens are tilted in order to be able to look only at the images of the protective polymeric layers and the new applied coating, and not the fibres from the backing paper.

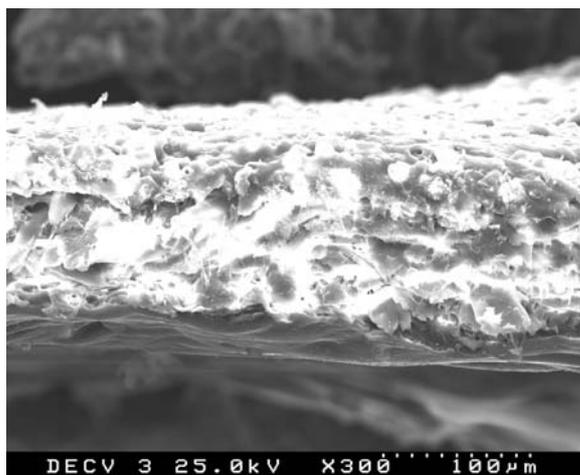


Figure 28. SEM image of uncoated backing paper.

The coating thickness on the backing paper differs from one coating to another depending on the coating density. The protective polymeric barrier on the backing paper is around 120 μm as in **Figure 28**, while the bigger thickness on the right side of the same figure is due to the possible bending of the sample which gives the more broad area.

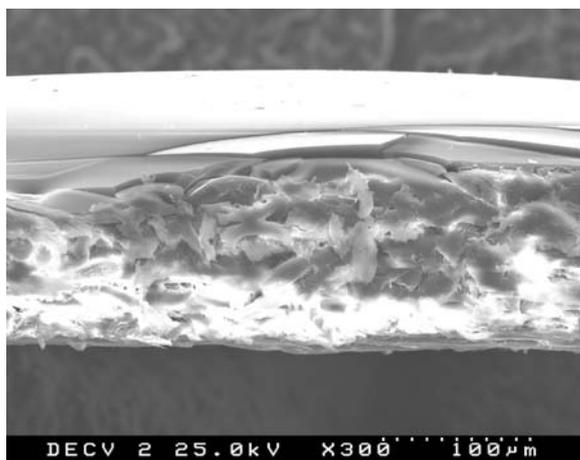


Figure 29. SEM image of phenolic resin formulation.

Another sample of the coating thickness is around 225 μm as in the coating made by phenolic resin formulation as in **Figure 29**.

The same image shows that there is a breaking of the layer due to its expected rigidity.

Figure 29 also shows that the fibres in the backing paper and the polymeric layer making the paper waterproof are very compressed - in close contact with each other. The barrier layer is very thin and evenly spread. It is not possible to see any penetration of this layer into the fibres.

Cutting a sample with scissors can damage the edges of the samples and compress the layers, making them very difficult to analyse. The overall observation is that according to these images, no penetration of the coating is observed, which proves that the penetration of the layers is not the reason for the results obtained by the previously performed mechanical tests but different instrumental factors.

5.5 Economics concern

The next step is to look into economic concerns and financial issues. Cost and prices are important when developing a new product. To avoid going into the details of the abundant and detailed business literature, this section briefly outlines the financial arguments that are likely to be put forward [24].

To estimate the economic viability of this modified phenolic resin with, for example, suberic acid, the following information is obtained from several suppliers:

Prices of different chemicals:

- Phenolic resin costs €1/kg,
- Epoxy resin (including hardener) costs €3/kg
- Suberic acid costs €50/kg
- Lauric acid costs €33/kg
- Ethanol costs €25/L
- Modified phenolic resin costs €5/kg

To modify 1.0 kg of phenolic resin 0.24 kg of suberic acid is needed. Thus, 1 kg of phenolic resin will cost 1 € plus the 12.2 € that the needed amount of suberic acid will cost, which gives a total cost of 13.3 €. Assuming that it will need some ethanol to dissolve this amount of diacid, the total cost will be up to 15 € for modifying 1 kg of phenolic resin.

So now we must think about whether it is worth finding another modifier that will be cheaper. For example, chemical modification with lauric monoacid gives promising results as well. When using this acid to modify 1 kg of phenolic resin, the same amount of monoacid is needed. Thus, 1 kg of phenolic resin will cost 1€ plus the 9.2 € that the needed amount of lauric acid costs, which gives a total cost of 10 € including the needed amount of ethanol for modifying 1 kg of phenolic resin.

It is to be assumed as well that for simplification and obtaining a cheaper product, it is desirable to recover the ethanol completely by a further industrial process and reuse it.

The overall conclusion is that it is quite expensive to perform this kind of modification and ordering an already modified phenolic resin that will have a price of 5 €/kg can be a cheaper solution. However, it will not be necessary to invest in any new equipment and the company is not dependent on this specific supplier. The existing batch equipment which is used for several different products may already be fully reused. This makes the overall cost for the new product more acceptable. Though capital is spent when starting the marketing of the new product, the investment is expected to be paid off, where the profit will most probably be affected by different factors, such as labour required, etc.

Although the economics outlined in this section can be a useful start, they are only a sketchy estimate. More detailed estimates are needed, and more factors must be discussed.

6. Conclusion and future work

All conclusions drawn from the test results are to be found in section 6.1. The proposed future work that can be performed in this study area is to be found in section 6.2.

6.1 Conclusions

In the first part of the report, a detailed literature survey is presented in order to summarize the latest approaches to chemically modifying phenolic resin to improve its flexibility. The overall impression is that many attempts have been made to make phenolic resin more flexible, but not all of these ideas can be applied.

In the second part of the report, experimental work with its analyses and results are presented.

The basic conclusions from the work are the following:

- A phenolic resin has been chemically modified with diacids, monoacids, dimethylethanol amine and poly(ethyl glycol). However, better flexibility and spreading properties compared to the original resins are achieved only after the modification with diacids, particularly with suberic acid.
- There is a noticeable change in the spreading appearance of modified resin compared to the surface of the original resin film. There are no more of so-called “fisheyes”.
- Even though it has been assumed earlier that the phenolic resin VPR1470 shows better performance than unmodified phenolic resin, the structural analysis shows no difference in those two resins. The only explanation for such behaviour is that VPR1470 is a milky watery dispersion that gives different spreading properties.
- Rheology studies are performed on unmodified phenolic resin to predict time temperature-viscosity parameters. The viscosity of 603 cP measured at 25°C is not stable at this temperature for a minimum of five days. After three weeks the viscosity is

measured to be 1140 cP. In addition, it is very possible that this change of viscosity can have an effect on some of the obtained results.

- Several formulations have been investigated and optimised quantitatively to give higher flexible surfaces of the modified phenolic film. The best results are obtained when suberic diacid is reacted with phenolic resin in the ratio 0.0014 moles to 1g for three hours.
- IR analysis of the product obtained from phenolic resin/diacid reaction indicates that carbonyl acid is transformed into ester linkage to react with methylol group of phenolic resin during esterification.
- Statistical analysis of the results from the double folds tests gives the results with the high coefficient of variance up to 76% for the film of modified resin, which makes this test not usable. Smaller coefficients of variance for measuring bursting strength of different films makes this test more reproducible and more reliable.
- Achieving such good results within the time and facilities available, proves that following some basic steps of Product Engineering solves Chemical Engineering problems much faster. The new product is developed to meet the needs specified by “Indasa”.
- The analysis performed on phenolic resin involves some uncertainties, as there are still many questions that need to be answered about the properties of unmodified phenolic resin. This will be the main issue of future work.

6.2 Future work

The following testing can be performed in future to gain better results and to confirm some of the conclusions stated above:

- Determining how many of the “available” OH-groups have reacted with diacids and how many can react at all to give the best results. It is desirable to find the best method to measure those groups.
- Detecting changes in the chemically modified surface structure of the resin film on the backing paper
- Surface characterization methods like XPS and TOF-SIMS can be investigated on the films of modified resin to give a proper surface analysis aiming i.e. to know how the thickness variation effects the spreading properties of the films.
- If the esterification of the phenolic resin is controlled, the unreacted OH groups that are retained after the reaction can therefore work as an initiator for further polymerization. The next step can be to verify this “reactiveness”.
- If formation of a stable emulsion is another possibility to obtain a more flexible phenolic resin, then the next step will be to look more closely at the miniemulsion process to synthesise stable phenolic resin dispersions.
- Trying to see how the results of measuring zeta potentials can be used in this case.
- Finding a new recipe for the phenolic primer coat formulation that instead of original phenolic resin will use modified phenolic resin.
- Sol-gel studies can be performed to determine the degree of crosslinking within the resin networks. Such studies will provide information that may be used to better understand the mechanical and thermal properties of modified resin.
- Dynamic mechanical analysis (DMA) may be used to obtain accurate glass transition temperatures, which would provide further insight into the performance capabilities of the resin.

7. List of abbreviations

2,4,6-DHMP	2,4,6-trihydroxymethylphenol
2,4-DHMP	2,4-dihydroxymethylphenol
2,6-DHMP	2,6-dihydroxymethylphenol
2-HMP	2-hydroxymethylphenol
4-HMP	4-hydroxymethylphenol
Abrakoll	Crosslinker
Araldite GZ	Epoxy resin
CNSL	Cashew nutshell liquid
CNSLF	Cashew nutshell liquid formaldehyde
DMAE	Dimethylamino ethanol
DA2	Malonic acid
DA4	Adipic acid
DA6	Suberic acid
EG	Ethylene glycol
F/P	Formaldehyde/phenol ratio
IR	Infrared spectroscopy
ISO	International standard
K54	Commercial product - a curing agent
MA6	Caproic acid
MA12	Lauric acid
MA18	Stearic acid
NMR	Nuclear magnetic resonance
NR	Natural rubber
PBA	poly(butylene adipate)
PDA	poly(decamethylene adipate)
PEA	poly(ethylene adipate)
PEG	Polyethylene glycol
PHA	poly(hexamethylene adipate)
POA	poly(octamethylene adipate)
SEM	Scanning electron microscope

TOF-SIMS	Time-of-flight Secondary ion mass spectroscopy
VOC	Volatile organic compounds
VPR 1740	New phenolic resin offered by another supplier
XPS	X-ray photoelectron spectroscopy

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Appendix A: Synthesis of unmodified phenolic resin

This part describes a detailed synthesis of phenolic resin, resole, produced in the factory “EuroResinas” for the sandpaper manufacturer “Indasa”.

This section presents all the materials used and all steps that need to be followed to produce a resin with previously determined properties.

1. Materials

Phenol (90% aqueous solution), formaldehyde (55% aqueous solution) and barium hydroxide are commercial products used without further purification.

Process water, which has been previously treated, is used for the adjustments of the formaldehyde concentration. The pH of the final resin is adjusted by using 50 % sodium hydroxide.

2. The reaction vessel

A cylindrical vessel or reactor with dished top and bottom is used, and is proved with a jacket of steam-heating and water cooling. Accessories, such as the condenser, with which the reactants may come into contact, as a vapour or a liquid, are constructed of the proper material as well as the vessel itself.

Through an air-tight gland in the centre of the top, there passes the vertical shaft of the stirrer, which is driven by an electronic motor and may be arranged for various speeds. Other things preset are a charging-line for raw material, an “eye” for inspection of the reaction, vapour-outlet and condensate return-lines to the condenser, connections for temperature- and pressure- recording instruments, and a pressure safety-valve.

The condenser is of the tube type, with the vapour going through the tubes, fixed in a horizontal position with a wide vapour-pipe from the still to the top end of the condenser. A pipe from the lower end leads back to the top of the still through a U-bend trap. However, by altering the settings of two valves, the distillate can be led into a distillate-received tank. In the first position the condenser system is used as a reflux condenser, and in the second it can be used for distillation.

For this resin it is necessary to operate under reduced pressure, the pipe-lines and valves are provided to enable both reflux and distillation to be carried out at lower pressures.

3. Resin preparation

Step 1: Calculations

The amount of the resin that can be produced in the pilot reactor is 50 kg. For these experiments, it is to obtain 25 kg of phenolic resin after extraction. Using an already existing excel worksheet, the exact amount and concentration of the formaldehyde is written in it and the amount of the other components is calculated according to that amount, by using the right molar ratio F/P and percentage of the components in the resin.

The molar ratio F/P is calculated by using the following equation:

$$F/P = 3.13 \cdot \frac{C(F) \cdot m(F)}{C(P) \cdot m(P)} = 3.13 \cdot \frac{0.55 \cdot m(F)}{0.90 \cdot m(P)} \quad \text{Eq. 1}$$

The molar ratio F/P is set to be approximately 1.75. The amount of process water in the reaction mixture is previously calculated to adjust the final concentration of formaldehyde to be 41.5 %. The amount of the catalyst is around 1.0 % of the total mass.

The worksheet calculates the amount of the water that need to be extracted from the final resin to obtained wanted solid content and viscosity of the final product, as well as the amount of the sodium and barium hydroxide that will be necessary to adjust pH value and catalyse the reaction.

The following table presents an example of the amount of the raw material that can be used in the synthesis of phenolic resin:

Table 1: The amount of the used raw material

Components	Concentration [%]	Mass for resin nr. 1[g]	Mass for resin nr. 2 [g]
Formaldehyde	55.40	17150	17450
Phenol	90.00	18868	19226
Process water*	-	3841	3939
Barium hydroxide	-	350	450
Sodium hydroxide	50.00	100	150
Total amount before extraction [g]		40309	41185

*To adjust the concentration of the formaldehyde to be from around 55.0% to 41.5 %

Step 2: Checking the set up

Before starting the reaction, check if all valves are closed. Firstly, the stirrer is started and secondly, the vacuum pump as well as the valve of the water to seal it (note that the valve has to be opened slowly and carefully).

Step 3: Addition of formaldehyde

Formaldehyde is placed in the reactor through the reactors "eye", and all the containers that have been in touch with formaldehyde are washed properly with plenty of water.

Step 4: Adjustment of the concentration

The process water is added to adjust the concentration of the formaldehyde from being around 55% to 41.5%. After this addition, these two components are mixed for a few minutes.

Step 5: Addition of the phenol

The addition of phenol is performed in the same manner as that of formaldehyde. As soon as the phenol is added, it is necessary to check the temperature, as the reaction starts the same moment these two components begin mixing. If there is a high increase of the temperature, cold water is to be let into the system, through internal serpentines.

Step 6: Addition of the catalyst

The amount of the catalyst that is used is weighed and added into the reactor. It is preferable not to put in the whole amount at the same time, as it is not always necessary to use the whole amount to be able to reach the right pH value of 8.5. Due to this, it is always better to start with some small portions and check the pH value after each addition. When the resin has the pH = 8.5, proceed to the next step.

Step 7: Reaction

Hot water is introduced into the system, through external lair, to slowly heat up the resin and speed the reaction. The temperature has to be maintained at 89°C. However, as the reaction gives an increase of the temperature itself, it is preferable to turn off the hot water valve as soon as the temperature has reached 70°C and wait a few minutes for the last increase of the temperature. When the temperature reaches 89°C, the temperature is maintained for 15 min. after which a new pH value of the sample is to be checked, which has to be higher than 7,0. It is very important to remember that all samples of the resin taken directly from the reactor have to be cooled in a water bath at 25°C before being used for any further analysis.

Step 8: Checking the vacuum

Meanwhile, while waiting for the temperature to rise, it is possible to check for the vacuum in the system. This is done by checking if it is possible to reach 0.2 bar absolute (which is equal to 0.8 bar below atmosphere pressure, knowing that atmosphere pressure is equal to 1 bar) in the vacuum chamber.

Step 9: Checking the water tolerance

After the pH reaches above 7.0, a new sample is taken to measure the water tolerance. It has to be minimum 200%. There are sequences of the samples taken every 15 min. to check this tolerance. When this percentage of the tolerance is reached, the cooling of the resin starts by turning off hot water and turning on cold water fully.

In this case, the water tolerance is measured by the following formula:

$$\text{water_tolerance} = \frac{V}{V^1} \cdot 100 = 20 \cdot V$$

where V is the volume of added distilled water while performing the test, and V¹ is equal to 5 mL of the sample.

The water tolerance, which is affected by the content of alkali and solvents, depends mainly upon the extent of resin condensation and represents therefore a good criterion for molecular weigth.

Step 10: Water extraction

Reaching the right solid content of the final resin, the previously calculated amount of the water is to be extracted. It is very important that the extraction is carried out under reduced

pressure, so that the temperature does not rise sufficiently to cause rapid hardening of the resin.

Using at the same time the plan of the pilot reactor, the extraction is performed in the following way:

- a) At 60°C, all the valves should be closed, especially V13 which has been used earlier, to seal the reactor.
- b) Close V20 to reach and control the vacuum at 0.2 bar a (a= absolute).
- c) After the pressure is stabilized, the hot water valve is opened to start reflux. Wait for a few minutes to clean the system with the condensates.
- d) The extraction accumulation is performed in the extraction container of 4 litres, where V7 is open and V10 is closed. Wait until a certain amount is obtained.

Note that the container has a scale from 2 to 3 litres with a “glass window” that is necessary

to be able to observe the water volume and appearance.

- e) To empty the extraction container, close V7, open V10, and close V6 to be able to isolate the container from the reactor without losing any pressure in the system. Opening V8/V9, it pressure is let out from the container into the atmosphere.
- f) Opening V2 and V1 is to let the extracted water out. Measure the quantity of each extraction.
- g) To re-establish the vacuum inside the container, V2, V1 and V8/V9 are closed. Open V6 and wait to stabilize the pressure again. After a few minutes, the reflux starts again.
- h) Steps from d) to g) are repeated until the wanted volume of the water is extracted.

p.s. All valves are numbered according to an already existing sketch of the pilot reactor!

When performing this extraction, it is very important that the temperature and pressure are kept constant, because any changes in these two parameters can influence the final properties of the phenolic resins.

The extraction process is necessary to adjust the solid content of the phenolic resin, and it is always related to the final viscosity as well. It depends on the resin application, and in some cases if the final viscosity is more important, during the extraction, samples are taken and the stop point is determined by viscosity and not solid content.

