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AN ANALYTICAL VIEW OF PARTICLEBOARD WITH SPECIAL REFERENCE TO PHENOL-FORMALDEHYDE RESINS

LALANTHA A. PANAMGAMA

Supervisor: *Professor A. Pizzi* - Polymer Chemistry

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A Dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg in fulfillment of the requirement for the degree of Master of Science (Chemistry).

Dedication

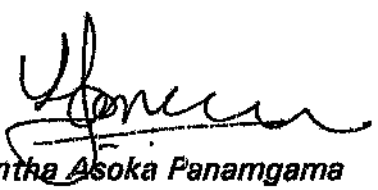
to

my wife *Rasika* and the family

who makes my dreams come true!

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not previously been submitted for any degree or examination in any other university.



Lalantha Asoka Panamgama

14th day of December 1993.

ABSTRACT

This research work represents a new simple concept to correlate the ^{13}C NMR relative peak intensity data of different characteristic chemical groups known or supposed to contribute to Phenol-formaldehyde (PF) resins' strength to its wood adhesive performance.

To explore the practicability of the method, two series of PF resins were prepared with the same final F:P molar ratio but with different syntheses approach. A- series a single step, addition of formaldehyde to phenol with F:P molar ratios 1.1:1, 1.3:1, 1.5:1, 1.8:1, 2.0:1, 2.2:1 and B- series a multi step addition, of formaldehyde to phenol respectively. ^{13}C NMR data and physical characteristics of the resins were recorded. Particleboards were produced from the above set of resins and physical, and chemical properties were evaluated.

At high F:P molar ratio (>2.0) some NMR spectra were not highly resolved due to the very high degree of polymerisation. Generally the particleboards produced with the higher F:P molar ratio resins gave average higher I.B. strength values and boards with low F:P molar ratio resins (<1.8) showed lower resistance to wet tests. Other boards gave more or less the same results for the thickness swell test.

^{13}C NMR spectra indicated that above 1.5 F:P molar ratio less than 100% of the charged formaldehyde content has reacted in the resins. Experimental formaldehyde emission data from the particleboards were very low at microscopic level. A- series resins gave a relatively higher emission values than the B-series.

(I) Potentially interesting functional groups and sites for bond formation in PF resins can be divided into four main categories viz., methylol (Mo), methylene bridges (Me), *ortho* plus *para* free sites in the phenolic ring (o+p), and *meta* plus blocked (already reacted) sites in the phenolic ring (m+B). (II) Methylene ether groups, unreacted free formaldehyde, and methylol groups are potentially important for the formaldehyde emission from the boards.

Due to the different spinning rate for different regions of the ^{13}C NMR spectrum individual peak intensity data cannot be used for direct correlation. Thus peak intensity ratios were considered. Seven possible peak ratio combinations for the I.B. strength tests and three combinations for the formaldehyde emission tests were considered. The group intensity ratios correlated well with the variation in F:P molar ratio. Then regression analysis of the mechanical and chemical properties of the boards with all the possible ^{13}C NMR peak intensity

ratio data was carried out. The correlation coefficients in most cases were above 0.9, which is acceptable.

Mo/Me peak ratio gave a good correlation with I.B. Strength dry test, which is valid up to F:P molar ratio of 2.0:1 only. But the correlation coefficient of Mo group in combination with the same set of groups versus the I.B. strengths were found to be valid for the whole range of molar ratio values. Experimental formaldehyde emission data correlated well with the predicted peak ratio data.

The same method can be extended to correlate the sum of a number of different ^{13}C NMR peak ratios with the properties of the particleboard. The results indicated that simple equations describing the sum of a number of different peak ratios can be presented to evaluate internal bond strength of both dry and wet tested particleboards, as well as formaldehyde emissions levels. Several relevant equations in this respect, were presented. This approach will help researchers in designing and formulating PF resins to meet the performance properties wanted. The results can be achieved in a reasonably short time, and the parameters of the equations can be determined by a commercial desktop computer programme.

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CHAPTER ONE

LITERATURE REVIEW

1.1 INTRODUCTION

Polymers of phenol-formaldehyde in aqueous solutions with sodium hydroxide dominate the market place as adhesives for exterior-grade particleboard and plywood. This dominance stems from their ease in processing, low cost relative to alternative adhesives, minimal pollution from either formaldehyde or solvents (generally water) emission, and good glueline properties. The glueline is waterproof, infusible, and very durable when properly cured in particleboard and plywood manufacture.

Although the technology for formulating phenol-formaldehyde resin adhesives for particleboard and plywood manufacture is well established, it has for the most part been developed empirically. Their structure is far from being completely clear. The polymers derived from the reaction of phenol and formaldehyde differ in one important aspect from other polycondensation products Polyfunctional phenol can form a variety of isomerides with different chain lengths.

Other products derived from polycondensation reactions such as polyamides and polyesters are mixtures of molecular chains of various lengths. However in this case only one structure is possible for a molecule of a certain length. For this reason kinetics and related studies are feasible if one assumes that the growth of a chain proceeds from one molecule to the next in a smooth and regular manner.

Polyfunctional phenol may react with formaldehyde in both the ortho and para positions to the hydroxyl group. Thus condensation products exists positional isomerides for any chain length. This makes kinetics studies extremely difficult and the same time the organic chemistry of the reaction very complex and tedious to unravel.

A PF resin is a mixture of polymer molecules differing in molecular weights, shapes and degree of substitution. The ingredient ratios and parameters of resin formulations are frequently adjusted empirically to tailor the resin's tolerance to the production environment. Little knowledge of molecular structure is available to guide that tailoring process.

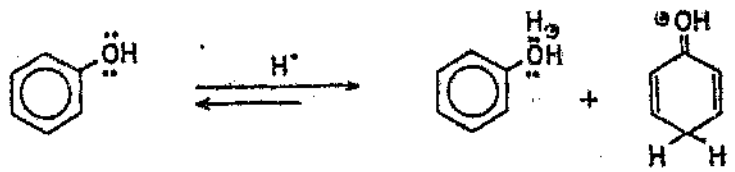
Most analytical tools such as wet chemistry, gas, paper, GPC chromatography and IR spectroscopy are not suitable to detect and quantify these products, during the formation and cure of PF resins. Thus knowledge of phenolic resin chemistry remains an invaluable asset to the adhesive formulator in designing resins with specific properties.

1.2 CHEMISTRY.

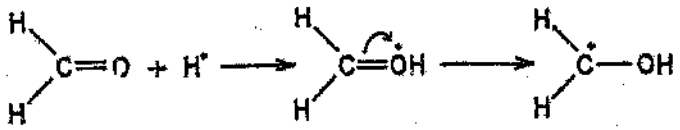
1.2.1 Reaction Mechanisms

Phenols condense initially with formaldehyde in the presence of either acid or alkali to form a methylolphenol or phenolic alcohols, and then dimethylolphenols. The initial attack may be at 2-, 4- or 6- positions. The second stage of the reaction involves the reaction of the methylol groups with other available phenol or with methylolphenol, leading first to the formation of linear polymers [1] and then to the formation of hard-cured, highly branched structures.