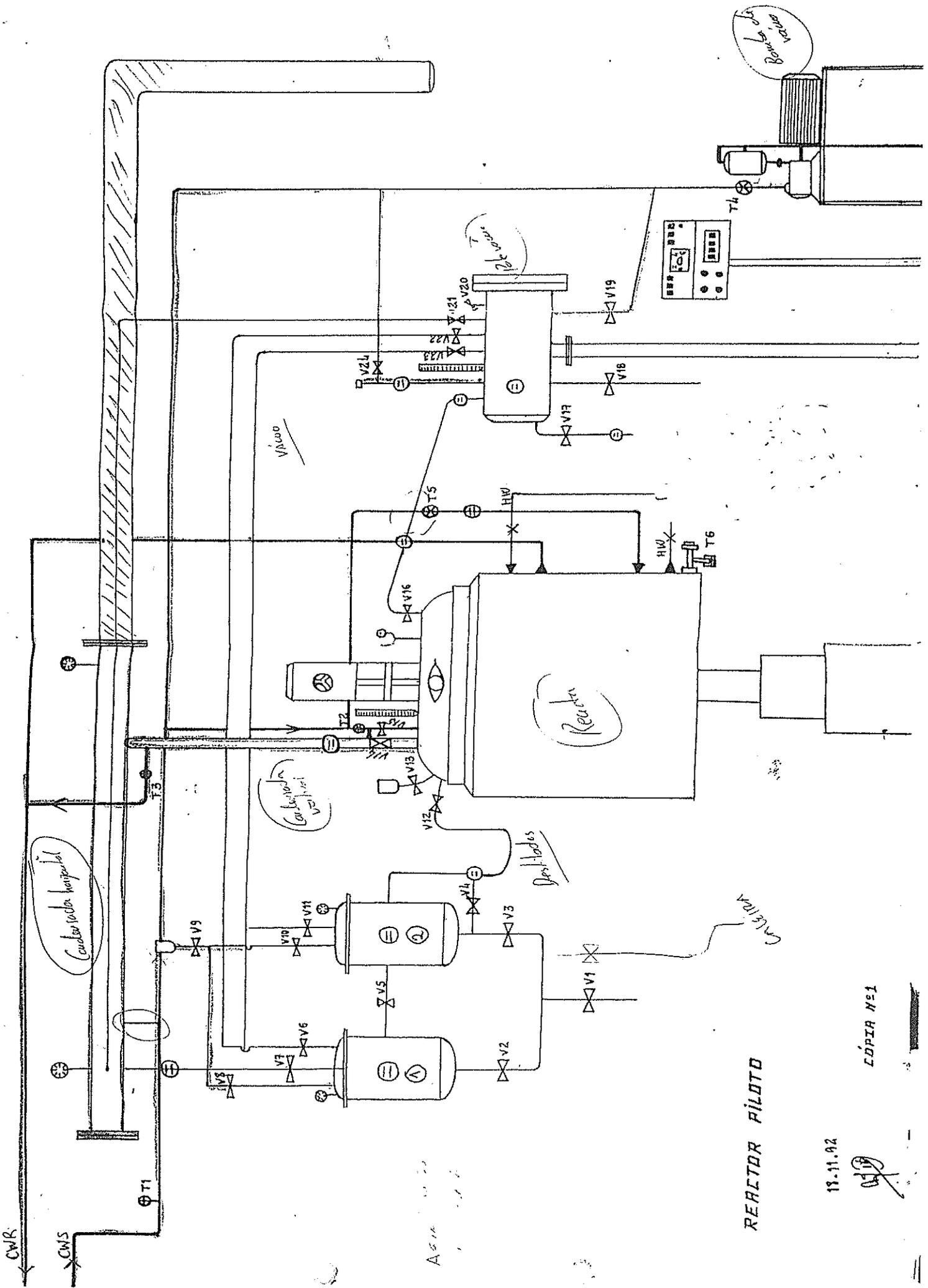
Step 11: Finishing

After the extraction, a new measurement of the pH is performed, which is to be at around 8.00. When this pH is reached, the resin is to cool further down. At 30°C, the viscosity, pH, density and the water tolerance are checked and confirmed. The final product is discharged through an outlet valve at the bottom of the reactor as soon as the end-point is reached. The resole catalysed by hydroxide becomes reddish due to the formation of phenolate ions through the extraction of the phenolic proton by the hydroxyl anion of the catalyst.

Step 12: Qualitative analysis

The resin is tested by different standard methods. The normal tests on resins for control and inspection purposes are:

- Gel time
 - Solid content
 - Viscosity, density and pH measurements
 - Water tolerance
 - Content of free phenol and formaldehyde
-



REACTOR PILOTO

19.11.92

CÓPIA Nº 1

[Handwritten signature]

Appendix C: General facts about "EuroResinas"

The history

"EuroResinas" - Industrias Quimicas S.A. is a member of the Portuguese Sonae Group, a company which is situated at a new industrial site in Sines, south of Lisbon. SONAE comes from the original name of the firm created on 19 August 1959. At that time the Company was known as SONAE - Sociedade Nacional de Estratificados, SA, and it was concerned with the production of decorative laminated products. This has further developed into the production of high pressure decorative laminates, which it still manufactures today, under the name of LAMINITE in one of the Sonae Indústria group of companies. In 1975, the process has been expanded with the production of melamine and phenolic resins among many other products.

Production and products

Sonae Indústria holds the following industrial activities in Portugal:

- high pressure decorative laminates (HPL);
- value added products and services - components, solutions and systems - for the furniture, building, decoration and DIY industries;
- chemical products (formaldehyde and synthetic resins with formaldehyde, urea, phenol and melamine bases) is undertaken by EuroResinas.

Working environment

Sonae Indústria is committed to integrate environmental management as part of its associated companies' management systems, assuming eco-efficiency as the management reference for:

- natural resources sustainable use by saving, reducing, reusing and recycling wastes;
- the compliance with legislative requirements relating to all environmental issues;
- safety, hygiene and health at the workplace improvement;
- minimization of its industrial facilities' impacts on their locations and on the environment.

For any further information it is possible to visit their web site:

<http://www.sonaeindustria.com/ing/index.htm>

Appendix D: General introduction about "Indasa"

History

INDASA was founded in December 1979 by Mr. Benjamim Santos and a group of investors and professionals linked to the abrasives sector for the manufacture of high quality coated abrasives and focusing mainly on the export markets of the automotive refinishing industry. Its production was initiated in November 1980 and commercialised in April 1981.

Following a Management Buy-Out (MBO) led by Mr. Benjamin Santos in 1997, INDASA's shareholding structure was altered. Today, INDASA is owned by a group of people involved in the project for a long time. On May 1999, INDASA consolidated its position in the market by acquiring Luzostela S/A - a one-hundred-years-old Portuguese coated abrasives producer and with a dominant position just 25 years ago. On 31 December 2003, Luzostela stopped operating with all its activities being integrated in INDASA.

Today, INDASA exports 80% of its production capacity to over 50 countries all over the world. Key markets are served within Europe and America with the continuing expansion of their subsidiary companies in UK, Spain, France, Germany, Poland, USA, and Brazil.

Production and products

Research & Development plays a crucial role, in producing a range of technically advanced and innovative materials developed specifically to satisfy the needs of today's refinishing industry with a continuous and high-standard quality

INDASA coated abrasives systems incorporate the very latest in materials technology to provide the optimum in sanding performance. Product range from the very specialised for the automotive aftermarket, to others directed to different industrial markets such as wood industry, metal industry, stone industry, leather industry, glass industry and others.

INDASA has a range of products that satisfies all coated abrasive needs for the Automotive Refinishing Trade segment. Devoting special attention to application and customer needs. INDASA has been able to develop products that compete successfully with any coated abrasives manufacturer operating in this segment.

Progressively, INDASA continues to widen its product range to satisfy other industrial applications. Their sales figures and international presence certify the high market recognition gained by INDASA's RHYNO brand.

Working environment

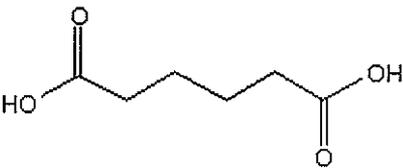
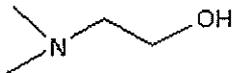
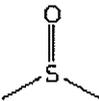
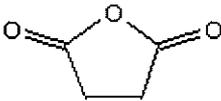
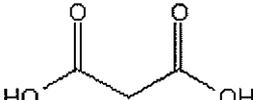
INDASA aims to develop products with fewer resources and less environmental, health and safety impact. In this sense, Environmental Division develops programs in the following areas:

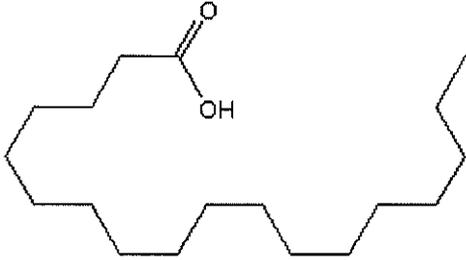
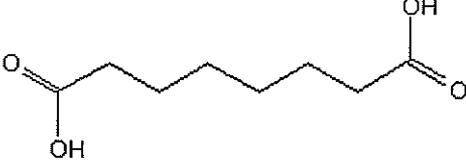
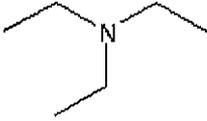
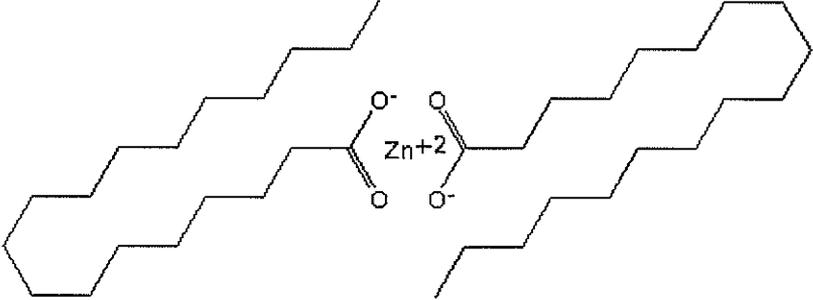
- Reduction in the consumption of natural resources:
 - Reduction of water consumption by reintroducing treated wastewater into the system.
 - Studying the viability of treating and recycling internally some effluent outlets.
 - Studying and developing environmental friendly raw materials.
- Waste outlet control:
 - Classification of solid waste and selection of the best available solution.
 - Treatment of both household and industrial wastewater using a water treatment plant.
 - Monitoring discharges in the atmosphere.
- Guaranteeing compliance with all legal requirements.

For any further information it is possible to visit their web site:

<http://www.indasa.pt/cgi-bin/ncommerce3/ExecMacro/catalogo/index.d2w/report?L=1>

Appendix E: Structures of the used chemicals

Chemical name	Structure
Adipic acid	 <chem>OC(=O)CCCCC(=O)O</chem>
Dimethyl amino ethanol	 <chem>CN(C)CCO</chem>
Caproic acid	 <chem>CCCCCC(=O)O</chem>
Dimethyl sulfoxide	 <chem>CSC(C)=O</chem>
Lauric acid	 <chem>CCCCCCCCCCCC(=O)O</chem>
Maleic anhydride	 <chem>O=C1OC(=O)C=C1</chem>
Malonic acid	 <chem>OC(=O)CC(=O)O</chem>
Oleic acid	 <chem>CCCCCCCC=CCCCCCCCC(=O)O</chem>

Stearic acid	 <chem>CCCCCCCCCCCCCCCC(=O)O</chem>
Suberic acid	 <chem>OC(=O)CCCCCCCC(=O)O</chem>
Tetrahydrofuran	 <chem>C1CCOC1</chem>
Triethylamine	 <chem>CCN(CC)CC</chem>
Zinc stearate	 <chem>CCCCCCCCCCCCCCCC(=O)[O-].[Zn+2].[O-]C(=O)CCCCCCCCCCCCCCCC</chem>



Bursting Strength Tester

Burst-o-Matic → LORENTZEN & WETTRE (SWEDEN)

CODE 04 BOM

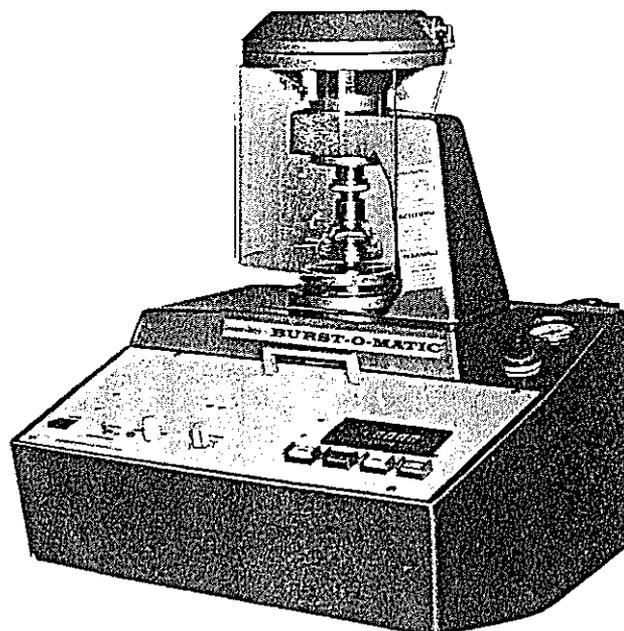
AUTOLINE Compatible

The optimum instrument for determining the bursting strength of paper and board.

The Burst-o-Matic provides rapid test sequences thanks to coordinated automatic controls for clamping and testing cycles. An electronic pressure transducer provides a high level of accuracy and excellent reproducibility of measured values.

Specification

- Panel meter display with 4 1/2 decades for displaying measured value.
- Memory for retaining peak value, with automatic or manual zero-setting.
- Rapid electronic calibration check.
- Automatic or manual testing.
- Adjustable pause during automatic testing.
- Automatic return after rupture saves testing time and increases diaphragm life.
- Adjustable clamping pressure.
- Dimensions: 0.5x0.5x0.6 m.



Measuring ranges and accuracy

Type	Intended for	Measuring range	Accuracy
PD	Paper	0-2 000 kPa	±1 % read-out of value reading within 200-2 000 kPa range.
JD	Board	0-6 000 kPa	±1 % of read-out value within 600-6 000 kPa range. The effect of the diaphragm must, however, be taken into consideration.

Connections

Power supply 220 V, 1-phase, 50 Hz, 150 W.
Instrument air 600 kPa.

Options

BCD output and/or analog output for connection to graphic recorder, printer or computer.
Measuring range for paper 0-1 000 kPa, with accuracy ±1 % of read value within 100-1 000 kPa range.
Other power supplies.

ORDERING DATA

Code No.
Type
Voltage
Frequency

SHIPPING DATA

Net weight	52 kg
Gross weight	90 kg
Approx. volume	0.4 m ³

Folding Endurance Tester

System Köhler-Molin

CODE 06

This tester is used for determining the folding endurance of paper, but can also be used for fatigue tests on textiles, plastics and other thin sheet materials.

The Köhler-Molin Folding Endurance Tester dominates the market in Scandinavia for carrying out folding endurance tests on paper, but is also well-known and widely accepted all over the world.

Specification

- Two strips are tested simultaneously.
- Folding clamps of stainless steel for a strip width of 15 mm.
- Loading clamps with weight bars and weights in steps of 50 g give loads between 1.96 N and 9.32 N.
- Standard load according to SCAN and ISO is 7.85 N (corresponding to a weight of 800 g).
- Folding angle 312°.
- Folding speed 200 double folds per minute.
- Pulley with round belt for drive from separate motor, 1 380 rpm.
- Dimensions 0.3×0.3×0.4 m.

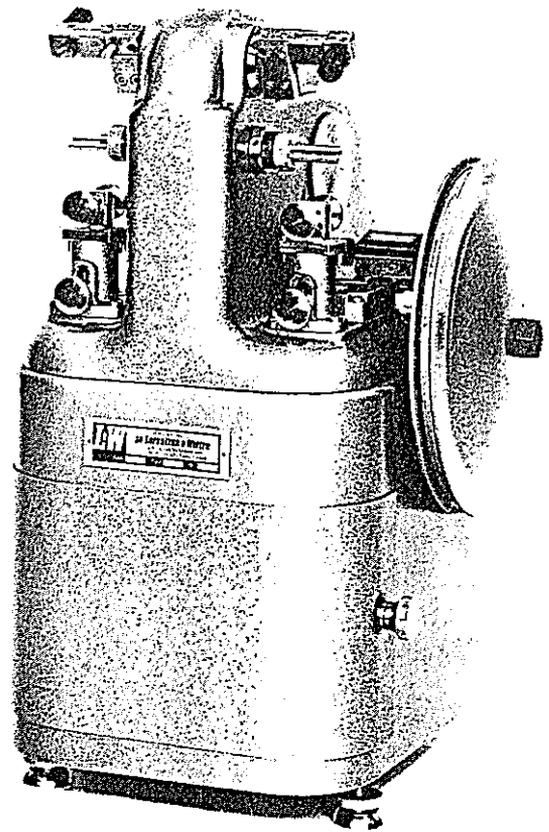
Options

Motor with motor pulley as standard for 220/380 V, 3-phase or 220 V, 1-phase.

Folding endurance

► Definition: The number of double folds which a sample of paper can withstand when tested under standard conditions before rupture occurs (SCAN-P 17:66).

Dimensionless number. According to ISO, the report shall include the logarithm of the number to the base 10. This is used for statistical calculations, e.g. of the mean value.



ORDERING DATA

Code No.
Voltage
No. of phases
Frequency

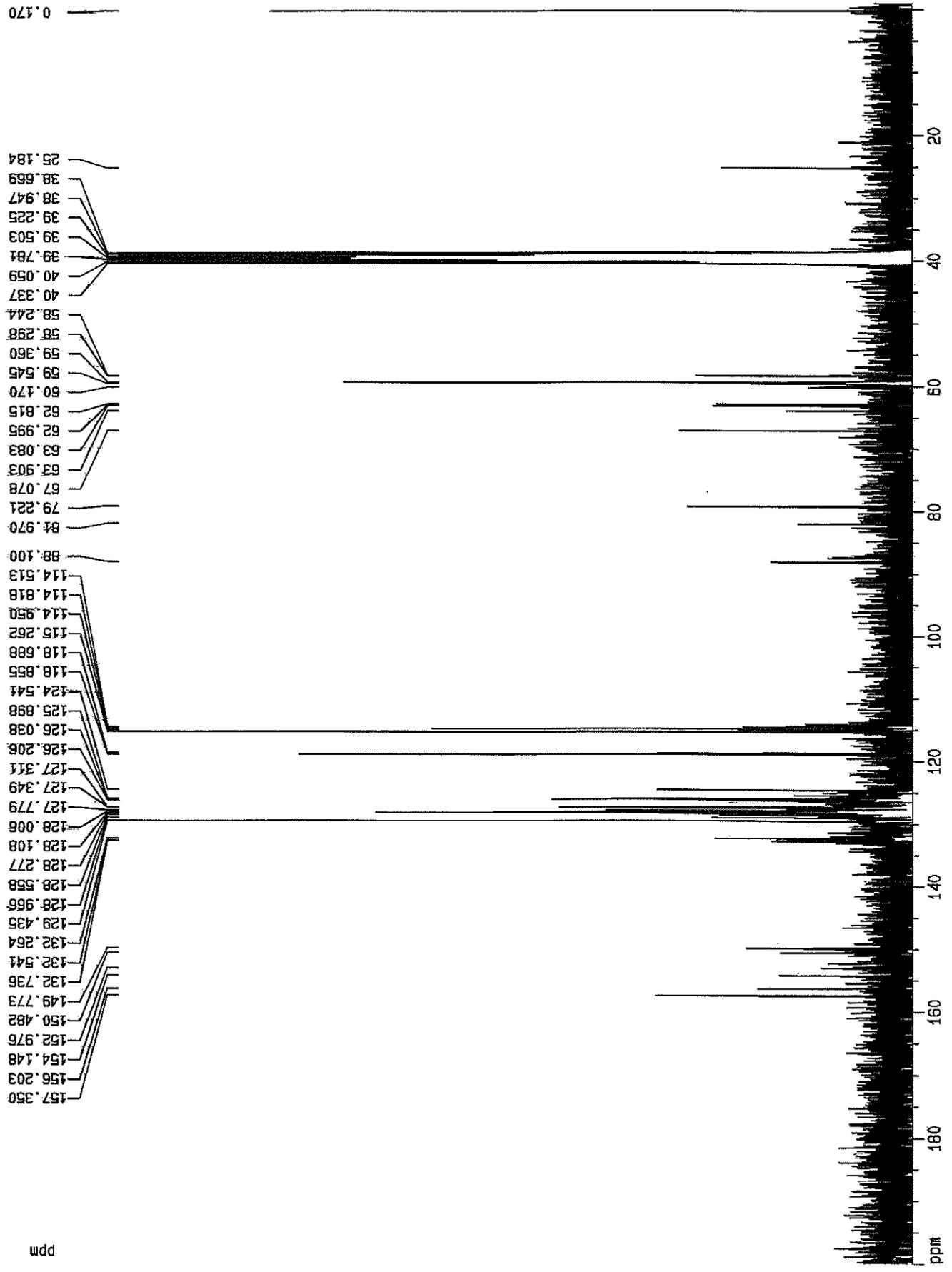
SHIPPING DATA

Net weight 11 kg
Gross weight 25 kg
Approx. volume 0.25 m³

⊕ ~ 3000 scans

Date: 20040325
RG: 16384
NUC1: 13C
SF01: 75.4747190 MHz
A11: 0.0300000 sec

R 158



ppm

Date_ 20040325
 RG 16384
 13C
 SFO1 75.4747190 MHz
 d11 0.0300000 sec

25.1838

40.3368
 40.0592
 39.7811
 39.5031
 39.2249
 38.9468
 38.6686

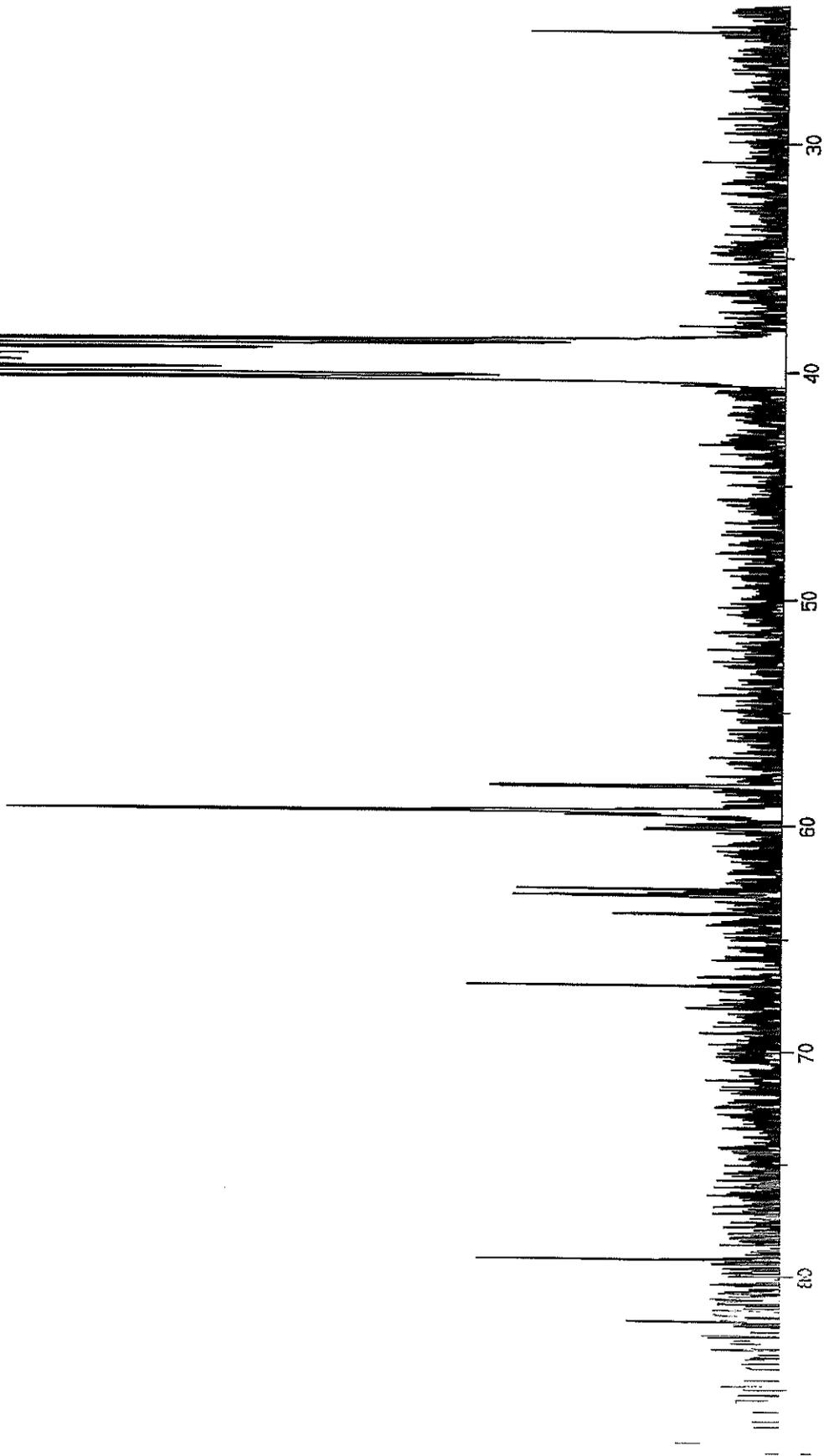
58.2439
 58.2983
 59.3604
 59.5448
 60.1702
 62.8147
 62.9951
 63.0831
 63.9032

67.0784

79.2205

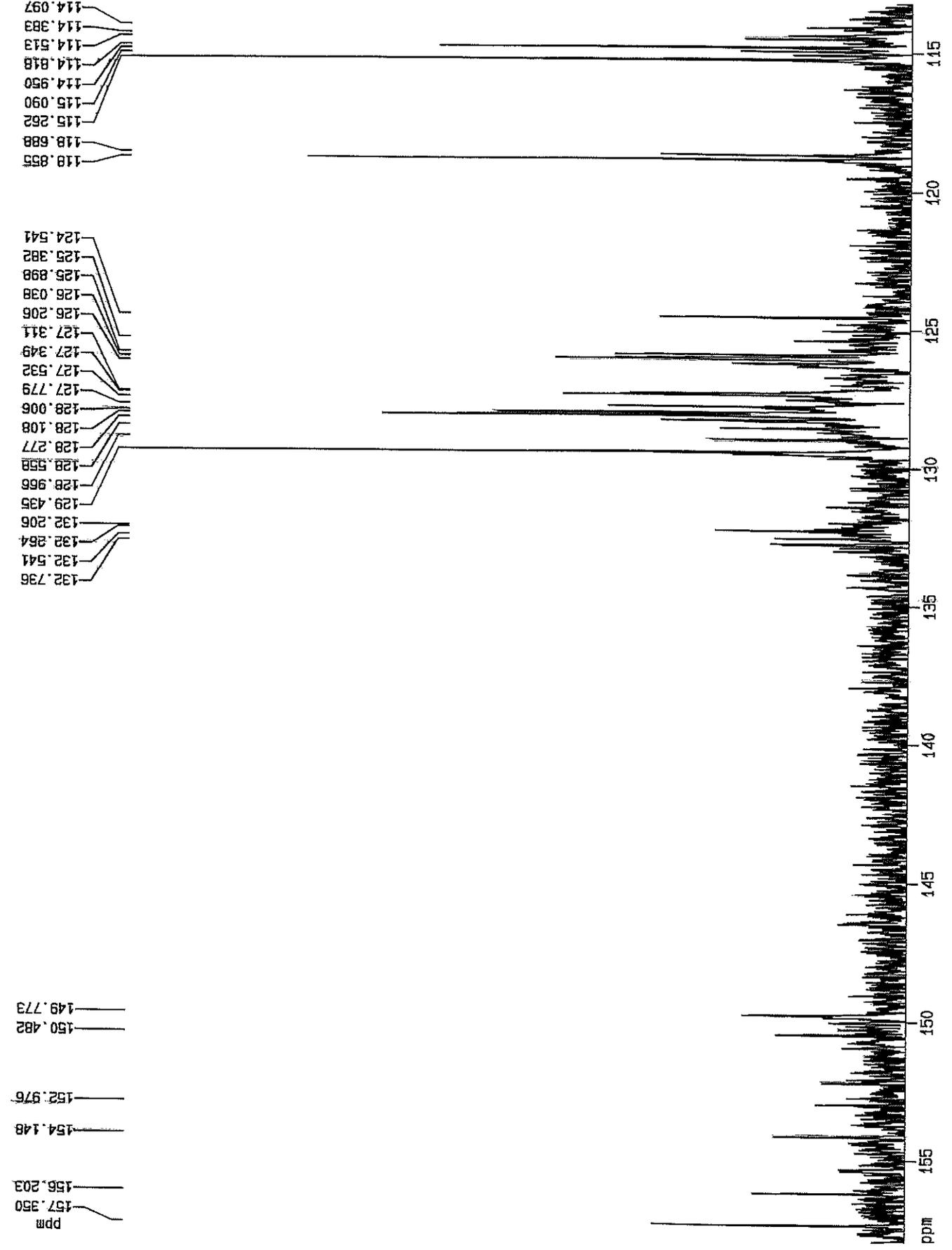
81.9699

R 158



R 158

Date 20040325
 RG 16384
 NUC1 13C
 SF01 75.4747190 MHz
 411 0.0300000 sec



118.855
 118.688
 115.262
 115.090
 114.950
 114.818
 114.513
 114.383
 114.097

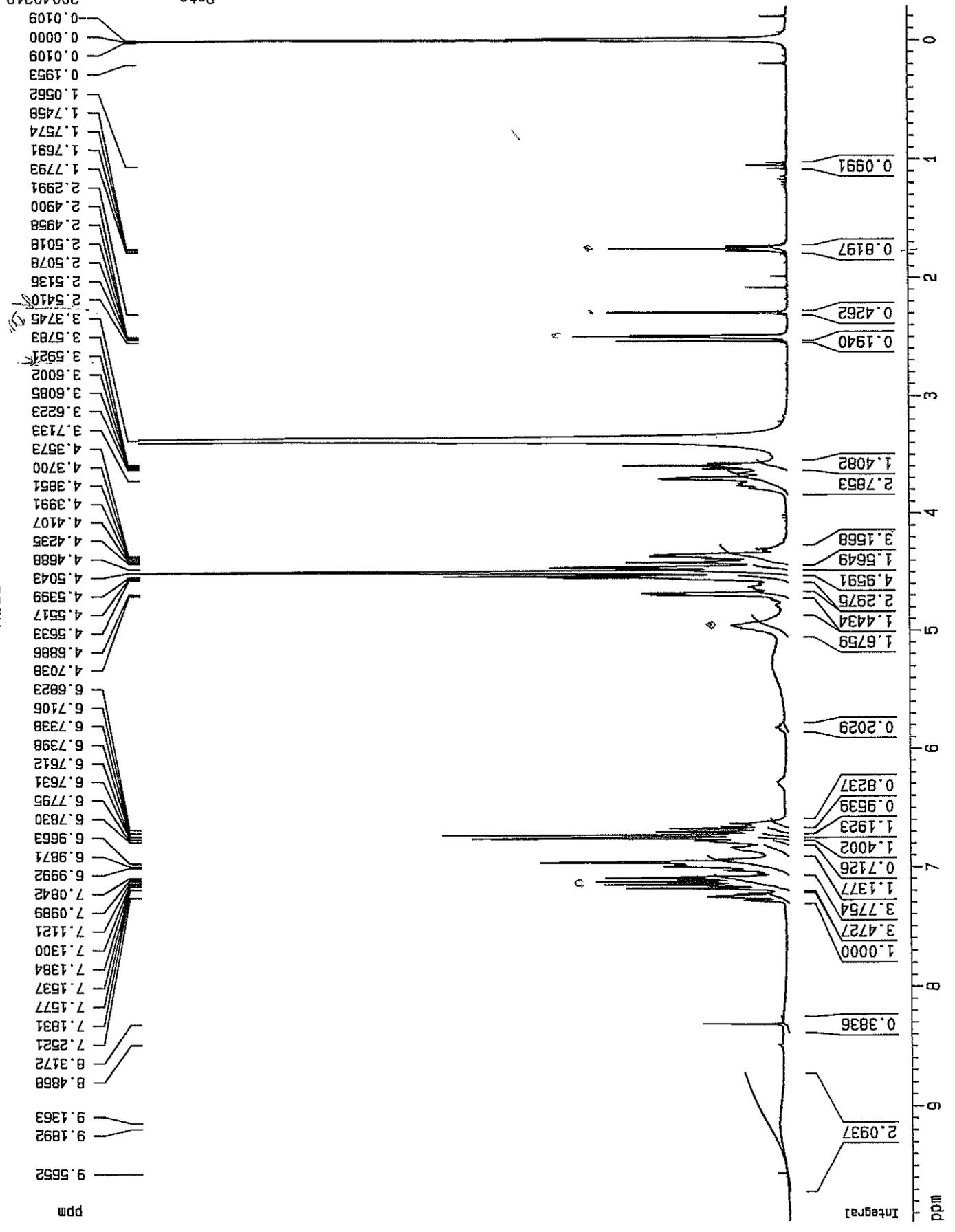
124.541
 125.382
 125.898
 126.038
 126.206
 127.311
 127.349
 127.532
 127.779
 128.006
 128.108
 128.277
 128.558
 128.966
 129.435
 132.206
 132.264
 132.541
 132.736

149.773
 150.482
 152.976
 154.148
 156.203
 157.350
 ppm

111
P-111

Date_ 20040219
RG 322.5
NUC1 1H
SFO1 300.1325000 MHz

R158



Date: 20040219
 RG 322.5
 NUC1 1H
 SF01 300.1325000 MHz

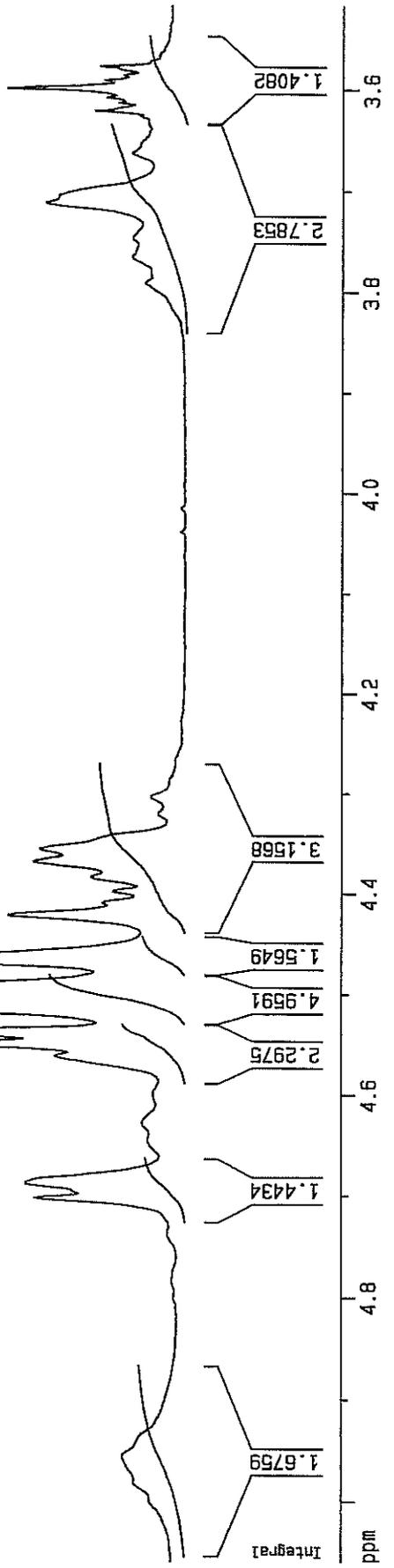
R158

- 3.79167
- 3.76616
- 3.74679
- 3.71334
- 3.66362
- 3.63577
- 3.62731
- 3.62226
- 3.61375
- 3.60852
- 3.60024
- 3.59214
- 3.58687
- 3.57830

- 4.30445
- 4.32078
- 4.35730
- 4.36995
- 4.38507
- 4.39911
- 4.41074
- 4.42350
- 4.46884
- 4.50433
- 4.53986
- 4.55166
- 4.56334
- 4.60071
- 4.62869
- 4.64613
- 4.68858
- 4.70375
- 4.73854

4.95680

ppm

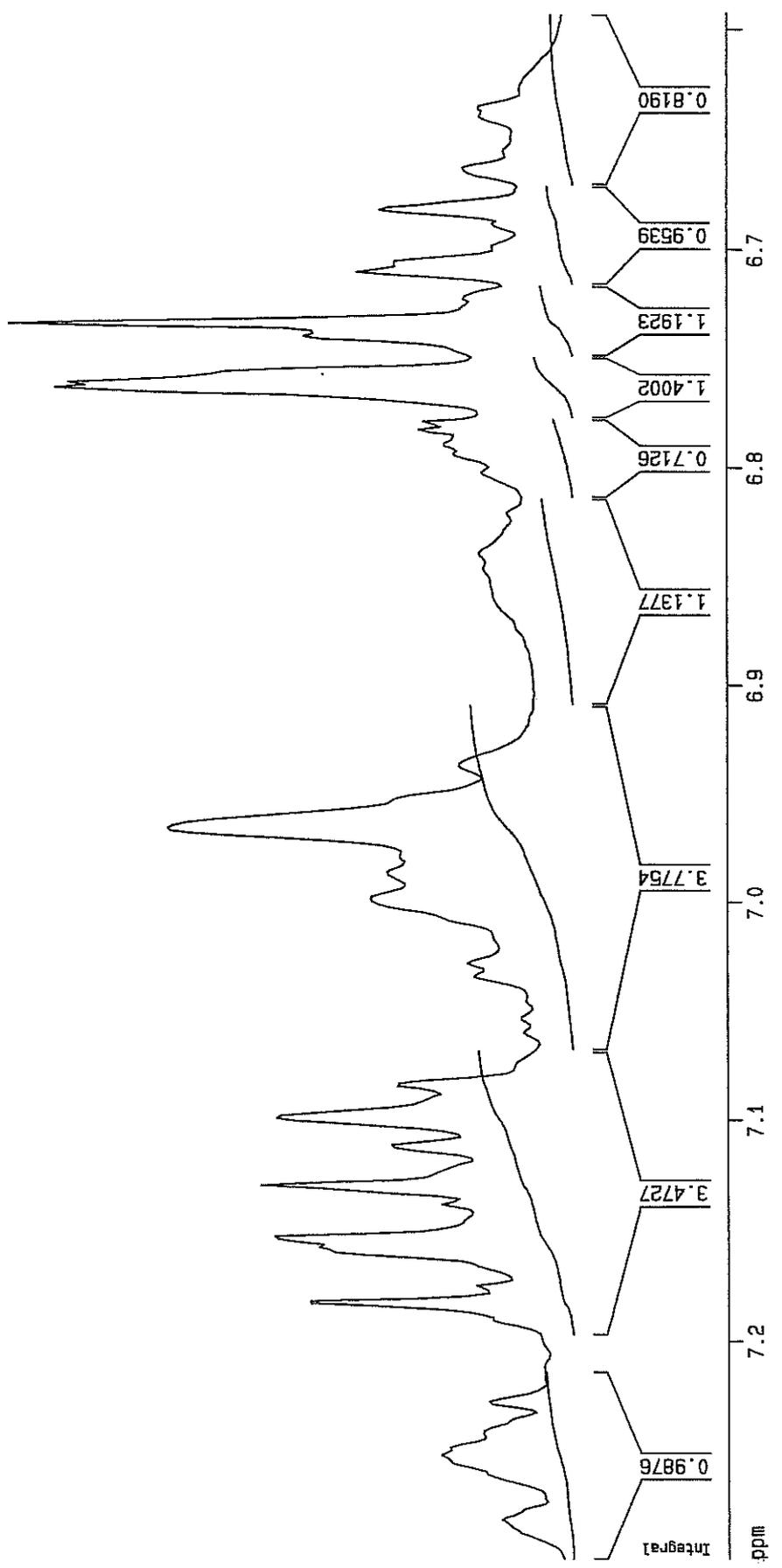


Date: 20040219
 RG 322.5
 NUC1 1H
 SF01 300.1325000 MHz

R158

6.84680
 6.83967
 6.82106
 6.80251
 6.79378
 6.78958
 6.78302
 6.77951
 6.76305
 6.76116
 6.73982
 6.73383
 6.72266
 6.71060
 6.68879
 6.68226
 6.66352
 6.65551
 6.63945
 6.63578

7.28134
 7.25207
 7.24195
 7.22811
 7.21201
 7.18306
 7.17545
 7.15773
 7.15369
 7.13839
 7.12998
 7.11206
 7.09894
 7.08417
 7.05998
 7.05357
 7.03431
 7.02839
 6.99916
 6.98715
 6.96631
 6.93749



PHYSICAL PROPERTY SPECIFICATIONS

Grade Spec: 5454P0
110 GSM Tan BC/BS A+ WT WP Paper

		<u>Target</u>	<u>Limits</u>	<u>Munising Test Method</u>
Basis Weight (gsm)		111.3	102.2 - 120.3	101
Caliper (mm)		0.168	0.147 - 0.188	102
Dry Tensile (kg/15mm)	MD	8.5	6.4 min.	203
	CD	7.0	5.3 min.	303
Dry Stretch (%)	MD	2.8	4.5 max.	205
	CD	8.2	13.1 max.	305
Elmendorf Tear (g/16 sht.)	MD	95	68 min	201
	CD	90	62 min	301
Smoothness (mL/min)	Wire	130	195 max.	501
Wet Tensile, Cured (kg15mm)	MD	4.7	3.3 min	250
Wet Stretch, Cured (%)	MD	8.5	13.5 max.	206

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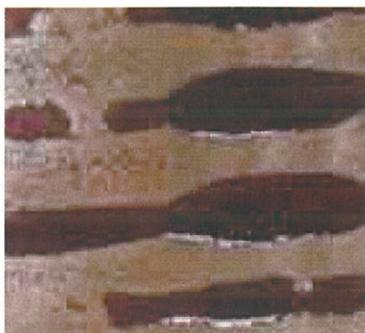
"(C) 2003 Kimberly-Clark Corp. This document has not been published."