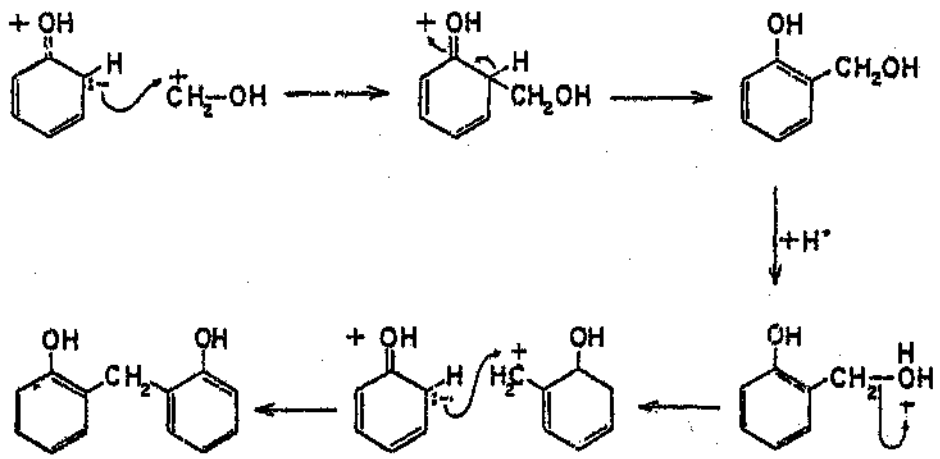
Novolak resins are obtained with acid catalysis with a deficiency of formaldehyde. A novolak resin has no reactive methylol groups in its molecules, and therefore is incapable of condensing with other novolak molecules on heating without hardening agents. To complete resinification, further formaldehyde is added to cross-link the novolak resins. Phenolic resins are consequently less active as nucleophilic centres at an acid pH, due to hydroxyl and ring protonation.



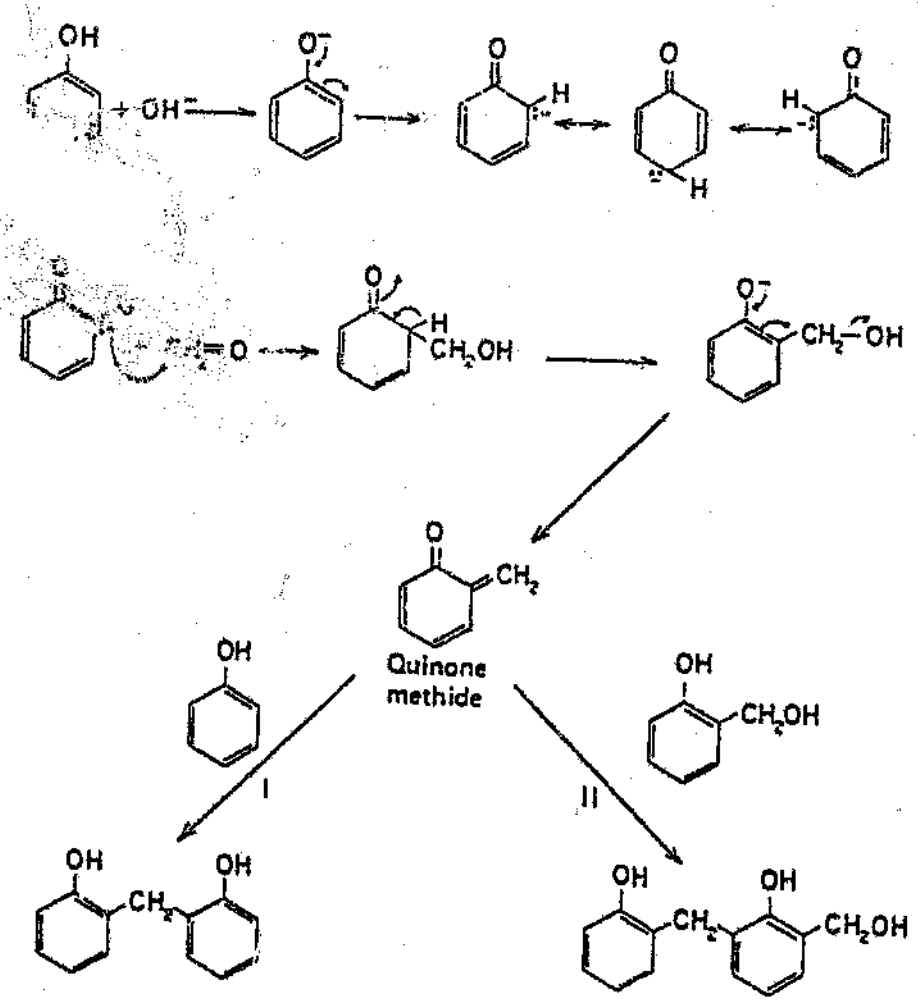
However, the aldehyde is activated by protonation, which compensates for this reduction in potential reactivity. The protonated aldehyde is a more effective electrophile.



The substitution reaction proceeds slowly and condensation follows as a result of further protonation and the creation of a benzylcarbonium ion which acts as a nucleophile.



Resols are obtained as a result of alkaline catalysis and an excess of formaldehyde. A resol molecule contains reactive methylol groups. Heating causes the reactive resol molecules to condense to form large molecules, without the addition of a hardener. The function of phenols as nucleo-philes is strengthened by the ionization of phenol, without affecting the acdivity of the aldehyde.



Phenolic nuclei can be linked not only by simple methylene bridges, but also by methylene ether bridges. The latter generally revert to methylene bridges if heated during curing, with elimination of formaldehyde.

The difference between acid-catalysed and base catalysed processes is (1) in the rate of aldehyde attack on the phenol, (2) in the subsequent condensation of the phenolic alcohols, and to some extent, (3) in the nature of the condensation reaction. With acid catalysis, phenolic alcohol formation is relatively slow. Therefore, this is the step that determines the rate of the total reaction. The condensation of phenolic alcohols and phenol forming compounds of the dihydroxydi-phenylmethane type is instead rapid. The latter are therefore predominant intermediate in novolak resins.

Novolaks are mixtures of isomeric polynuclear phenols of various chain lengths with an average of five to six phenolic nuclei per molecule. They contain no reactive methyl-ol groups and consequently cross-link and harden to form infusible and insoluble resins only when mixed with compounds that can release formaldehyde and form methylene bridges (such as paraformaldehyde or hexamethylenetetramine). In the condensation of phenols and formaldehyde using basic catalysts, the initial substitution (i.e., the formaldehyde attack on the phenol) is faster than the subsequent condensation reaction. Consequently, phenolic alcohols

are initially are predominant intermediate. These phenolic alcohols, which contain reactive methylol groups, condense with either methylol groups to form ether links, or more commonly, with reactive positions in the phenolic ring (ortho or para to the hydroxyl groups) to form methylene bridges. In both cases water is eliminated.

Mildly condensed liquid resols, which are the more important of the two types of phenolic resins in the formation of wood adhesives, have an average of less than two phenolic nuclei in the molecule. The solid resols average three to four phenolic nuclei but with a wider distribution of molecular size.