Carh
27.06.03

Donna J. Corey 26-June-2003
Specification Analyst
Kimberly-Clark Technical Paper

2006
27.06.03
[Signature]

Appendix K: Digital photos of different coatings



PR+PEG



PR+MA12



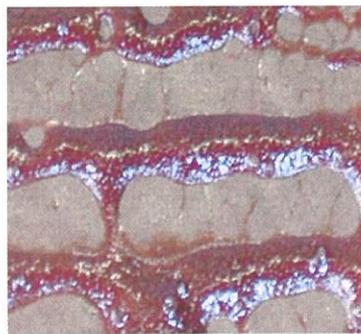
Pure phenolic resin



Pure epoxy resin



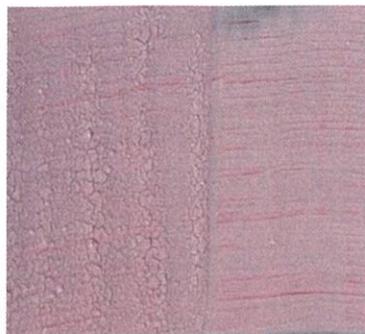
PR+DA6



PR + DMEA



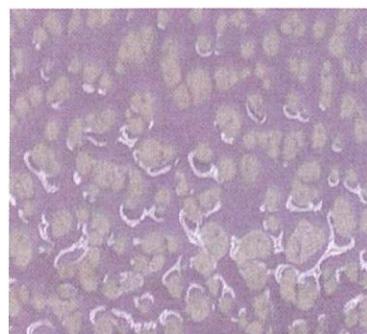
Phenolic production formulation



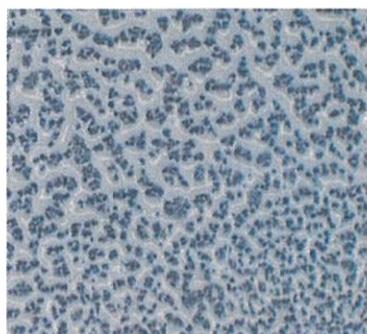
Modified PR + all fillers



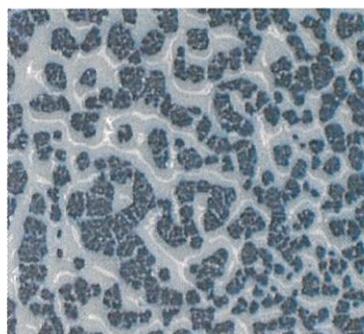
PR with ½ fillers



PR on different backing paper



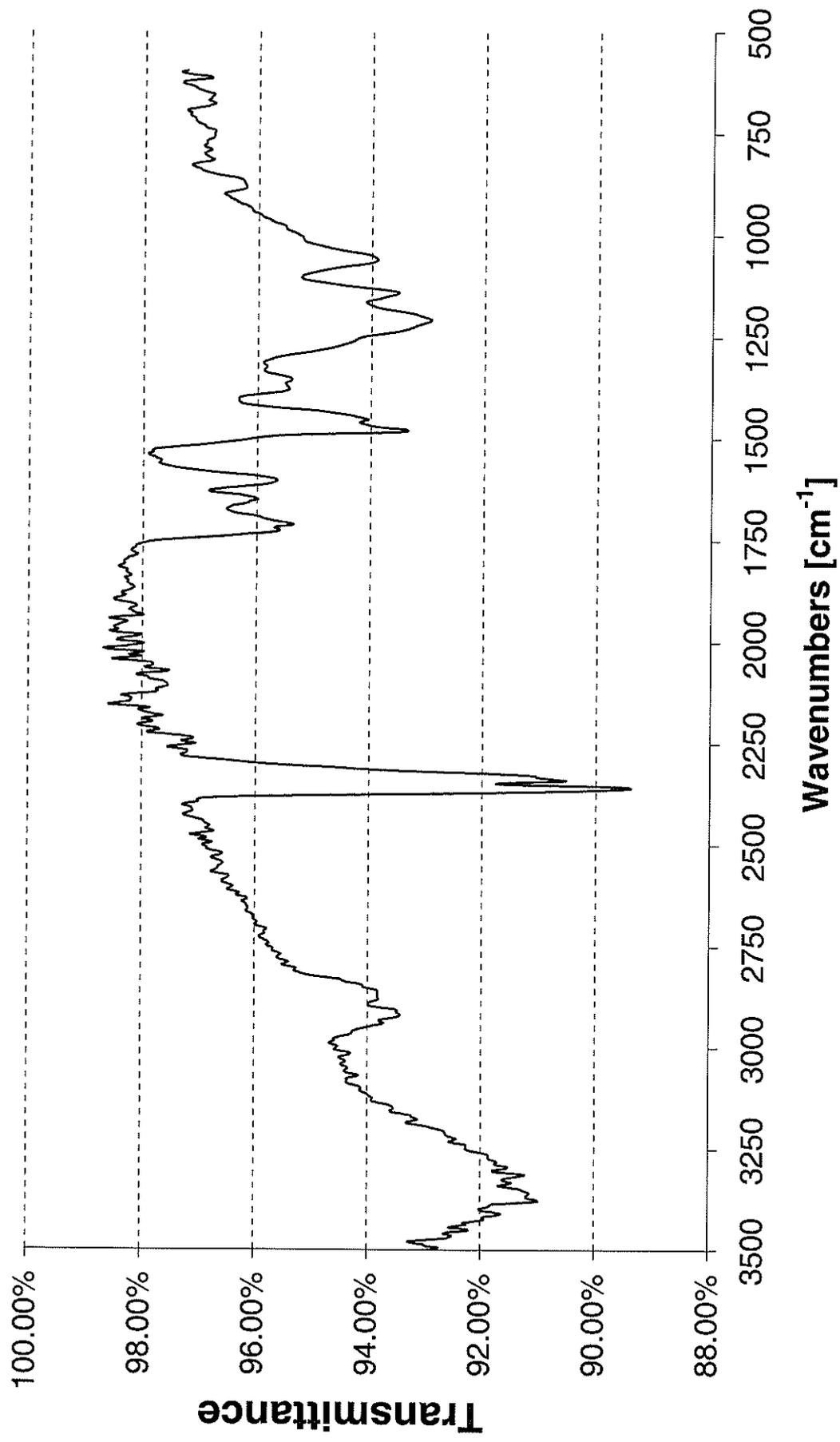
PR with 10% TiO₂



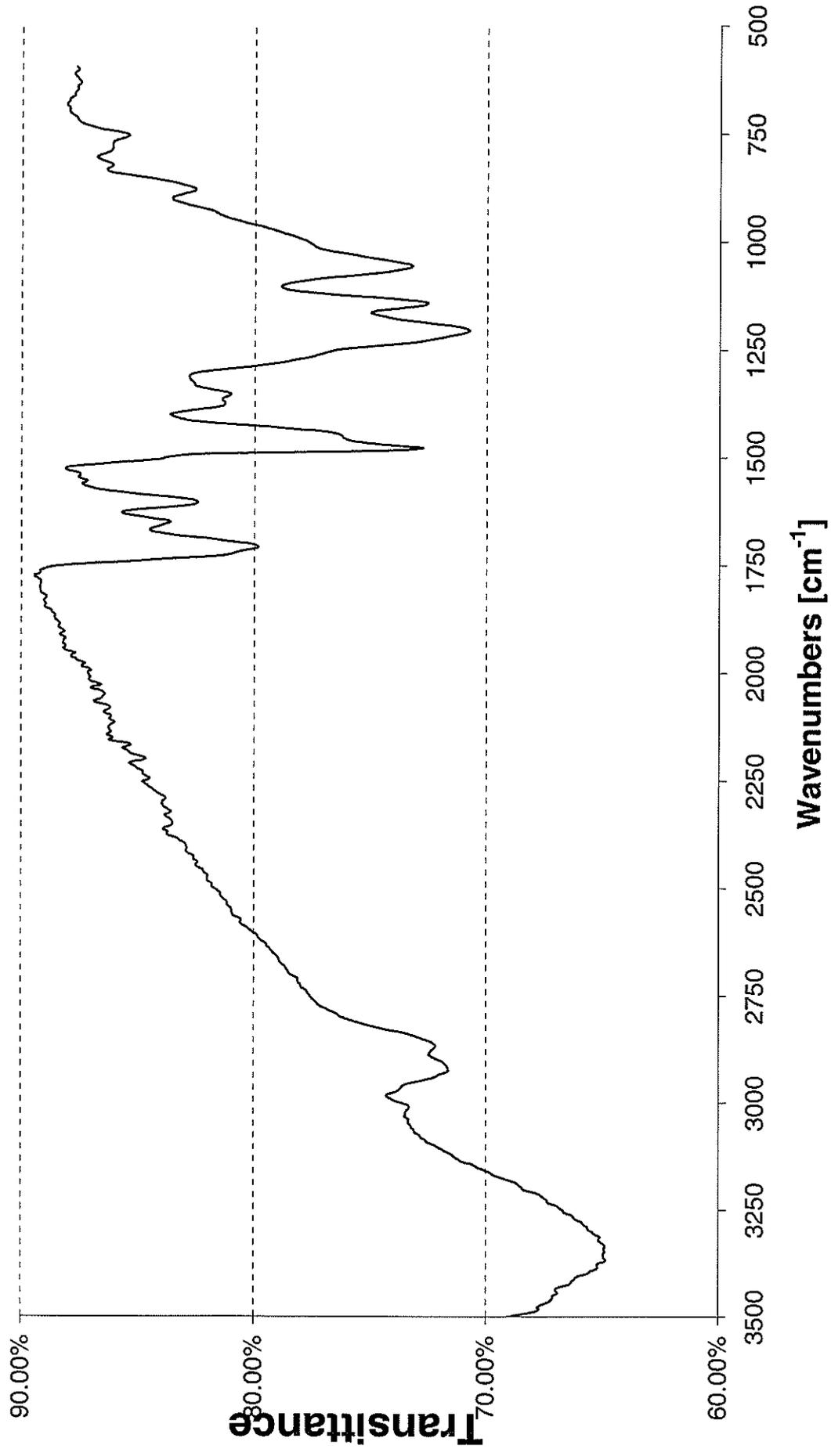
PR with 20% TiO₂

Note: PR refers to the unmodified phenolic resin.

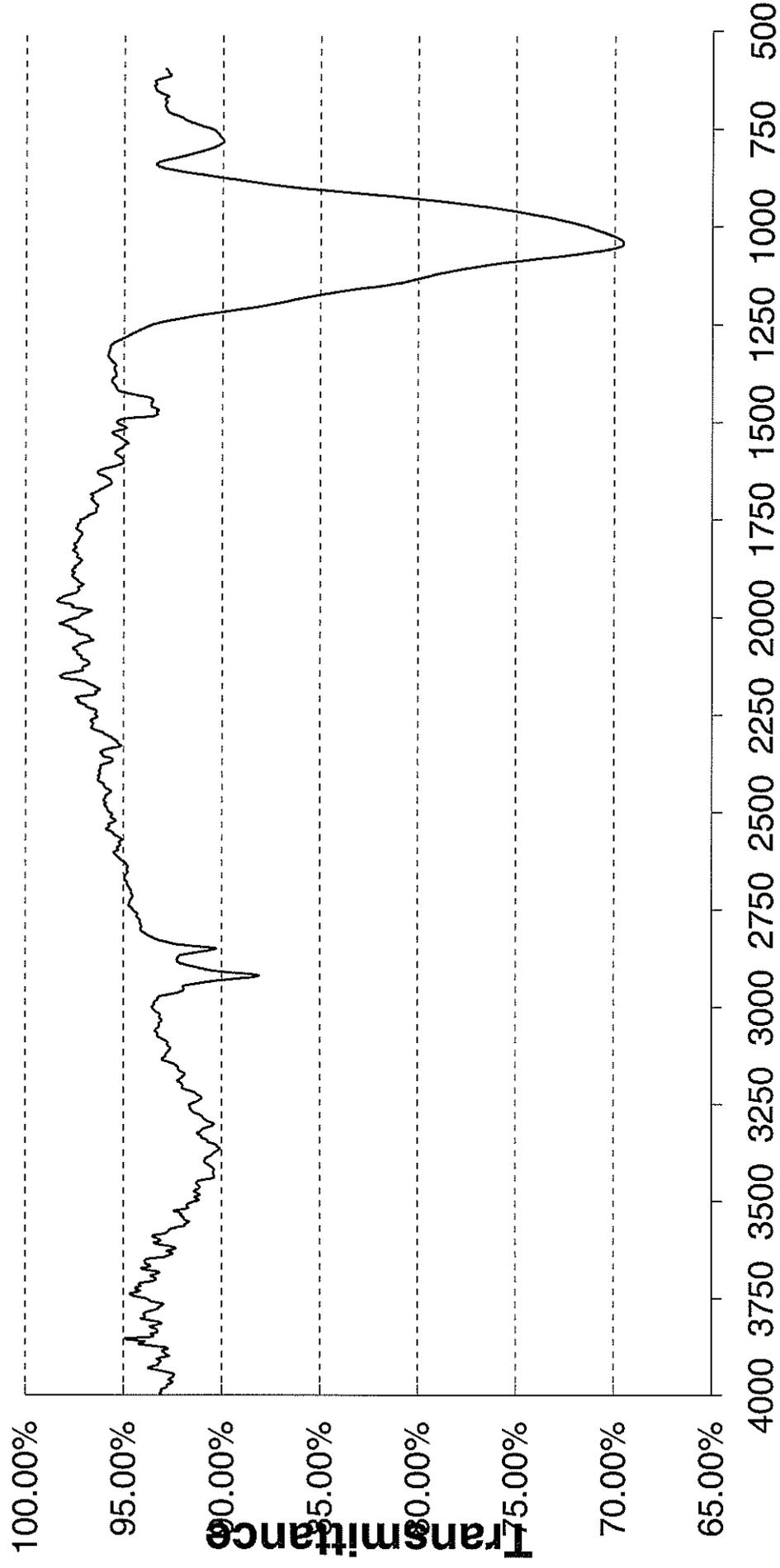
PR-DA4



PR-DA6

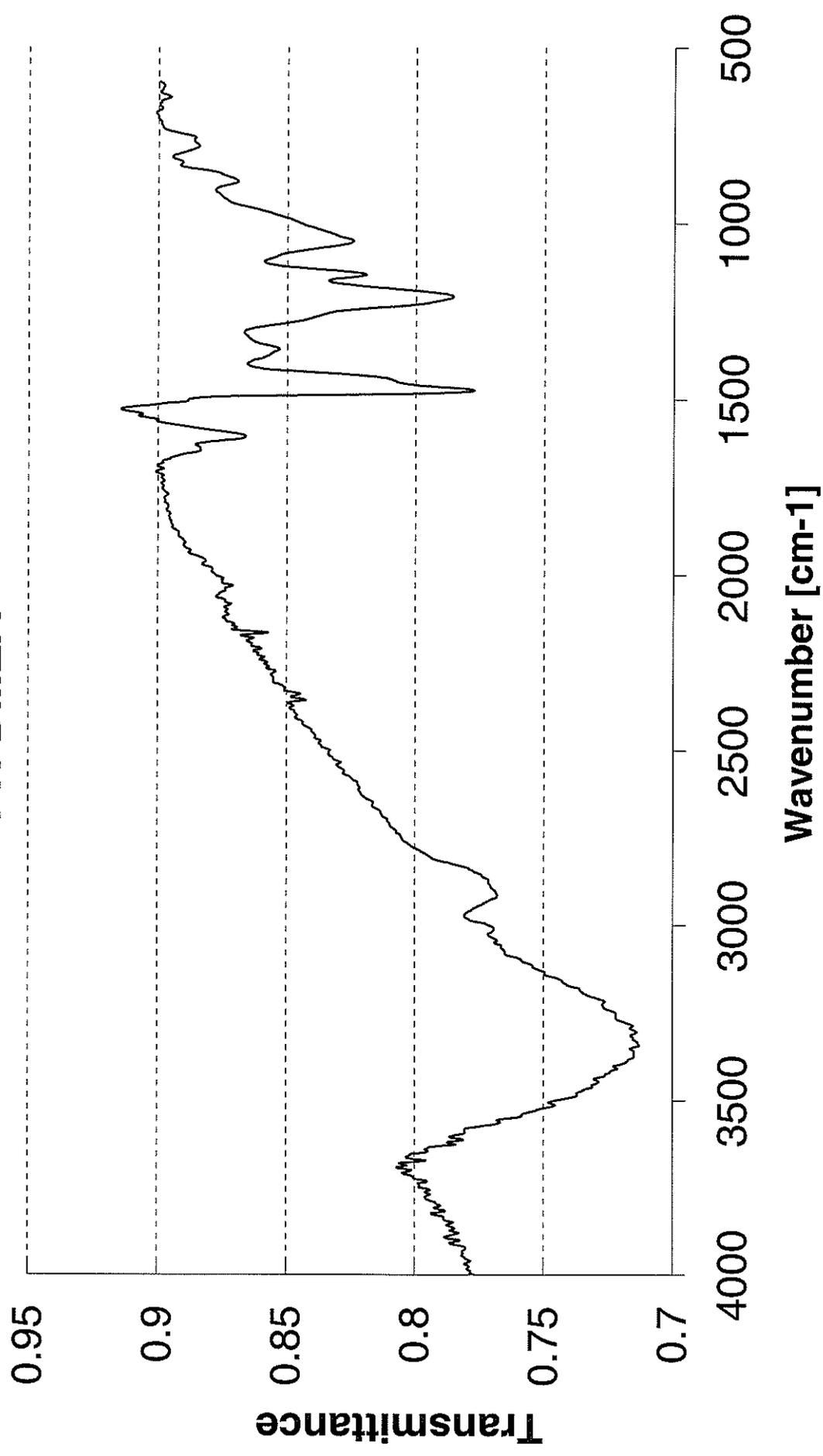


PR-MA12

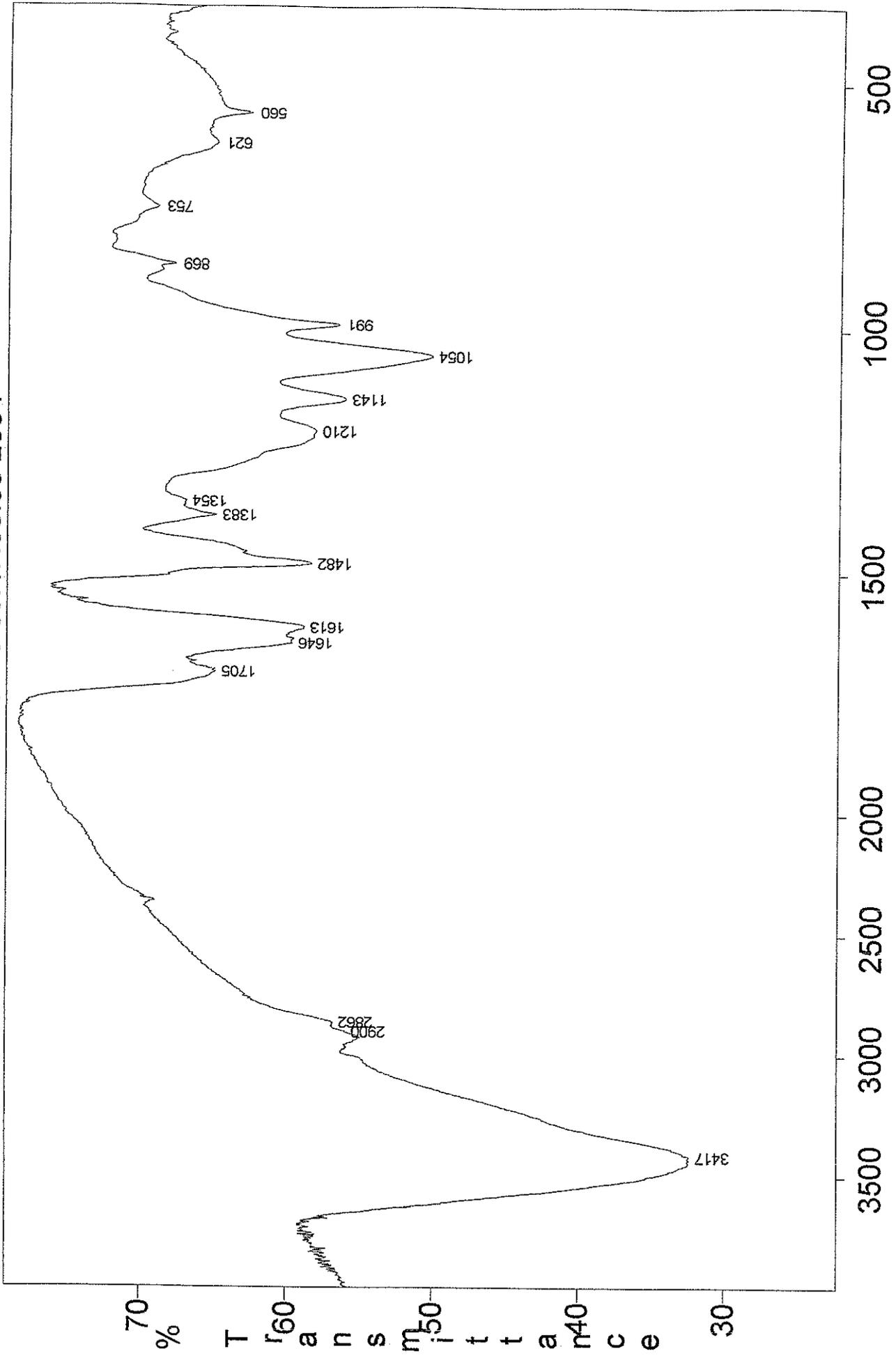


Wavenumbers [cm⁻¹]

PR-DMEA



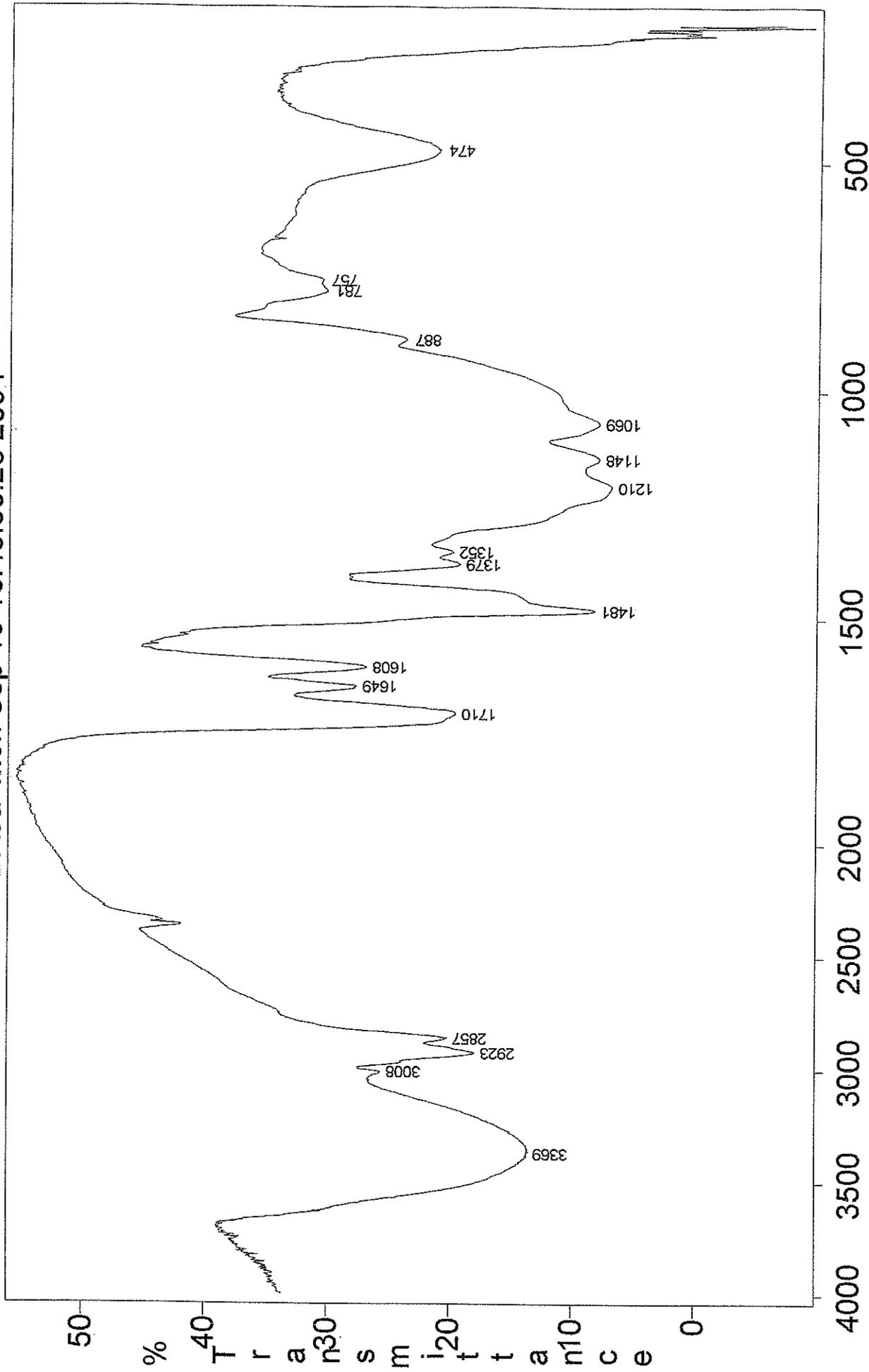
DA4-PR Thu Jul 15 09:47:38:06 2004



Wavenumbers

1: da4-pr: DA4-PR Thu Jul 15 09:47:38:06 2004

PR+DA6a Mon Sep 13 16:43:30:26 2004

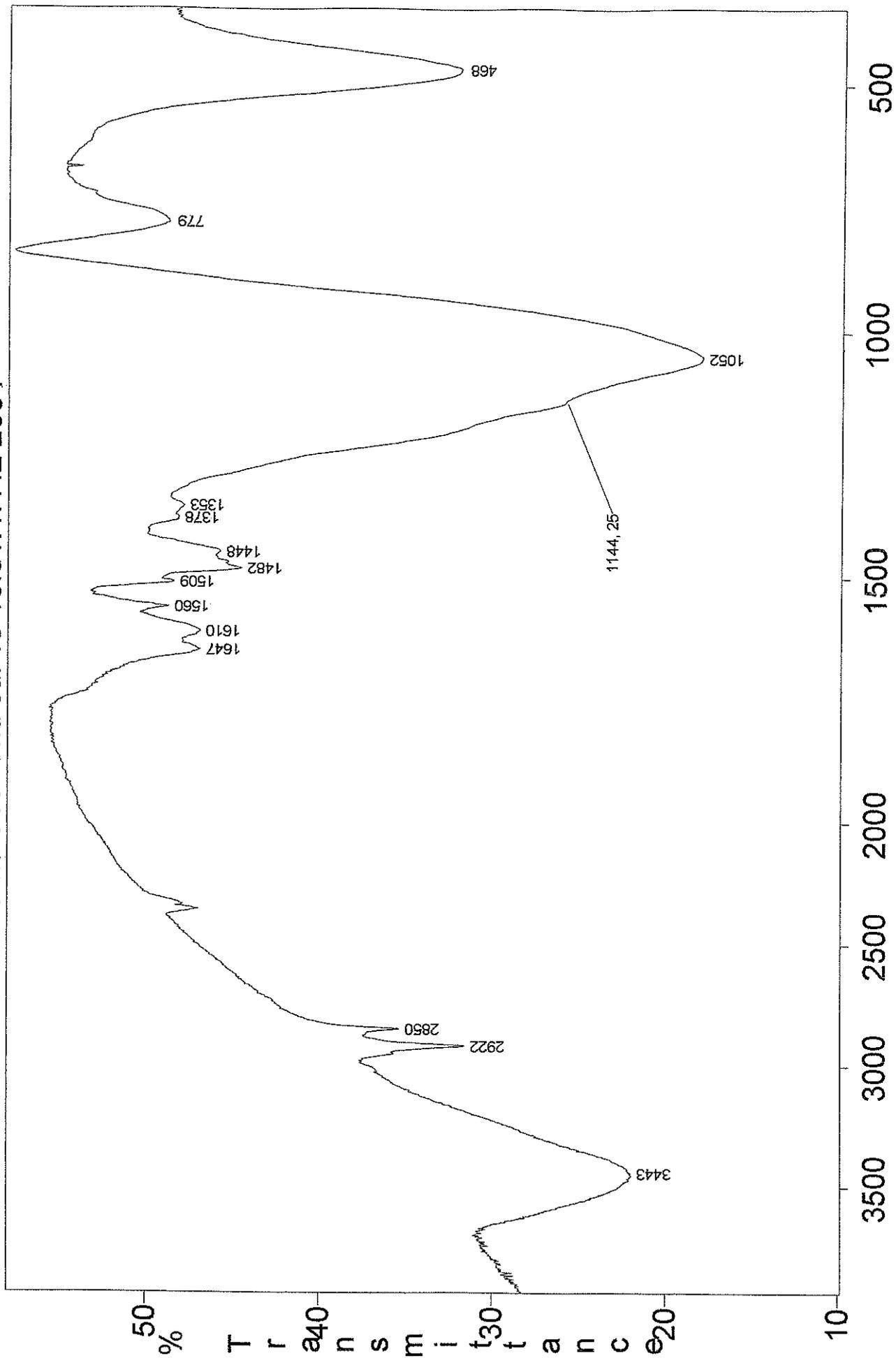


Wavenumbers

1: PRDR6A: PR+DA6a Mon Sep 13 16:43:30:26 2004

Date: Mon Sep 13 16:43:30:26 2004 Resolution: 2.0 Scans: 32

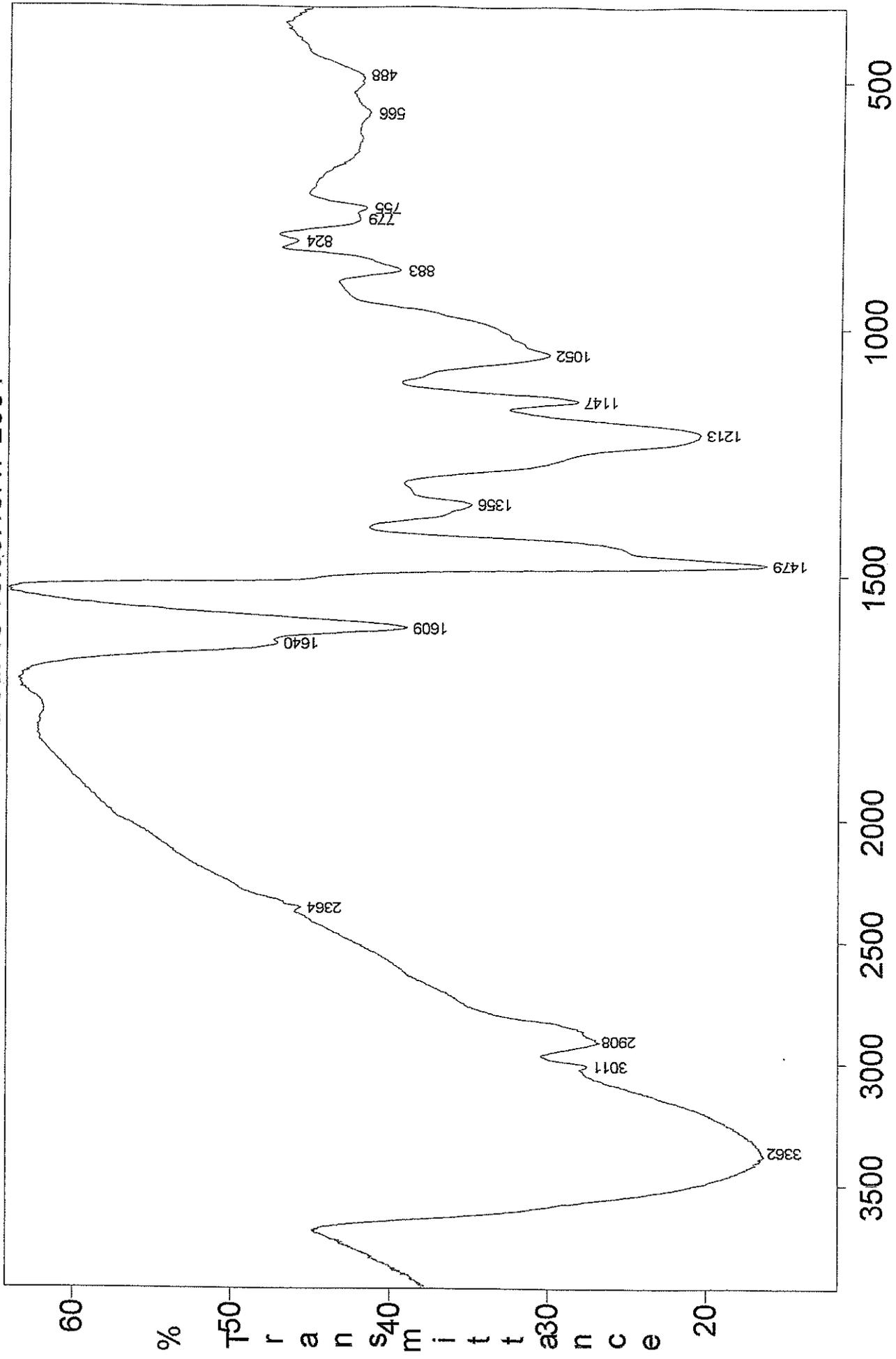
MA12-PR Thu Jul 15 10:01:47:42 2004



Wavenumbers

1: ma12-pr: MA12-PR Thu Jul 15 10:01:47:42 2004

DMEA-PR Thu Jul 15 10:05:15:47 2004

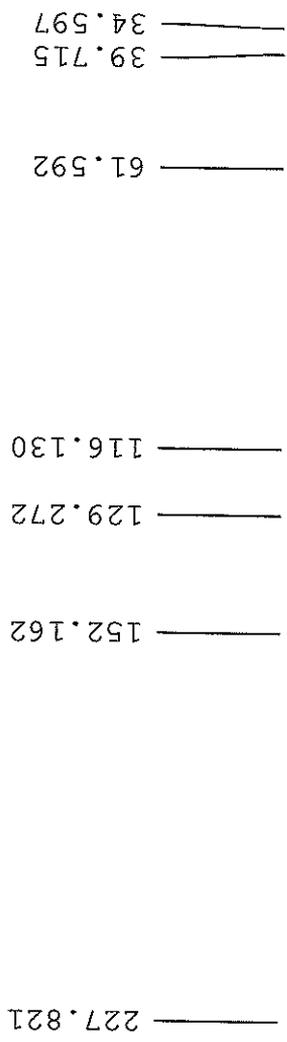


Wavenumbers

1: dmea-pr: DMEA-PR Thu Jul 15 10:05:15:47 2004

Dr. K. G.