Heating or acidification of these resins causes cross-linking through uncondensed phenolic alcohol groups, and possibly also through reaction of formaldehyde liberated by the breakdown of the ether links.

As with novolaks, the methylolphenols formed condense with more phenols to form the methylene-bridged polyphenols. The latter however, quickly react in an alkaline system with more formaldehyde to produce methylol derivatives of the polyphenols. In addition to this method of growth in molecular size, methylol groups may intereact with one another, liberating water and forming dimethylene-ether links ($-CH_2-O-CH_2-$). This is particularly evident if the ratio of formalde-hyde to phenol

is high. The average molecular weight of the resins obtained by acid condensation of phenol and formalde-hyde decreases hyperbolically from over 1000 to 200, with increase of the molar ratio of phenol to formaldehyde from 1.25:1 to 10:1 (fig. 1.1).

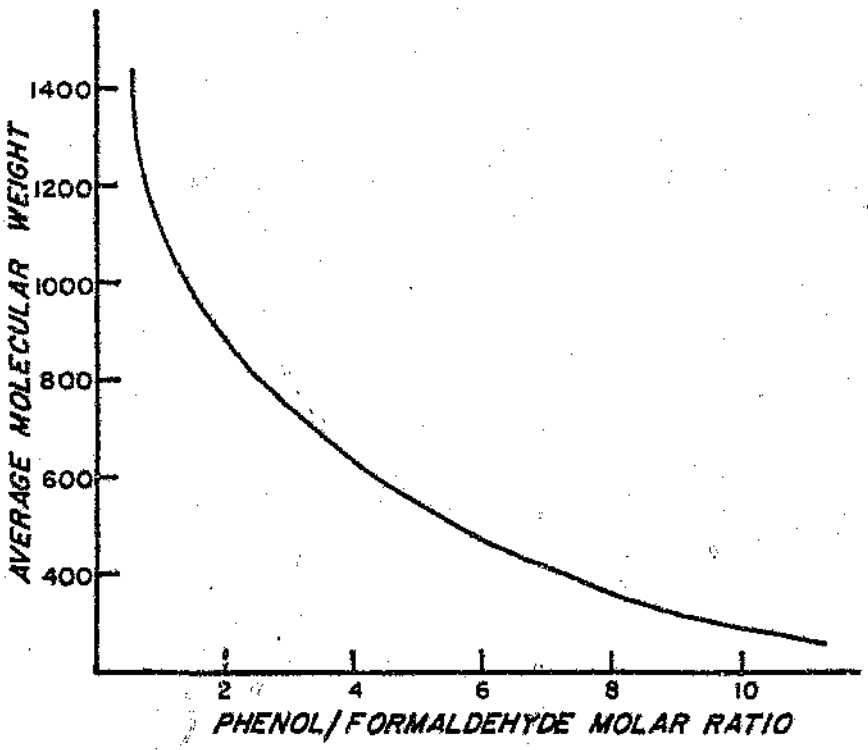
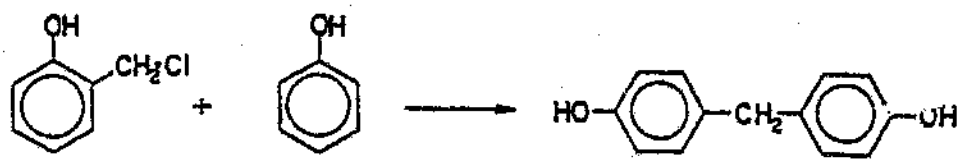


Fig. 1.1. Average molecular weight of PF resins as a function of Phenol/Formaldehyde molar ratio.

1.1.2 CATALYSIS USED IN THE PF RESIN CHEMISTRY

(a) Acid Catalysis

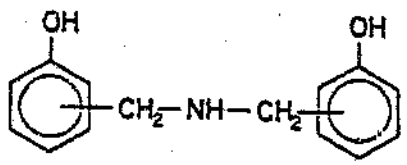
Condensation must be given to the possibility of direct intervention by the catalyst in the reaction. Hydrochloric acid is the most interesting case of acid catalyst. When the phenol-formaldehyde reaction is catalyst by hydrochloric acid, two mechanisms possibly come into operation. One reaction route passes through the formation of bischloromethyl ether (Cl-CH_2-O-CH_2-Cl) and the other route via the formation of a chloromethyl alcohol (Cl-CH2-Cl) as the intermediate [2,3,4]. The second route appears to be the possible one. Both hypoth-eses agree that chloro-methlyalphenols are the principal intermediate. The chloro-methlyalphenols have been prepared and isolated by various means. They are highly reactive compounds which, with phenols, form dihydroxydiphenylmethanes and complex methylene-linked multiring polyphenols. Reaction is highly selective and takes place in the para position.

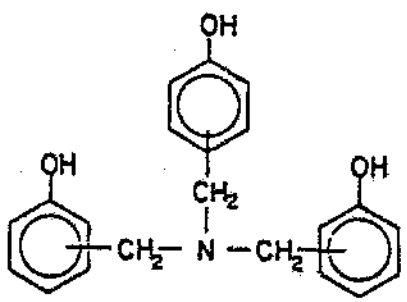


(b) Alkaline Catalysis

Different mechanisms of alkaline catalysis have been suggested according to the alkali used. In the case where caustic soda is used as the catalyst, the type of mechanism which seems the most likely is that which involves the formation of a chelate ring [5]. The chelating mechanism may initially cause the formation of a sodium-formaldehyde complex or of a formaldehyde-sodium phenate complex.

When ammonia is used as a catalyst, the resins formed are very different in some of their characteristics from other alkali-catalysed phenol formaldehyde resins. The reaction mechanism appears to be quite different to that of sodium hydroxide catalysed resins. An obvious deduction is that intermediates containing nitrogen are formed. Several such intermediates have been isolated from ammonium-catalysed phenol-formaldehyde reactions by various researchers [6-8]. Similar types of intermediates are formed when amines or hexamethylenetetramine are used instead of ammonia. In the case of ammonia, the main intermediates are dihydroxy-benzylamines and trihydroxybenzylamines.





These intermediates contain nitrogen and have polybenzylamine chains. They react further with more phenol, causing the splitting and elimination of the nitrogen as ammonia or amines, and producing nitrogen-free resins. This, however requires a considerable excess of phenol and a high temperature. With phenol-hexamethylenetetramine resins of molar ratio 3:1, the nitrogen content of the resin cannot be reduced to less than 7% when heated at 210°C. When the ratio is increased to 7:1, the nitrogen content on heating at 210°C can be reduced to less than 1%.