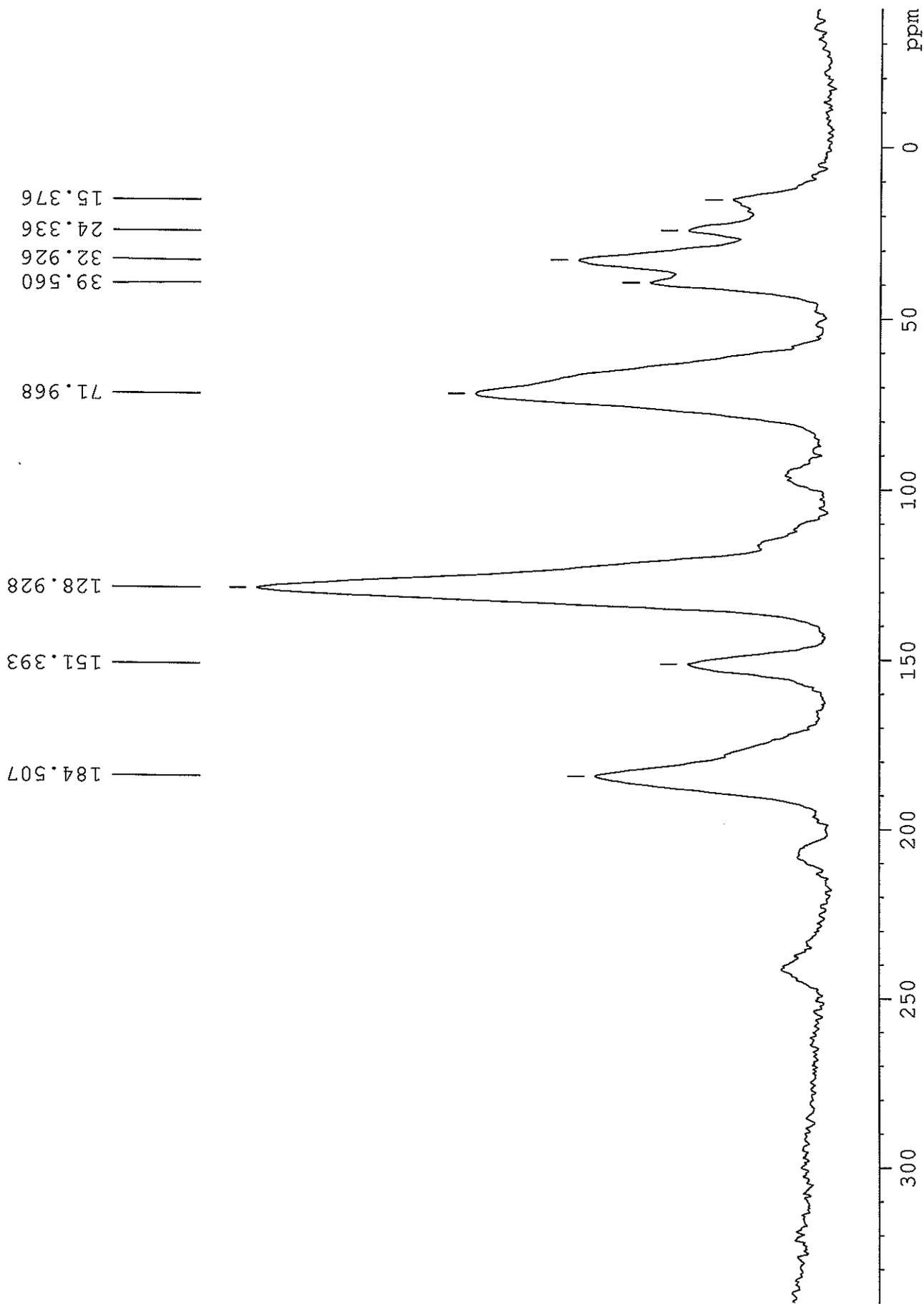
AnaB400.2



VPR 1740; CP/MAS 10kHz

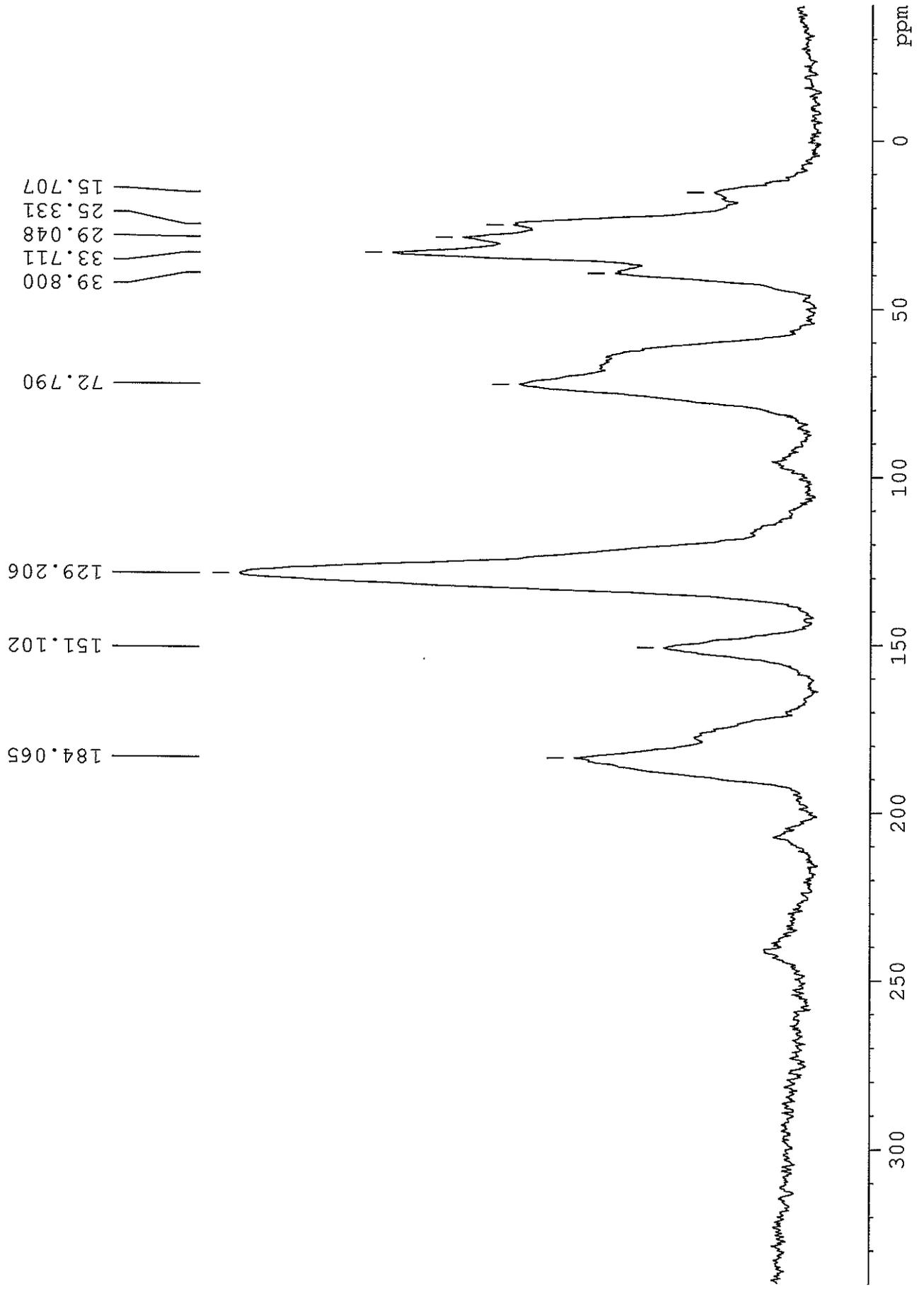
* spinning sideband





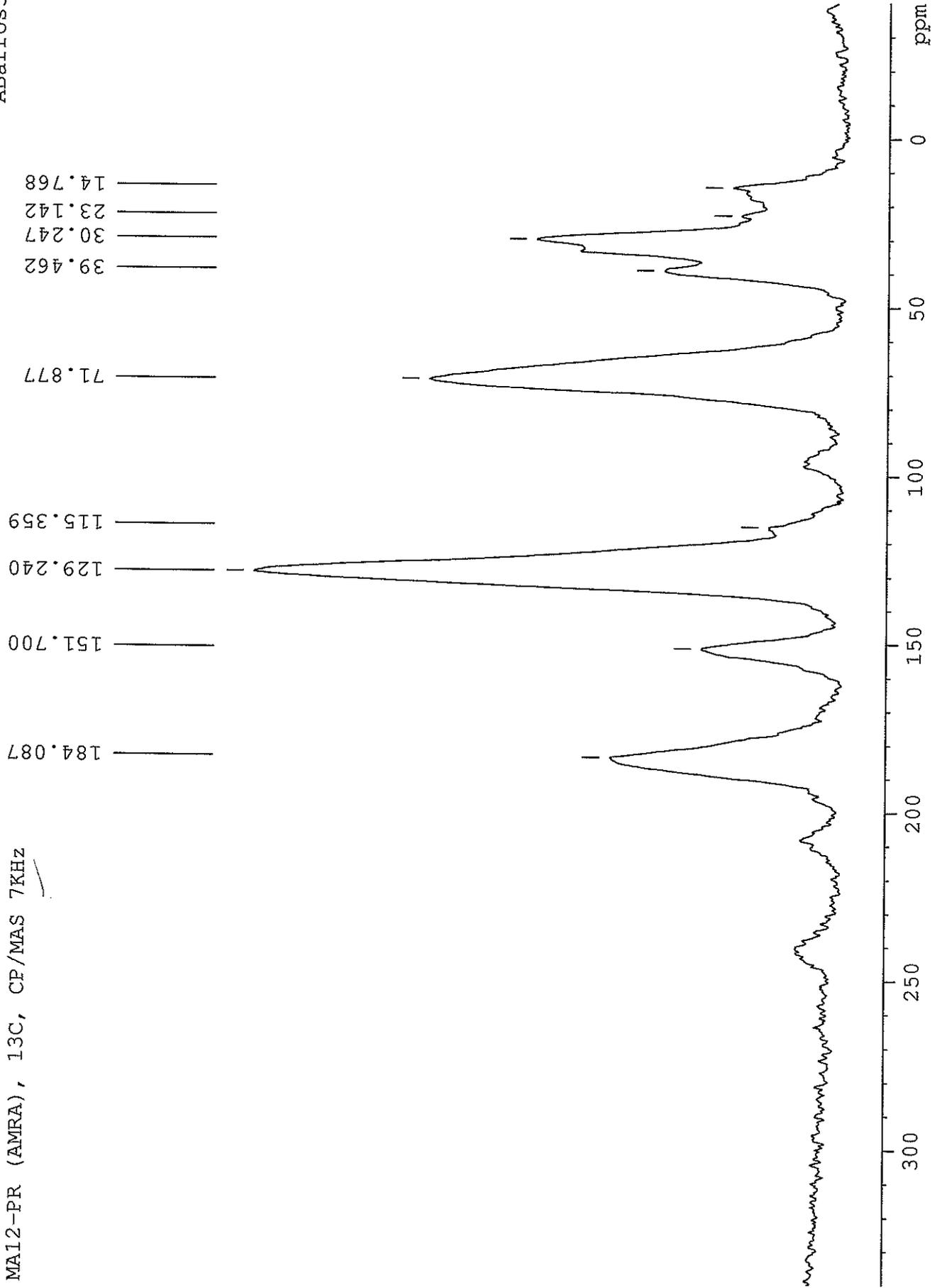
DA6_PR, AMRA; CP/MAS 7kHz

ABarros500.3 1



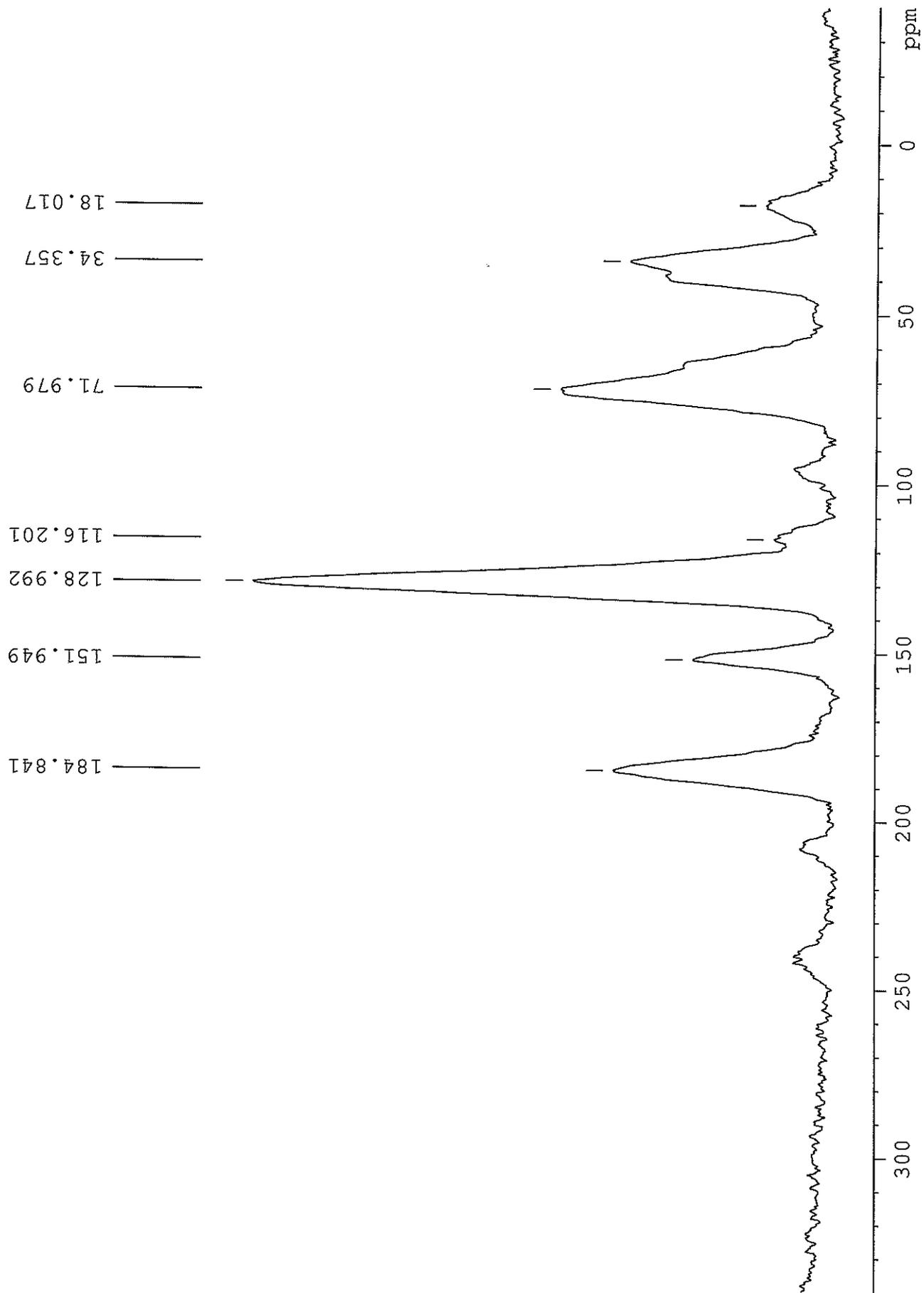
ABarros500.1

MA12-PR (AMRA), ¹³C, CP/MAS 7KHZ



DMAE_PR, AMRA; CP/MAS 7kHz

ABarros500.5



Appendix O: Statistical calculations on double folds test

Short general theory behind the calculations

The following procedure compares the data in given columns, where various statistical tests and graphs are constructed to compare the samples. The F-test in the ANOVA table tests whether there are any significant differences amongst the means, average. The ANOVA table decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio is a ratio of the between-group estimate to the within-group estimate. When the P-value of the F-test is smaller than or equal to 0.05, there is a statistically significant difference between the means of the variables at the 95.0% confidence level. As in the most cases there are, the Multiple Range Tests is run to tell which means are significantly different from which others.

Due to the fact that in those tests results there are many outliers, the Kruskal-Wallis Test is chosen to compare medians, measures of the central tendency of the data, instead of means. The Box-and-Whisker Plot displays a graphical summary of the presence of outliers in the data. The data are divided into four areas of equal frequency (quartiles). A box encloses the middle 50 percent, where the median is drawn as a vertical line inside the box.

The various plots help judge the practical significance of the results, as well as allow to look for possible violations of the assumptions underlying the analysis of variance.

• **Modification with suberic acid**

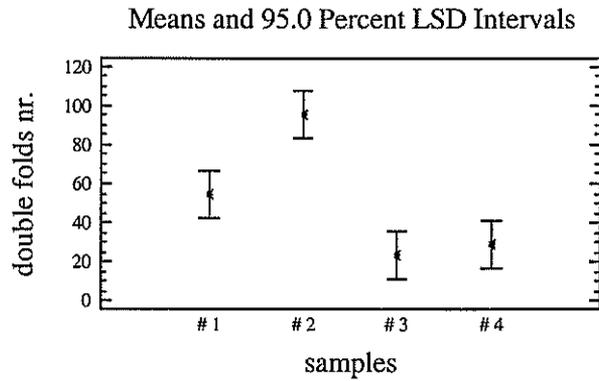
	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
50	172	25	19	
69	60	20	21	
72	45	25	25	
80	160	11	25	
32	27	20	27	
32	127	11	33	
44	69	37	33	
42	99	36	34	
58	70	18	37	
68	122	31	40	

Table of Means with 95.0 percent LSD intervals

	Count	Std. error		Lower limit	Upper limit
		Mean	(pooled s)		
# 1	10	54.7	8.40631	42.6447	66.7553
# 2	10	95.1	8.40631	83.0447	107.155
# 3	10	23.4	8.40631	11.3447	35.4553
# 4	10	29.4	8.40631	17.3447	41.4553
Total	40	50.65			

This table shows the mean for each column of data. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean.

The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95.0% of the time. The intervals is displayed graphically as following:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	31863.3	3	10621.1	15.03	0.0000
Within groups	25439.8	36	706.661		
Total (Corr.)	57303.1	39			

The F-ratio, which in this case equals 15.03, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

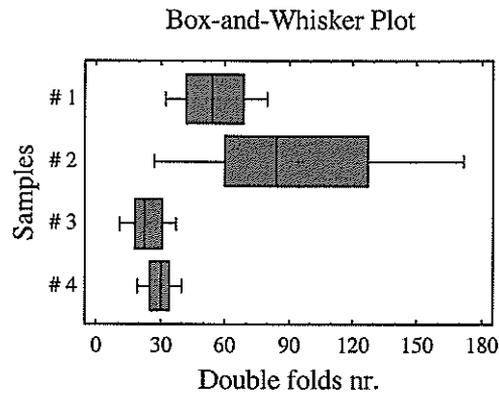
Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	10	26.55
# 2	10	32.2
# 3	10	9.15
# 4	10	14.1

Test statistic = 25.1578 P-Value = 0.0000143108

The Kruskal-Wallis test tests the null hypothesis that the medians within each of the 4 columns is the same. The data from all the columns is first combined and ranked from smallest to largest. The average rank is then computed for the data in each column. Since the P-value is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence

level. To determine which medians are significantly different from which others, the following Box-and-Whisker Plot is presented:



The results shows that there the medians of the sample 2 differs the most from any other means.

• Epoxy production

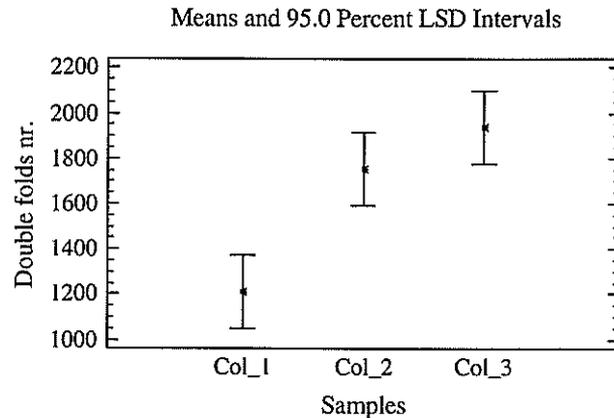
:

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>
	1647	1315	1756
	1037	1990	2265
	953	1450	1729
	579	1599	1509
	1414	2005	1725
	1129	1189	2201
	1279	2240	2004
	1258	2001	2349
	1589	2005	1890

Table of Means with 95.0 percent LSD intervals

	Count	Mean	Std. error (pooled s)	Lower limit	Upper limit
# 1	9	1209.44	110.745	1047.82	1371.07
# 2	9	1754.89	110.745	1593.27	1916.51
# 3	9	1936.44	110.745	1774.82	2098.07
Total	27	1633.59			

This table shows the mean for each column of data, as well as the standard error of each mean, which is a measure of its sampling variability. The intervals is displayed graphically as



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	2.577E6	2	1.2885E6	11.67	0.0003
Within groups	2.64914E6	24	110381.0		
Total (Corr.)	5.22615E6	26			

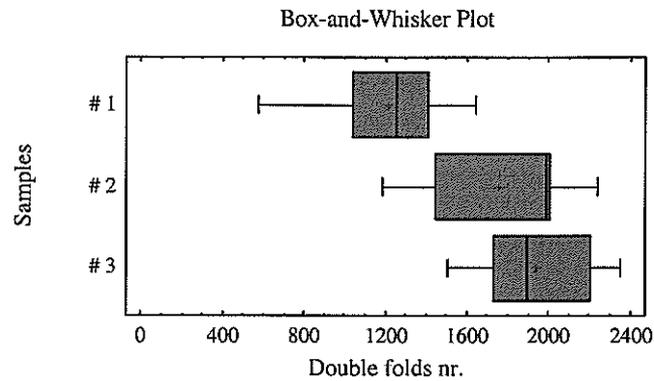
The F-ratio in this ANOVA table case is equal to 11.6732, and is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 3 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	9	6.44444
# 2	9	16.1111
# 3	9	19.4444

Test statistic = 13.0304 P-Value = 0.00148074

The Kruskal-Wallis test tests the null hypothesis that the medians within each of the 3 columns is the same. As previously, since the P-value is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, Box-and-Whisker Plot is plotted:



The results shows that there the mean of the sample 1 differs the most from any other means.

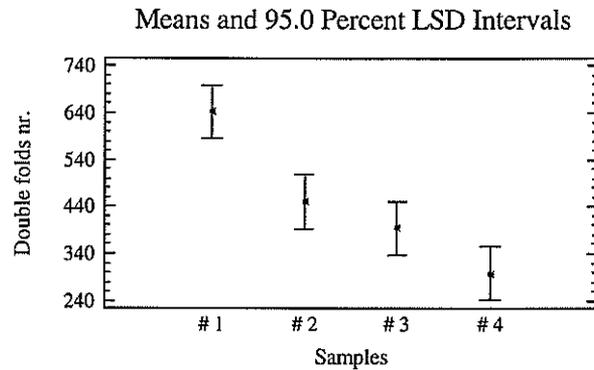
• Epoxy pure

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
793	492	593	349	
589	415	220	270	
826	455	360	199	
434	306	307	316	
476	419	330	151	
664	580	190	249	
670	495	520	396	
635	592	509	362	
690	299	520	390	

Table of Means with 95.0 percent LSD intervals

	Count	Mean	Std. error (pooled s)	Lower limit	Upper limit
# 1	9	641.889	39.5057	584.988	698.79
# 2	9	450.333	39.5057	393.432	507.235
# 3	9	394.333	39.5057	337.432	451.235
# 4	9	298.0	39.5057	241.099	354.901
Total	36	446.139			

The table shows the mean for each column of data and the standard error of each mean, which is a measure of its sampling variability. The table also displays an interval around each mean. They are constructed in such a way that if two means are the same, their intervals will overlap 95.0% of the time. Those intervals are graphically displayed as following:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	566681.0	3	188894.0	13.45	0.0000
Within groups	449481.0	32	14046.3		
Total (Corr.)	1.01616E6	35			

In this ANOVA table, the F-ratio is 13.45, which is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

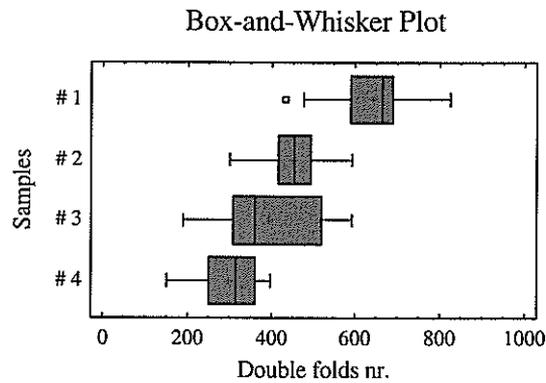
Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	9	29.8889
# 2	9	19.0
# 3	9	16.0
# 4	9	9.11111

Test statistic = 18.1935 P-Value = 0.000401217

The Kruskal-Wallis test results shows that the P-value is less than 0.05, and thus there is a statistically significant difference amongst the medians at the 95.0% confidence level.

Testing of which medians are significantly different from which, the following Box-and-Whisker Plot is displayed:



The results shows that there the mean of the sample 1 differs the most from any other means.

• Phenolic production

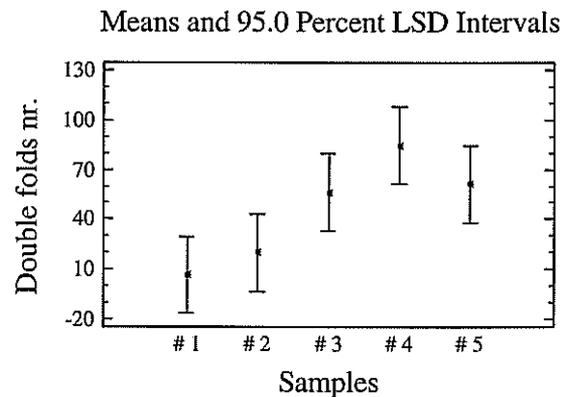
	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>	<u>Sample 5</u>
	5	3	25	175	78
	4	3	29	7	148
	2	34	4	98	96
	2	3	146	3	109
	35	20	67	87	3
	2	110	54	73	102
	2	2	6	5	7
	2	2	103	123	5
	2	2	73	192	3

Table of Means with 95.0 percent LSD intervals

	Count	Mean	Std. error (pooled s)	Lower limit	Upper limit
# 1	9	6.22222	16.2496	-17.0004	29.4448
# 2	9	19.8889	16.2496	-3.33369	43.1115
# 3	9	56.3333	16.2496	33.1108	79.5559
# 4	9	84.7778	16.2496	61.5552	108.0
# 5	9	61.2222	16.2496	37.9996	84.4448
Total	45	45.6889			

The table shows the mean for each column of data and the standard error of each mean, which is a measure of its sampling variability. The table also displays an interval around each mean. They are constructed in such a way that if two means are the same, their intervals will overlap

95.0% of the time. Those intervals are graphically displayed as following:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	36952.1	4	9238.02	3.89	0.0093
Within groups	95057.6	40	2376.44		
Total (Corr.)	132010.0	44			

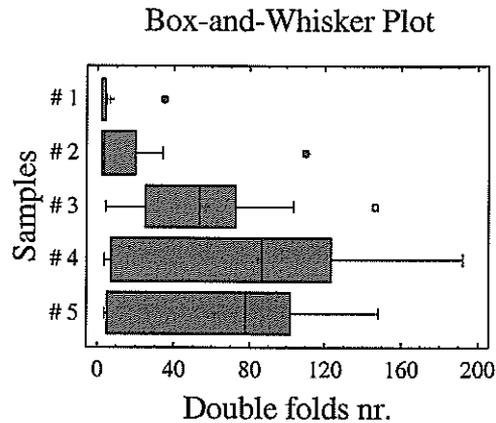
The F-ratio in this ANOVA table is calculated to 3.88734. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 5 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	9	10.3889
# 2	9	15.9444
# 3	9	28.7778
# 4	9	31.7222
# 5	9	28.1667

Test statistic = 18.1929 P-Value = 0.00113146

The Kruskal-Wallis test tests the null hypothesis that the medians within each of the 5 columns is the same. Since the P-value is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, the following Box-and-Whisker is presented:



The results shows that there the medians of the sample 1 and 2 differ the most from other two medians.

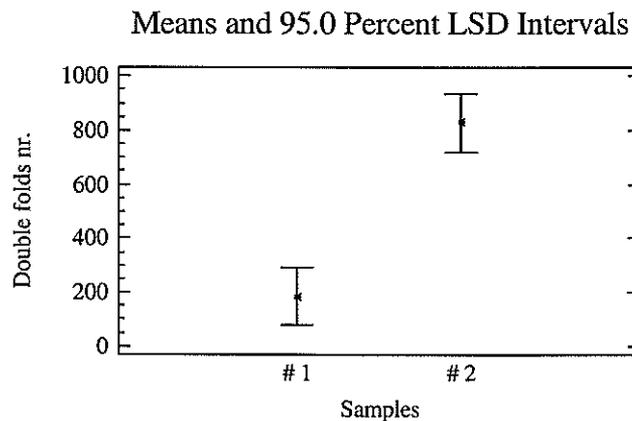
• Phenolic pure

	<u>Sample 1</u>	<u>Sample 2</u>
	83	1411
	95	538
	170	865
	143	603
	338	630
	240	840
	181	860
	218	874

Table of Means with 95.0 percent LSD intervals

	Count	Std. error		Lower limit	Upper limit
		Mean	(pooled s)		
# 1	8	183.5	71.1189	75.6414	291.359
# 2	8	827.625	71.1189	719.766	935.484
Total	16	505.563			

The table shows the mean for each column of data and the standard error of each mean, which is a measure of its sampling variability. The table also displays an interval around each mean. They are constructed in such a way that if two means are the same, their intervals will overlap 95.0% of the time. Those intervals are graphically displayed as following:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	1.65959E6	1	1.65959E6	41.01	0.0000
Within groups	566484.0	14	40463.1		
Total (Corr.)	2.22607E6	15			

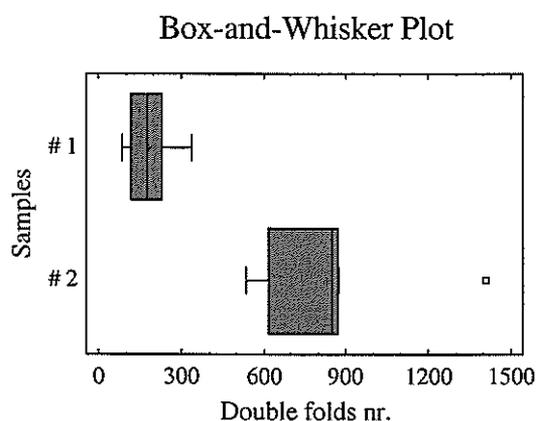
The ANOVA table presents the F-ratio equals to 41.01. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 2 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	8	4.5
# 2	8	12.5

Test statistic = 11.2941 P-Value = 0.000777099

The Kruskal-Wallis test tests the null hypothesis that the medians within each of the 2 columns is the same. Since the P-value is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, a Box-and-Whisker Plot is presented:



The results shows that the two calculated means are very different from each other.

The similar calculations are performed with backing paper before and after being heated. As there are only one set of the numbers, the statistical calculations give the following results:

- **Unheated backing paper** Mean value of one set of data: 2151
 - **Heated backing paper** Mean value of one set of data: 1574
-

Appendix P: Statistical calculations on bursting strength test

Short theory behind the calculations

This procedure compares the data in given columns of the current data file. Various statistical tests and graphs are constructed to compare the samples. The F-test in the ANOVA table tests whether there are any significant differences amongst the means. The ANOVA table decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio is a ratio of the between-group estimate to the within-group estimate. When the P-value of the F-test is smaller than or equal to 0.05, there is a statistically significant difference between the means of the variables at the 95.0% confidence level. As in the most cases there are, the Multiple Range Tests is run to tell which means are significantly different from which others. As there are often many outliers, the Kruskal-Wallis Test is chosen to compare medians instead of means.

The various plots help judge the practical significance of the results, as well as allow to look for possible violations of the assumptions underlying the analysis of variance.

• Modification with suberic acid

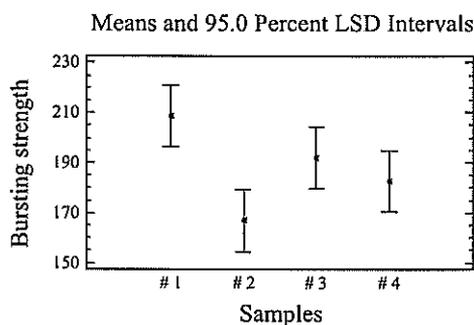
	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
	231	172	219	183
	215	154	194	194
	179	171	174	175
	210	170	180	179

Table of Means with 95.0 percent LSD intervals

	Count	Std. error		Lower limit	Upper limit
		Mean	(pooled s)		
# 1	4	208.75	7.95953	196.487	221.013
# 2	4	166.75	7.95953	154.487	179.013
# 3	4	191.75	7.95953	179.487	204.013
# 4	4	182.75	7.95953	170.487	195.013
Total	16	187.5			

This table shows the mean for each column of data. It also shows the standard error of each mean, which is a measure of its sampling variability. The standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The table also displays an interval around each mean.

The intervals currently displayed are based on Fisher's least significant difference (LSD) procedure. They are constructed in such a way that if two means are the same, their intervals will overlap 95.0% of the time. The intervals are displayed graphically as:



ANOVA Table

Analysis of Variance					
Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	3691.0	3	1230.33	4.85	0.0195
Within groups	3041.0	12	253.417		
Total (Corr.)	6732.0	15			

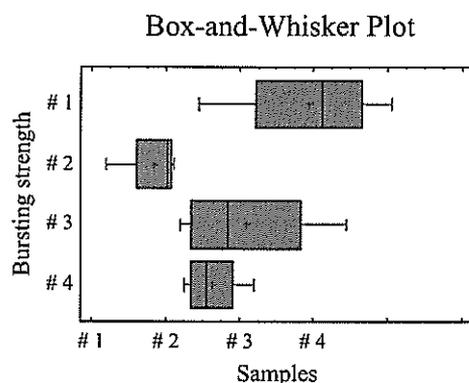
The ANOVA table decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio equals 4.85, is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	4	12.625
# 2	4	2.5
# 3	4	10.125
# 4	4	8.75

Test statistic = 9.86173 P-Value = 0.0197781

The Kruskal-Wallis test tests the null hypothesis that the medians within each of the 4 columns is the same, where the data from all the columns is first combined and ranked from smallest to largest. The average rank is then computed for the data in each column. Since the P-value is less than 0.05, there is a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, the following Box-and Whisker Plot is presented:



The results show that the median of the sample 2 differs the most from the other medians.

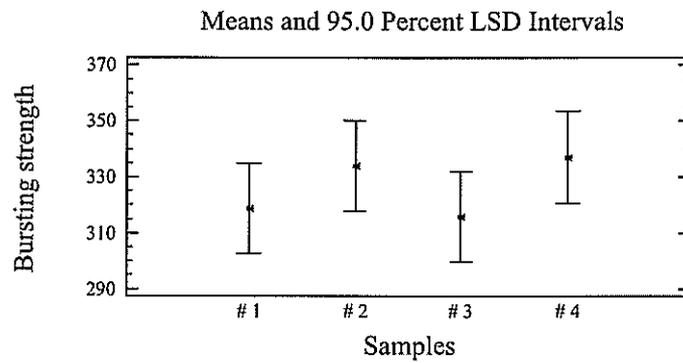
• Epoxy production

Sample 1	Sample 2	Sample 3	Sample 4
336	361	348	351
302	364	326	328
367	298	298	338
298	324	299	331
290	323	308	337

Table of Means with 95.0 percent LSD intervals

	Count	Std. error			
		Mean	(pooled s)	Lower limit	Upper limit
# 1	5	318.6	10.8536	302.33	334.87
# 2	5	334.0	10.8536	317.73	350.27
# 3	5	315.8	10.8536	299.53	332.07
# 4	5	337.0	10.8536	320.73	353.27
Total	20	326.35			

The table shows the mean for each column of data and the standard error of each mean, which is a measure of its sampling variability. Those intervals are graphically presented by the following Means Plot:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	1716.55	3	572.183	0.97	0.4305
Within groups	9424.0	16	589.0		
Total (Corr.)	11140.6	19			

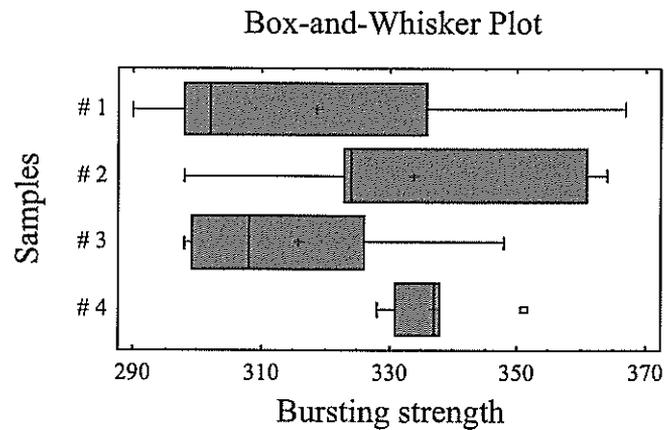
In this ANOVA table, calculated F-ratio is equal to 0.97. Since the P-value of the test is greater than 0.05, there is not a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	5	8.6
# 2	5	11.4
# 3	5	8.2
# 4	5	13.8

Test statistic = 2.95173 P-Value = 0.399123

In Kruskal-Wallis test, the data from all the columns is first combined and ranked from smallest to largest and the average rank is then computed for the data in each column. Since the P-value is greater than 0.05, there is not a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, a Box-and-Whisker Plot is shown:



The results show that the medians of the sample 2 differs the most from the other medians.

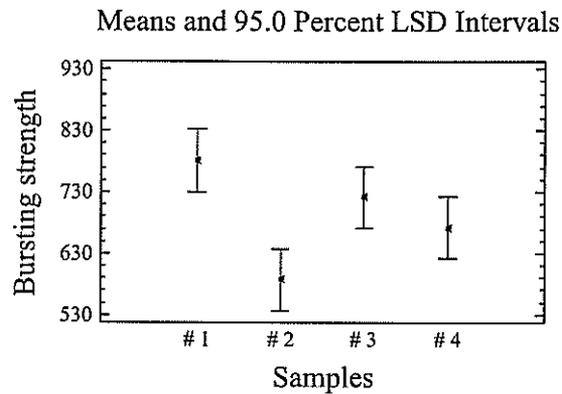
- Epoxy pure

Sample 1	Sample 2	Sample 3	Sample 4
802	573	831	673
799	548	770	570
744	599	607	745
780	630	678	700

Table of Means with 95.0 percent LSD intervals

	Count	Std. error		Lower limit	Upper limit
		Mean	(pooled s)		
# 1	4	781.25	32.8211	730.684	831.816
# 2	4	587.5	32.8211	536.934	638.066
# 3	4	721.5	32.8211	670.934	772.066
# 4	4	672.0	32.8211	621.434	722.566
Total	16	690.563			

This table shows the mean for each column of data, the standard error of each mean, which is a measure of its sampling variability, and the standard error is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The interval around each mean is displayed graphically by the following Means Plot:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	80591.2	3	26863.7	6.23	0.0085
Within groups	51706.8	12	4308.9		
Total (Corr.)	132298.0	15			

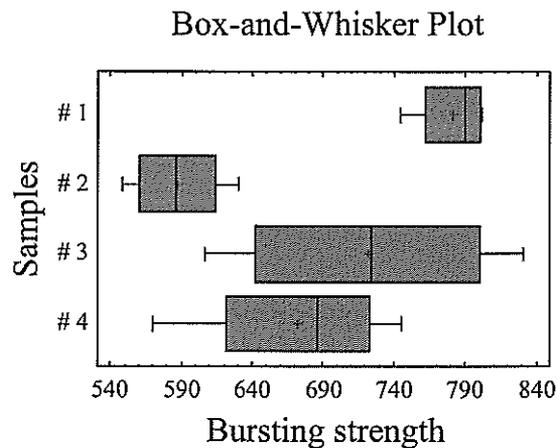
In this ANOVA table, calculated F-ratio is 6.23 and since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	4	13.0
# 2	4	3.5
# 3	4	10.25
# 4	4	7.25

Test statistic = 8.80147 P-Value = 0.0320492

Since the P-value is less than 0.05 in this test, there is a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, a Box-and-Whisker Plot is shown:



The results show that the medians of the sample 2 differs the most from the other medians.

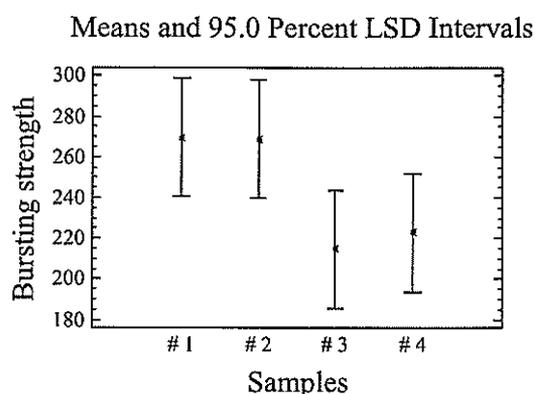
- **Phenolic production**

	Sample 1	Sample 2	Sample 3	Sample 4
	335	257	239	240
	248	197	210	217
	265	316	210	200
	230	306	200	234

Table of Means with 95.0 percent LSD intervals

	Count	Std. error		Lower limit	Upper limit
		Mean	(pooled s)		
# 1	4	269.5	18.855	240.451	298.549
# 2	4	269.0	18.855	239.951	298.049
# 3	4	214.75	18.855	185.701	243.799
# 4	4	222.75	18.855	193.701	251.799
Total	16	244.0			

This table shows as well the mean for each column of data, the standard error of each mean, which is a measure of its sampling variability, and the standard error that is formed by dividing the pooled standard deviation by the square root of the number of observations at each level. The interval around each mean is displayed graphically by the following Means Plot:



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	10329.5	3	3443.17	2.42	0.1166
Within groups	17064.5	12	1422.04		
Total (Corr.)	27394.0	15			

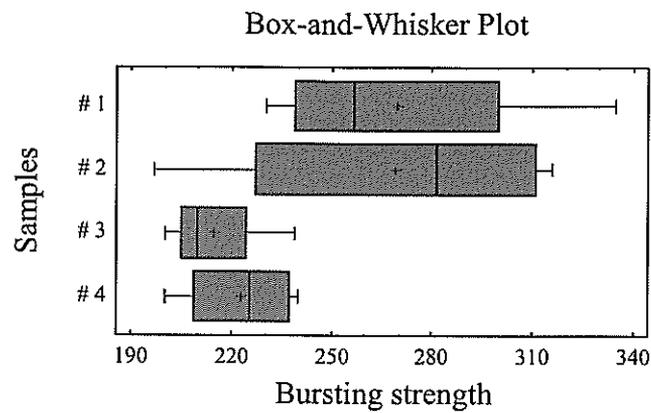
The F-ratio is calculated to be 2.42. Since the P-value of the F-test is greater than 0.05, there is not a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	4	11.75
# 2	4	10.5
# 3	4	5.125
# 4	4	6.625

Test statistic = 5.21571 P-Value = 0.156664

The Kruskal-Wallis test shows that the P-value is greater than 0.05, and thus there is not a statistically significant difference amongst the medians at the 95.0% confidence level. The following Box-and-Whisker Plot is presented to determine which medians are significantly different



The results show that the median of the sample 3 differs the most from the other medians.