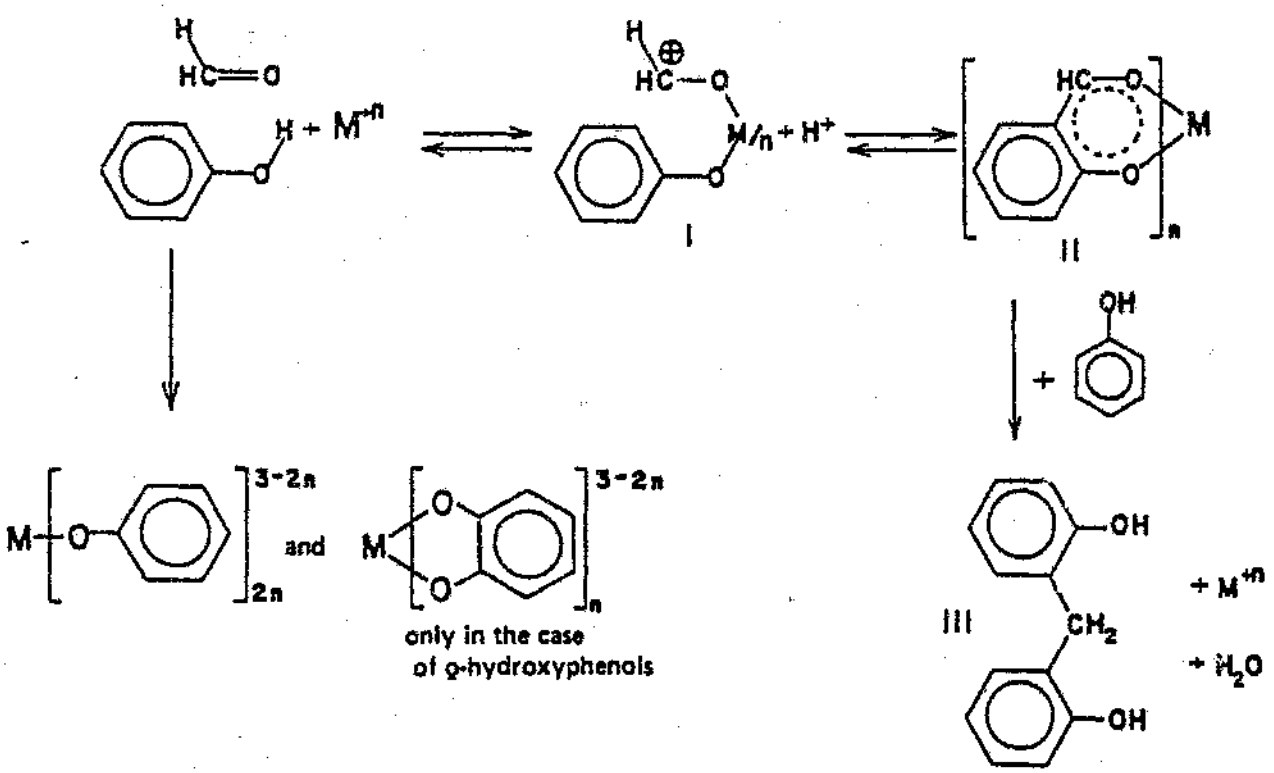
Ammonia-, amine-, and amide-catalysed phenolic resins are characterized by greater insolubility in water than that of sodium hydroxide-catalyst phenolic resins. The more ammonia used, the higher the molecular weight and melting point which are obtained without cross-linking. This is probably due to the inhibiting effect of the nitrogen- carrying groups (i.e., $-CH_2-NH-CH_3$ or $--CH_2-NH_2$), which is caused by their slow rate of subsequent condensation and loss of ammonia. Ammonia, amines, and amides (particularly dimethylformamide) are sometimes used as accelerators during the curing of phenolic adhesives for wood products.

(c) Metallic ion catalysis

Bender [9] shows that resins made under special conditions, where a high proportion of ortho-ortho links are formed in the phenol-methylene

chains, can be cured by hexamethylenetetramine at a much higher rate than resins made with conventional acid or alkali catalysis. This involves condensation within the pH range 4-7 by oxides or hydroxides of alkaline earth metals such as zinc, magnesium, and aluminium.

Normal condensation yields roughly equal quantities of para-para and ortho-para links, but uncured resins produced by metal ions catalysis yield approximately one ortho-para to two ortho-ortho links. They ascribes faster curing rates of phenolic resins prepared by metallic ions catalysis to the higher proportion of the free higher reactive para positions available for further reaction during the curing of the resin.



The rate of metal exchange in solution [10,11] and the instability of the complex formed determine the accelerating or inhibiting effect of the metal in the reaction of phenol with formaldehyde. The more stable the complex II is, the slower the reaction proceeds to the formation of resin III. A completely stable complex II should stop the reaction proceeding to resin III. If complex II is not stable the reaction will proceed to form phenol-formaldehyde resins of type II. The rate of reaction is directly proportional to the instability, or the rate of metal exchange in solution of complex II.

The metal catalyst does not change its valence, but interact with molecules or ions containing electron donor groups, and accelerates reactions like hydrogen ions do [12].

The effect of the metal is stronger than that of hydrogen ions, because of higher charge and greater covalency, since its interaction with donor groups is much greater [12]. This is important, because in the preparation of phenol-formaldehyde adhesives for wood, very high acid pH values cannot be used because they cause wood deterioration. Metal ion catalysts have the same catalytic effect on the preparation and setting of the of the resins at higher pH, which is shown by a higher concentration of hydrogen ions and therefore lower pH values.

This allow phenolic resin adhesives to set in milder acid conditions, with neither extension of the setting nor any wood deterioration. The gel times for formaldehyde obtained for resorcinol and catechol indicate that the metal catalysts effect is probably valid for most phenols with a free ortho position to the hydroxy group [10]. Most bivalent metallic ions accelerate phenol-formaldehyde reactions.

An extent of this effect is directly proportional to the quantity of metallic ion prese... [10]. First, bivalent metals do not inhibit the reaction, as the complexes they form are unstable and their rate of exchange in solution is high. Second, they accelerate the reaction in a manner similar to that of hydrogen ions, although it is even faster, due to their stronger charge and greater covalency. The formation of the identified stable complexes of type II and V slows down or inhibits the reaction from proceeding to the formation of phenol-formaldehyde resins, when trivalent metals are used.

It is consequently better to express the accelerating or retarding effect of the metal ions in the order of the rate at which they exchange in solution, rather than in the rate of their stability [10].

The metal complexes stability does not bear any relationship to the gel times obtained for phenol-formaldehyde condensations. The extent of

the metal ions accelerating effect is;

$Pb^{+2}, Zn^{+2}, Cd^{+2}, Ni^{+2} > Mn^{+2}, Mg^{+2}, Cu^{+2}, Co^{+2}, > Mn^{+3}, Fe^{+3} >> Be^{+2}, Al^{+3} > Cr^{+3}, Co^{+2}$

However, the most important conclusion to be drawn is that the acceleration effect is indeed present in both the manufacturing of the phenol-formaldehyde resin and its curing. Therefore the fast rate of curing of high-ortho phenolic resins can be only partially ascribed to the high proportion of para positions available. The other reason for the fast rate of curing is that the metallic ion catalyst is still present, and free to act, in the resin at the time of curing. In such a resin a considerable number of ortho positions (specially of methylol groups in ortho positions to the phenolic hydroxyls) are still available for reaction, and capable of complexing. The concept is also suggested in Fraser's articles on his discovery of the accelerating effect in the condensation of dihydroxydiphenyl methane, or phenolic "dimers", with formaldehyde.