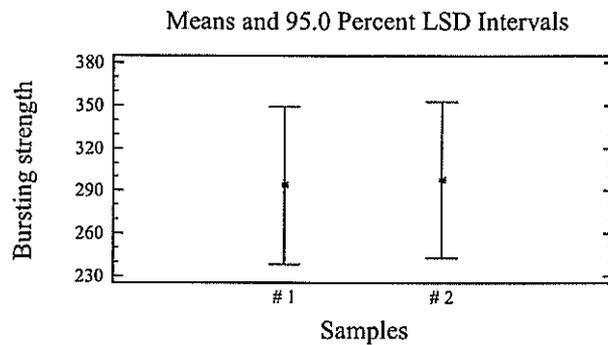
- **Phenolic pure**

	<u>Sample 1</u>	<u>Sample 2</u>
	300	388
	290	200
	280	358
	305	244

Table of Means with 95.0 percent LSD intervals

	Count	Std. error			
		Mean	(pooled s)	Lower limit	Upper limit
# 1	4	293.75	32.0076	238.369	349.131
# 2	4	297.5	32.0076	242.119	352.881
Total	8	295.625			

This table shows again the mean for each column of data, the standard error of each mean, and the standard error. The interval around each mean is displayed graphically by the following Means Plot:



ANOVA Table

Analysis of Variance

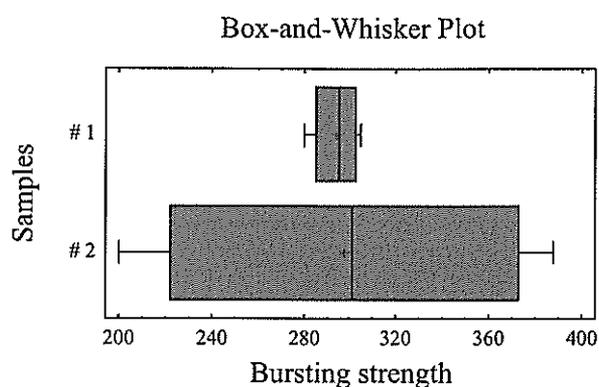
Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	28.125	1	28.125	0.01	0.9367
Within groups	24587.8	6	4097.96		
Total (Corr.)	24615.9	7			

The ANOVA table decomposing the variance of the data into two components: a between-group component and a within-group component calculates the F-ratio to be 0.01. Since the P-value of the F-test is greater than 0.05, there is not a statistically significant difference between the means of the 2 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	4	4.5
# 2	4	4.5
Test statistic = 0.0		P-Value = 1.0

Since the P-value calculated by this test is greater than 0.05, there is not a statistically significant difference amongst the medians at the 95.0% confidence level. To determine which medians are significantly different from which others, the following Box-and-Whisker Plot is presented:



The results show that the median in sample 2 is much bigger then in sample 1.

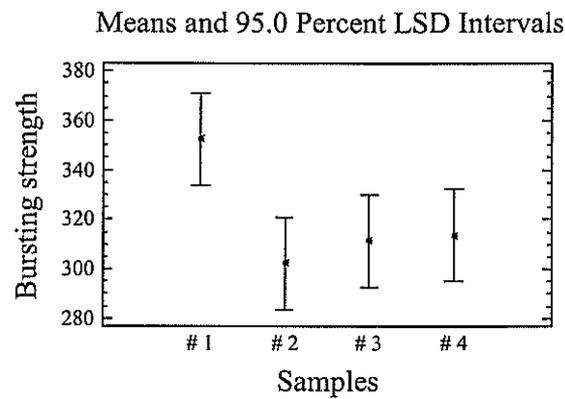
• **Baking paper untreated**

Sample 1	Sample 2	Sample 3	Sample 4
316	321	307	327
326	315	309	336
329	290	351	286
396	273	300	328
395	312	290	291

Table of Means with 95.0 percent LSD intervals

	Count	Std. error			
		Mean	(pooled s)	Lower limit	Upper limit
# 1	5	352.4	12.3705	333.857	370.943
# 2	5	302.2	12.3705	283.657	320.743
# 3	5	311.4	12.3705	292.857	329.943
# 4	5	313.6	12.3705	295.057	332.143
Total	20	319.9			

This table shows the mean for each column of data, as well as the standard error of each mean, which is a measure of its sampling variability. The intervals is displayed graphically as



ANOVA Table

Analysis of Variance

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	7407.4	3	2469.13	3.23	0.0505
Within groups	12242.4	16	765.15		
Total (Corr.)	19649.8	19			

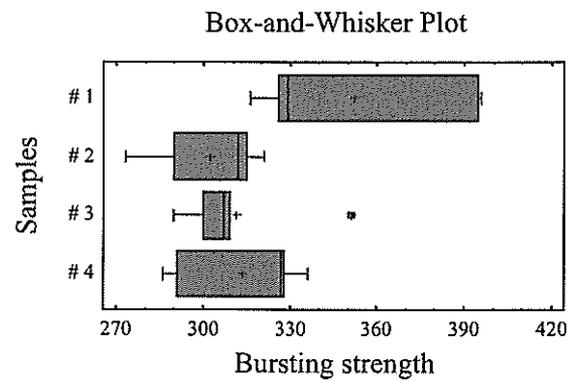
The F-ratio in this ANOVA table equals 3.23 and since the P-value of the F-test is greater than 0.05, there is not a statistically significant difference between the means of the 4 variables at the 95.0% confidence level.

Kruskal-Wallis Test

	Sample Size	Average Rank
# 1	5	15.8
# 2	5	7.1
# 3	5	8.5
# 4	5	10.6

Test statistic = 6.24184 P-Value = 0.100417

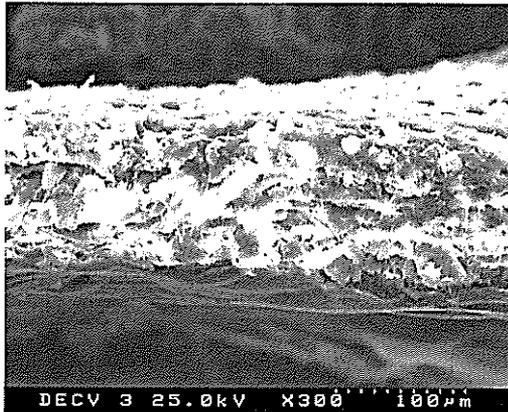
Since the P-value calculated by this test is greater than 0.05, there is not a statistically significant difference amongst the medians at the 95.0% confidence level. The following Box-and-Whisker Plot presents which medians are significantly different from which:



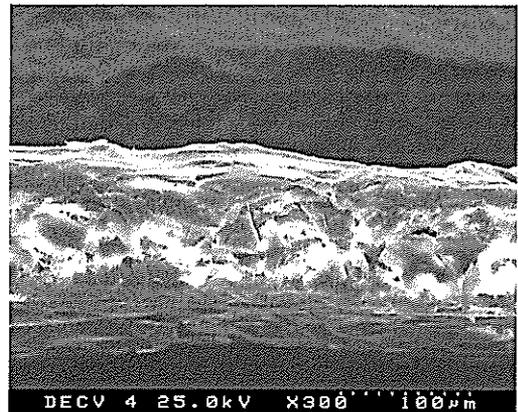
The results show that the median of the sample 1 differs the most from the other medians and has the biggest spreading.

- **Unheated baking paper** Mean value of one set of data: 320
- **Heated baking paper** Mean value of one set of data: 190

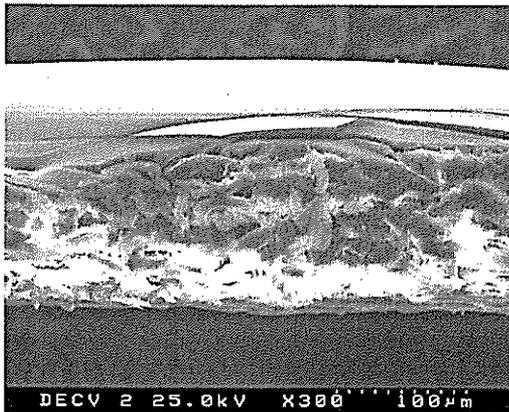
Appendix Q: SEM images of different coating formulations



Surface of backing paper



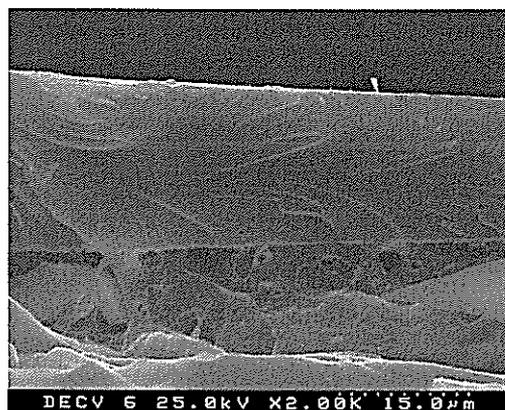
Pure unmodified phenolic resin



Phenolic production formulation



Epoxy production formulation



Modified phenolic resin

Appendix R: The 3M's disc P1500

General facts

A finishing film disc P1500 is produced by "Minnesota Mining and Manufacturing Company" for metal- and woodworking. This aluminium oxide disc constructed on a film backing is resin bonded for heat resistance. The used resin is most probably epoxy resin which needs to be investigated further for detailed confirmation. The used abrasive backing type is a polyester film. The abrasive mineral used in this case is improved aluminium oxide mineral, due to which the disc should last longer and should give nice cuts.

A coating that is applied to the discs to prevent clogging during use is most probably well used zinc stearate [$C_{36}H_{70}O_4Zn$]. Zinc stearate is a dry lubricant added during the size coat application which has a function to reduce any buildup of wood, metal, or paint residue on the sandpaper. This is going to be confirmed by melting point determination and by taking its IR spectrum.

Available as 5 inch and 6 inch discs, white in colour with a Hookit™ II attachment system and a strong film backing. The Hookit™ II attachment system provides longer disc life. The Hookit II attachment system, is the ultimate in re-usable attachment systems. Hookit™ II discs turn the Hook & Loop system upside down by reversing the hooks and the loops. In the Hookit™ II system the patented stems (hooks) are placed on the back of the disc, while the loops are placed on the back up pad. The advantages of the Hookit™ II system are as follows:

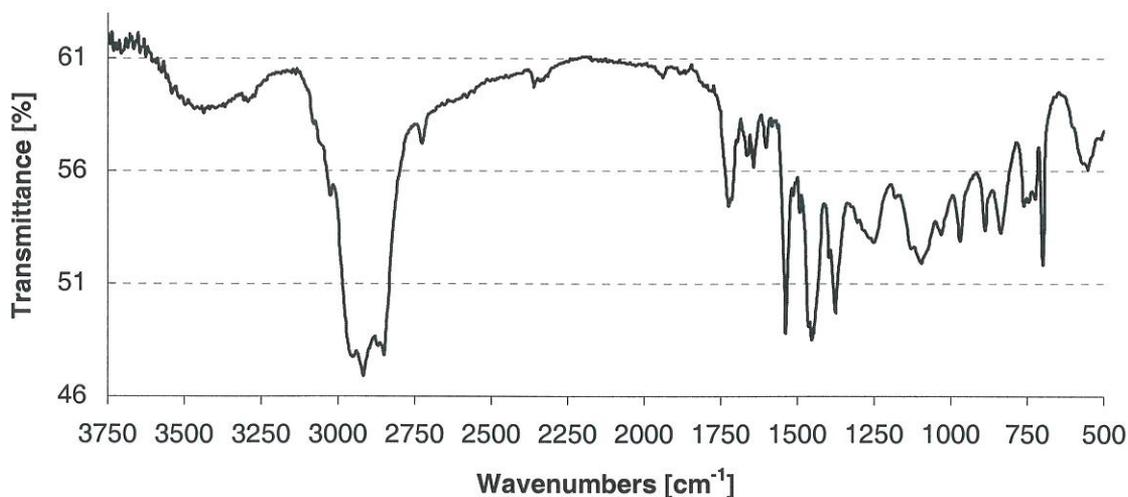
- Patented stems (hooks) are uniformly placed over the face of the disc for finer,
- The film backing of the stems on the back of the disc provides for greater tear resistance, increased durability and improved flexibility of the coated abrasive disc
- The loops on the back up pad provide for improved heat dispersal, more secure attachment, and up to four times the life of a conventional hook and loop back up pad.

Extraction with solvent and its IR spectrum

Procedure: The extraction is done by using a Soxhlet apparatus. A small sample of disk to be extracted is packed into a special “thimble” made of thick filter paper. The thimble is placed in the apparatus, and the whole Soxhlet extractor is placed on top of a well-supported round-bottomed flask containing organic solvent which in this case is toluene. The reflux condenser is placed on top of the Soxhlet extractor, and the flask is heated by using an electrical mantle, up to boiling temperature of the solvent. After about two whole days’ extraction, the material that is extracted from the disk sample is accumulated into the hot solvent. Recovering of the extractor from the solvent is done by evaporating toluene on a rotary evaporator.

Results: The result of the extraction is a sticky gel gummy. It is red due to the presence of the red pigment used for the logo printing on the backing.

IR spectrum of this gummy extract is as the following:



No further analysis than IR is performed on the obtained extract, because it is obvious due to its appearance that the extract is the rest of glue that is used to put different parts of the disk together. The extraction may be performed for too long time, so the result is a complete decomposition of the disk. Another try is given where the disks are washed in toluene at room temperature, but even this gives a complete decomposition of the disks.

IR analysis

Conditions: Surface IR-spectra are performed on a “Bruker IR” spectrometer. Before taking an IR- spectra, a background scanning is first done, after which a sample of the disk is placed on a diamond lens, and 128 scans in the area from 4000-650 cm^{-1} are performed.

IR-spectra using KBr plates are performed on a Mattson 700 Fourier transform infrared spectro-meter using a 2.0 cm^{-1} resolution and 64 or 128 scans.

Results of disks with powder: Results from the IR spectra performed on the disk are presented in Table 1, where due to the complexity that the IR spectra present in the fingerprint region, it is not possible to assign some of their bonds:

Table 1. The results from the original disk

Wavenumbers [cm^{-1}]	Assignment of the peaks
2915 and 2846	Aldehyde C-H stretch
1592	Shifted C=O stretch
1535	$\delta_{\text{in-plane}}$ C-H
1452 and 1396	CH ₂ scissoring

The results obtained from this spectra are compared to the spectra taken of pure zinc stearate. The same group of peaks are present which confirms its presence.

The intensities of the other peaks are too weak to be able to give any further assignment of them. It is because the surface of the disk is mostly covered by the powder of zinc stearete, and this is what has been detected, while everything under this layer is hidden.

An attempt to analysis the next layer that is under the layer of zinc stearete is performed by removing of zinc stearete and taking a new spectrum.

Results of disks without powder: The results from the IR spectra show that zinc stearate powder has not been completely removed from the surface of the disk, and the same peaks are detected as earlier. However, there are a few other peaks present, and their assignments are presented in Table 2, despite some noise that is present on the spectra:

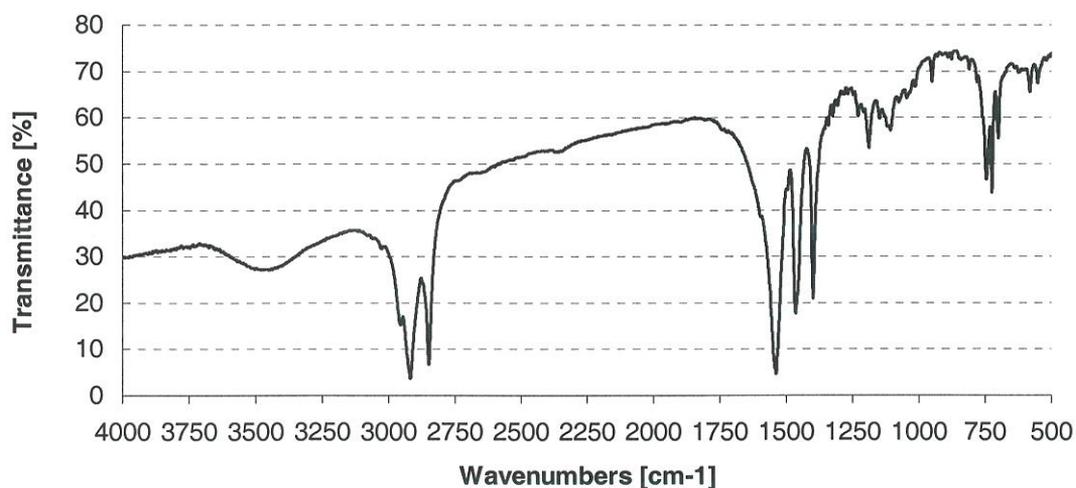


Table 2. The results from the disk without zinc stearate

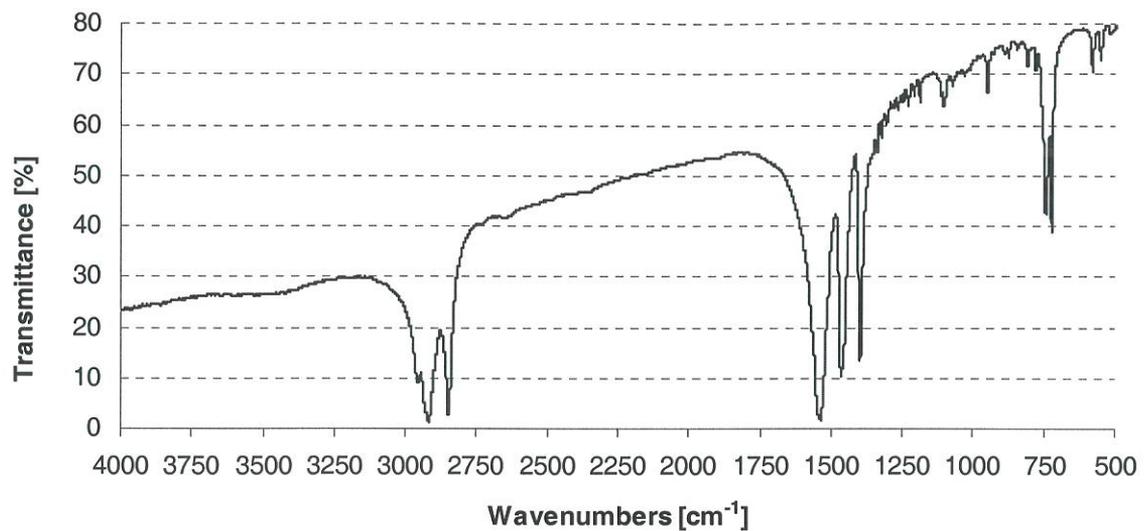
Wavenumbers [cm^{-1}]	Assignment of the peaks
2915 and 2846	Aldehyde stretch from zinc stearate
1722	ν C=O _{ester}
1600	ν C=C _{aromatic rings}
1535, 1452 and 1396	Stretchings C-H from zinc stearate
826	ν C-H _{aromatic ring}

At this point it is not possible to confirm which type of the resin is used.

IR spectrum of removed powder: The powder present on the top layer of the disk is carefully removed and the following IR spectrum is obtained:



The spectrum taken of zinc stearate that INDASA uses for its production is the following:



Looking closely at those two spectra, it is very convenient to say that the spectra are very much alike. The major and most distinguishable peaks are at 1400, 1466, 1544, 2850 and 2925 cm^{-1} , while the existing noise is due to the impurities and dirt that have appeared during the removal of the powder.

These results are confirmed by the melting point determination of the powder. The melting point is determined to be around 130°C, which is the actual theoretical value of zinc stearate, while the remaining impurities have melted at 180°C.