The accelerating effect is therefore a result of the stronger protonation effect of the formaldehyde, which causes a much faster attack of the aldehyde onto the phenol. The initial attack HCHO attack determines the rate of acid-catalysed phenolic reactions as it is the slower step. The

retarding effect is due to the effective blocking of the methylol group by the metal. Subsequent kinetic studies clearly confirm this. They also show that the trivalent metallic ions retarders accelerate the initial formaldehyde attack [13]. The accelerating effect of the metal ions is also present throughout the whole pH range, but is particularly evident in the range 2.5-7.0.

The decrease in the effect at lower and higher pH values can be ascribed to the "drowning" of the metal ion effect by the increased reactivity of the phenol-formaldehyde system. At lower pH values, the hydrogen ions are very abundant and consequently the metal ions contribute only minimally to the protonation of the formaldehyde and the acceleration of the reaction. At higher values the reaction of the phenol-formaldehyde system depends on formaldehyde protonation, and consequently the metallic ions have only a minimal bearing on the rate of the reaction.

The anion also influences the effectiveness of the metal as an accelerator of the reaction. For example, the following scale represents the decreasing accelerating effect for Zn^{+2} anions:

$$Zn(CH_3COO)_2 > ZnCl_2 + CH3COONa > ZnCl_2$$

The anion effect can be explained in terms of the relative affinities of the metal for the anion used and the complex formed. It should therefore be more difficult for a strong acid to release Zn^{+2} than a weak acid. A stronger acid salt slow down considerably the rate of exchange in solution of the metallic ion.

Another interesting way of producing high-ortho phenolic resins [14] without using a metallic ion catalyst is by reacting formaldehyde gas onto crystalline solid phenol with phenol with temperature between 20 and 40°C in the presence of naphthalene.

1.3 REACTION KINETICS.

Various researchers have investigated the reaction of phenols with formaldehyde and the results of earlier investigations have been controversial. Once all the methylol phenols had been synthesised it became possible to examine the individual steps in detail. This investigation was done by Freeman and lewis [15] which is considered to be one of the most comprehensive and detailed work ever carried out.

They reacted phenol, saligenin, para-hydroxybenzyl alcohol, or 2,4- or 2,6-dihydroxymethylphenol at 30°C with sufficient formaldehyde (as formalin) to bring about complete substitution, in the presence of one mole of caustic soda per mole of phenol. The compounds obtained

included all five methylate phenols, as well as tetramethyloldihydroxy-diphenylmethane towards the end of the reaction. The reactions that occurred are summarised in the following diagram, which shows the symbols used for the individual rate constants.

From the steady state, the Freeman and Lewis drew the following conclusions:

1. In phenol, the para position is slightly greater affinity for formaldehyde than the *ortho* position (i.e., 6.2:5.25). Nevertheless because two *ortho*

positions are available, saligenin is produced 1.7 times faster than *para*-isomeride.

2. The introduction of a methylol group decreases the reactivity of the remaining nuclear positions towards Formaldehyde. The decrease is bigger than one excepts. Thus para-hydroxybenzylalcohol is 50% less reactive than phenol (7.5:16.7) even though it has two-thirds the number of positions still available for reaction.

3. The introduction of a methylol group into the ortho position causes little deactivation. Therefore, saligenin is twice as reactive as para-hydroxybenzyl alcohol, and almost as reactive as phenol, even though it has one less position available. Similarly, 2,4 dihydroxymethylphenol.

Second order reaction rate constants for the base catalyst reaction of phenol with formaldehyde.

Rate constant	$k \times 10^{-5}$ litres $mole^{-1}$ sec^{-1}
ko	6.2
k'_o	10.5
k_1	7.5
k'_1	7.3

k''_1	8.7
k_2	9.1
k'_2	41.7

The relative reactivities of the ortho and para positions of phenol are 1.4 and 1.7, respectively, and are relative to a value of the ortho position of p-hydroxybenzyl alcohol of 1.0. Saligenin ortho and para positions have the relative reactivities of 2.3 and 2.0. The 2,4-dimethylolphenol ortho position has a value of 2.4. The 2,6-dimethylolphenol para position has a value of 11.1.

1.4 HARDENING OF PF RESINS.

When resols or A-stage resins made from phenols with three reactive positions, are heated to temperatures above 100°C, they become more viscous and eventually rubbery. They are then in the resitol or B- stage and they are insoluble in the usual solvents. However they will swell in acetone and will form flow under heat and pressure. Further heating causes further hardening of the resins until they reach the resite or C-stage when they are insoluble and infusible.

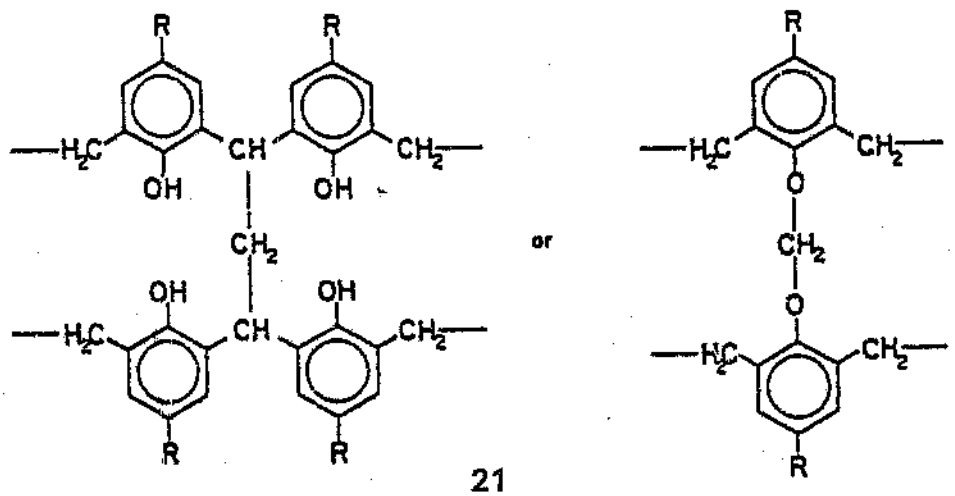
This change is accompanied by a change in structure from the low molecular weight mono- and polyalcohols of the A- stage, to the partly linked polymers of the B- stage. They finally change to the branched and cross-linked three-dimensional networks characteristic of the C- stage. Novolaks also pass through the same sequence of changes if heated with methylene-supplying agents under alkaline conditions.

Branched-chain novolaks are more reactive than linear novolaks, because of the higher proportion of monosubstituted phenol in branched structure. Branched chain novolaks cure faster than linear novolaks. The

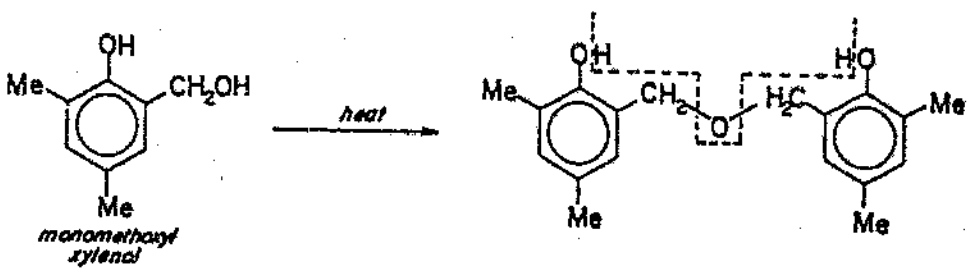
same changes can be obtained by adding strong acids to low molecular weight liquid resols. The acid-initiated condensation of the methylol groups with the phenolic nuclei may be exothermic enough to reach tempera-tures high enough to complete the hardening. With sufficient acid catalysis, resols will harden, if they are in thin films, at room temperature. Hardening mechanism of phenol-formalde-hyde resins [8,16,17] takes place in two stages. In the first stage of hardening ether-linked polymers are formed, with loss of water, by the condensation of two adjacent methylol groups.

The secondary stage of hardening at higher temperatures is accompanied by a change of colour from pale yellow-red to dark brown. This takes place either in air or in inert atmosphere. There is a reduction of solubility in aqueous alkali, chloform, and benzene. The products at first become partially soluble. Only the soluble portion contains either links.

But it seems that several different reactions occurs at the same time. If the ether links break down to methylene bridges, one molecule of formaldehyde should be set from each link. Since only about half of this is observed, the Zinke group concluded that the formaldehyde reacts with the remaining reactive positions on the phenolic nuclei, if any are still present; or if there are none, with the methylene bridges or the phenolic hydroxyl groups. This gives rise to the following structure:

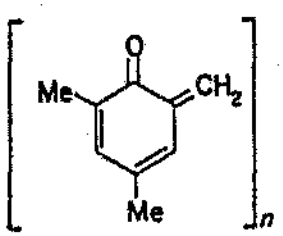


Hultzsch [17,18] disagrees with Zinke's theory that liberated formaldehyde causes cross-linking by condensing with methylene bridges. He found that the dihydroxydiphenlmethanes did not react with formaldehyde at 200-240°C. He also found that monomethylolxylenols, which have no free reactive positions, resinify on heating with a loss of water and formaldehyde. This initial product obtained on heating at 130-170°C is an ether, namely



monomethoxyl xylenol

On heating the alcohol (or the ether) further at 170-200°C, the products obtained are a small amount of the normal dihydroxydiariarylmethene and a considerable quantity of a polymeric quinone, formed by loss of water from the ether shown above and further polymerisation.



polymeric quinone methide

The polymeric quinone methide, which has a melting point of 200°C has an average degree of polymerisation of between 2 and 3. The polymeric quinone methide resinifies at 220°C and turns black without

liberating water or formaldehyde. Another produce of the hardening of the ether is the dihydroxy diarylethane. It is likely that hydrogenation and dehydrogenation at these reactions occur at fairly high temperature, (~ 200°C) simultaneously converting the polymeric and monomeric quinone methides to diphenylethanes, aldehydes, alkylphenols, and undistilliable resins [18].

The fully hardened resins are rigid three-dimensional structures in which cross-linking is random. There is no evidence of crystallites in the network, but it presumed that there are relatively large holes at certain points throughout the mass [19]. These forms points of weakness because all the cross-links theoretically possible have formed.

These points of weakness account for the fact the tensile strength of the hardened resin is very much less than in theory. Several researchers have concluded from these data that phenol-methylene chains are very irregular, and that they have only a few cross-links. During the harden process, the resin molecule is first a simple chain which grows slowly. Other chains subsequently condense onto it to form branches [20]. This process continues until separate molecule begin to entangle and form a gel. As the hardening continues, there is further growth and entanglement. The resin molecule become immobilised and therefore insoluble and infusible.

When the resin has hardened, the impact strength and flexural strength of phenolic resins increases with the number of methylene groups between the phenol nuclei. When the number of methylene groups is increased from 1 to 10, a more flexible cross-linked network is obtained [21]. The hardness of pheno-lic resins also decreases as the length of the polymethylene chain in the phenol increases. Several authors believe that the hardened resins first passes through two phases: first, the

formation of a highly condensed macromelecular gel structure, the second, a viscous liquid phase of lower molecular weight, or better continuous isogel structure, in the later, the cavities of a continuous net- or spongelike skeleton have filled with a viscous liquid condensate [22].

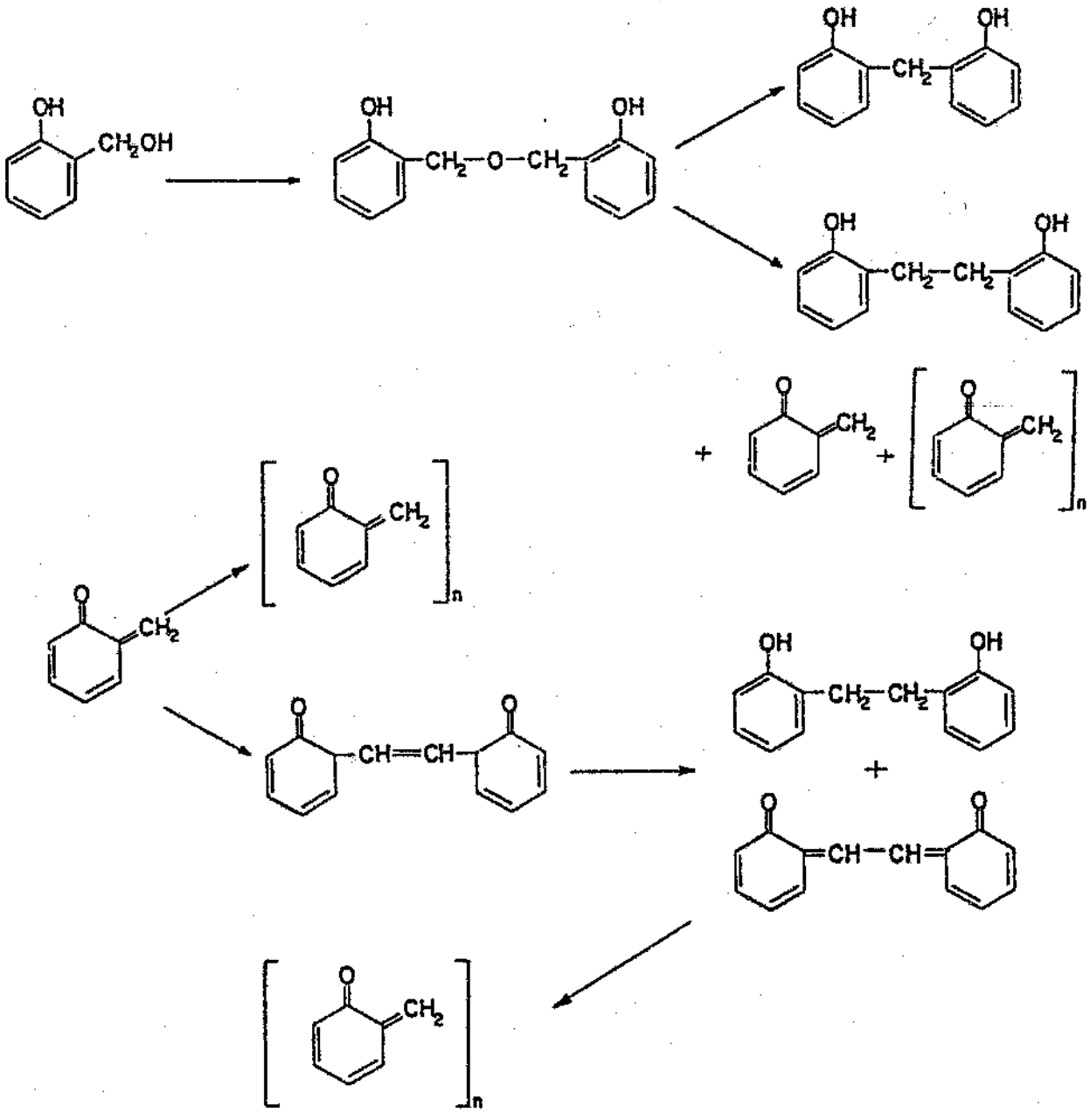


Fig 1.2: Schematic representation of Hultzsch's ideas on hardening of phenolic resins.

1.5 PHYSICAL PROPERTIES OF PHENOL-FORMALDEHYDE RESINS

Hardened phenol-formaldehyde resins have a specific gravity of in the range 1.2-1.3, a refractive index of 1.6, and a specific-heat of 0.5. They are typically brown in colour, and novolaks are lighter than resols. Resols are dark yellow, orange reddish, or brownish, even when made with pure raw materials. However, if the alkali is neutralised, resols become almost colourless. The best results were obtained with citric, lactic, and phosphoric acids. Pale-coloured, hardened resins can be prepared with them [23].

Phenolic resins are relatively stable up to about 200°C, although oxidation degradation takes the form of attack at the methylene bridges to produce substituted dihydroxy-benzophenones [24]. Above this temperature charring is more rapid. At about 400°C decomposition is rapid, yielding phenols and aldehydes, leaving a cokelike residue.

In the A stage, simple phenol-formaldehyde resins are readily soluble in common organic solvents like alcohols, esters, ketone, phenols and some ethers, and insoluble in hydrocarbons and oils. As a class, resols tend to be more soluble in alcohols and water, and novolaks tent to be more soluble in hydrocarbons. In the early stages of condensation, resols are often soluble in water, owing to the presence of methylol-phenols, specially polyalcohols. This is more pronounced with resols that are

derived from phenol. Cresilic resols are less soluble, and xylenolic resols almost insoluble in water. The solubility of A- stage resins in dilute aqueous sodium hydroxide or in mixture of water and alcohols follows the same trend.

Solubility in alcohols and insolubility in hydrocarbons appear to go together. The alcohol and water solubility can be reduced only by using acetaldehyde, or other aldehydes in the place of formaldehyde, and by introducing hydrocarbon chains, particularly in the ortho or para positions in the aromatic ring. B- stage resins are soluble in only a few solvents, such as boiling phenols, and acetone, aqueous sodium hydroxide, and deca- and tetrahydronaphtalenes.

Resins in the hardened or C- stage are very resistant to most chemical reagents. They are unaffected by all ordinary organic solvents and water, although a few percent of water may be observed in filled material, mainly by the filler, thus causing slight swelling. The C-stage resins dissolve slowly in boiling phenols such as naphtols. Resins from the simplest phenols can also be broken down and dissolved by hot, strong alkali solutions.

Simple phenol-formaldehyde resins are readily attacked by sodium hydroxide. However, cresol-formaldehyde and specially xylenol-

formaldehyde resins are much less susceptible to attack. Resins are often more resistant to strong alkaline solutions (i.e., 15-20%) than to dilute solutions (i.e., 5%). The filler has a considerable influence on the chemical resistance of the resins. Inert mineral fillers have a better resistance than cellulosic fillers. C- stage resins are resistant to most acids, except sulphuric acid stronger than 50%, formic acid, and oxidising acids such as nitric and chromic acids.

The insolubility of hardened resins in acetone is used to test the degree of cure of the resins. The curing temperature influences the amount of matter which is insoluble in acetone, after prolonged heating. [25]. The higher the hardening temperature, the lower the amount of acetone extractive. The mechanical properties of hardened phenol-formaldehyde resins are generally influenced by the moisture content. This applies even more to resins containing fillers, plasticizer, and other ingredients. The rate of water absorption decreases with time, but thick samples may not reach an equilibrium even after several days.

Therefore, in measuring the mechanical properties of resins, it is necessary to condition the test pieces under carefully controlled conditions (temperature, humidity) etc., prior to make the test. In many cases the mechanical properties of hardened resins are largely dependent on the type and orientation of the filler. This applies particularly to water

absorption, tensile strength, and impact strength etc.. It also applies to shear strength, with the condition that in the plane of the laminations the shear strength depends on the adhesion between the laminae of sheet material. The properties of the resin are more important in determining the compression strength than those of the filer.

1.6 CHEMISTRY AND TECHNOLOGY OF APPLICATION OF PHENOLIC RESIN ADHESIVES FOR WOOD

For the particleboard and plywood manufacture a resole type resin is used. For the production of resin phenol and formaldehyde (containing 37-40% formaldehyde) or paraformal-dehyde are charged into a reactor in molar proportion between 1:1.1 and 1:2.2 and mechanical stirring is started. The stainless reactor is normally equipped with an anchor type or turbine-blade agitator, a reflux condenser, vacuum equipment, heating and cooling facilities. An alkaline catalyst such as sodium hydroxide, is added to the mixture and then heated to 80-100°C. By applying vacuum or by cooling water in the reactor jacket the reaction temperature is kept under 100°C.

The reaction time varies between 1 and 8 hrs. This is govern by several factors such as pH of the reaction mixture, formaldehyde/phenol mole

ratio, temperature of the reaction mixture, presence or absence of retarding agents (alcohols etc.) Dehydration temperatures are kept below 105°C since resols can gel in the reactor.

After the resin has reached to the desired degree of advancement it is discharged. This can be calculated by the measurement of the gel time of the resin at 100°C in a water bath or on a 150°C hot plate. Measurement of the turbidity point, that is precipitating the resin in water or solutions is another method of evaluation.

Resins which are water soluble and which have a low molecular weight are finished at as low a temperature as possible (40-60) °C. It is important that the liquid, water-soluble resols retain their ability to mix with water easily since when they are used as particleboard adhesives, they are diluted further with water before they are sprayed onto the wood chips. The resols based on phenol are considered to be stable for 3-9 months. Properties of a typical resin are a viscosity of 100-200 cp at 20°C, a solids content of 60%. Novolak resins are less interest in the manufacture for wood products. The novolaks used in the wood industry are phenol-formaldehyde resols that have been transformed into novolaks by blocking the methylol groups present with resorcinol, or resorcinol-formaldehyde novolaks. The addition of paraformaldehyde as a hardener for the curing is needed for both cases. They are prepared in

the same way as for resols at acid or alkaline (or alternatively, both) pH values. A pH of about 4 is the point of lowest reactivity of for all phenolic resins. The effect of the pH and the phenol/formaldehyde molar ratio on the rate of polymerisation of phenolic resols is shown in figure 1.3.

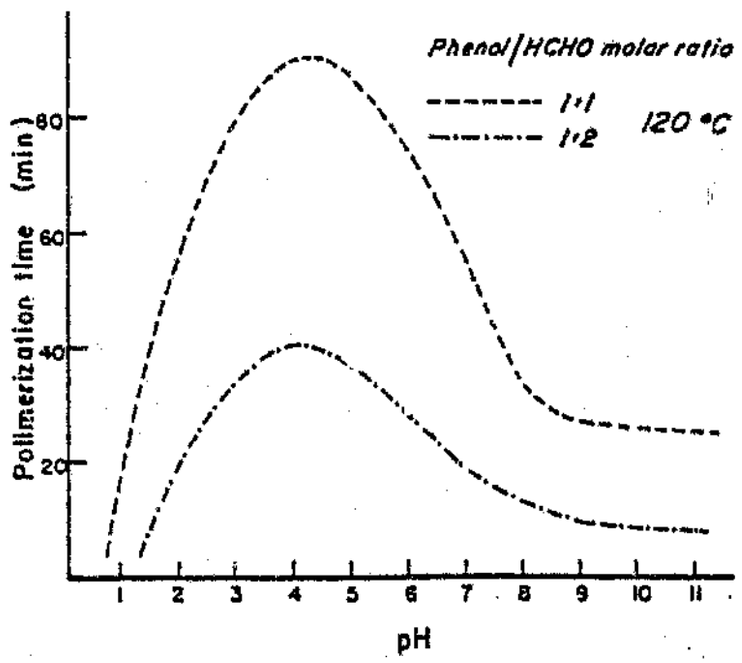


Figure 1.3: Rate of polymerisation as a function of pH for phenolic resols of different molar ratios at 120°C

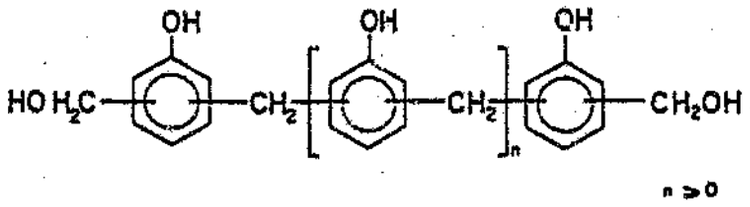
1.7 PARTICLEBOARD AND PLYWOOD ADHESIVES AND THE FACTORS REGULATING THEIR APPLICATION

The superior water resistance property provided by the Phenolic resins able them to used as binders for exterior-grade plywood and

particleboard manufacture. In the manufacture of plywood, the phenolic resin adhesives are usually applied to the wood veneers by roller or extrusion coating. The coated veneer is then cross-grained, stacked, and cured in a multidelight press for 5-10 min at 120-130°C and at 12-16 kg cm^{-2}.

In the manufacture of particleboard, the phenolic resin adhesives are sprayed onto the wood chips, or sprayed plus spread by continuous blenders. The glued wood chips are formed in a mat and then pressed for 4-7 minutes, according to the thickness and moisture content, at 170-195°C and 25-35 $kgcm^{-2}$.

The only type of phenolic resins commercially used for this application are resole-type resins, which have the following structure.



$n \geq 0$

They are hardened by heating after the addition of small amounts of wax emulsion and insecticide solution in the case of particleboard, and of vegetable or mineral fillers tackifiers in the case of plywood. Accelerators are often added in both types of glue mixes. There are aminic or amidic (e.g., dimethylformamide) in the case of particleboard and metallic salt catalysis (e.g., zinc acetate), in the case of plywood. Other accelerators are also some times used. The pH of these resins varies between 10 and 13.5 and generally between 12 to 12.5.

In dealing with wood-related factors that affect glue bonds, it is important to remember that adhesion is at least 95% chemical in nature. The mechanical aspects of bond formation (such as keying cured adhesive solids into the wood surface) contribute negligibly to the bond strength or wood failure. The main chemical forces in thermosetting resin adhesion are primary valence bonds, covalent bonds, and hydrogen bonds, plus secondary forces such as van der Waals' and London's forces, and any other types of electrostatic, dipolar, and associative forces. It is therefore essential that the resin contain significant number of functional groups and that the resin contain significant numbers of reactive sites to enable the resin to bond. Any factors that limit resin functionality or block reactive sites on the wood structure necessarily impede the adhesion.

1.8 THE CORRELATION BETWEEN PREPARATION AND PROPERTIES OF PHENOLIC RESINS IN RELATION TO WOOD [26]

Wood is a dimensionally anisotropic, chemically heterogeneous substrate, and its properties are strongly influenced by climatic conditions such as temperature and humidity. The composite's properties are influenced by wood particle size and geometry, and by the manufacturing process variables. The ability of the resin chemist to manipulate the chemistry of the resin system to fit the properties of the wood and the bonding process allows for the desired "marriage" of the wood and adhesive, resulting in an effective adhesive bond and useful wood/adhesive composite. Product performance optimization of a given manufacturing process generally results in a unique resin for that application. It is not possible to formulate a "universal resin" for all applications. Chemical instrumentation and characterisation techniques in conjunction with an inter-disciplinary appro-aches can be used to produce resins with superior product performance. The identification of variables that correlate to resin performance is the prime objective of resin synthesis and characterisation.

1.9. PLYWOOD

1.9.1 New Trends in Plywood Industry [27]

Plywoods are widely used in building and construction industry because its dense, homogeneous structure with good technical properties. Other plywood applications are reefer ships, livestock carriers, boats, furniture, toys, sports equipment, signboards etc.. Durable and elastic, plywood can be made to resist wear and tear, excess moisture and chemicals.

Lightness and self-supportiveness are properties appreciated by the transport industry. Plywood rules out corrosion and rust, major sources of maintenance cost and cargo damage, aggravated by the harsh winter conditions. Plywood's good thermal-insulation properties can also prevent moisture condensation on inner surfaces, providing excellent protection to cargo. As a lorry wall can be made out of one single panel there is no need for seams that could allow moisture penetration. Surface-treated plywood is easy to clean, checking the growth of germs and fungi and so adding to the panel's lifespan in damp climates. An added point in favour in plywood is that in comparison to steel and aluminium, it has good sound insulation properties. Therefore plywood has a great demand in commercial vehicle building industry. The ship-building and container industries have found plywood an attractive material for the same reason.

1.9.2 Properties of Phenolic Adhesives for Plywood [28]

Certain attributes of phenolic resins have been designed to give the strongest and most durable plywood bonds. Certain types of phenol-formaldehyde plywood resins perform significantly better on veneers than do others. This has been demonstrated by laboratory and field experiments. These superior resins have several properties in common.

1. They are relatively low in alkali content, generally about one-third to not mere than one-half molar.

2. They have a lower molecular weight for hardwood veneers than do phenolic resins designed for softwood gluing.

3. They are high in methylol group content. alternatively, they may contain free formaldehyde, or require a matching catalyst which contains paraformaldehyde.

4. Even in dried adhesive carrier films of powdered resins, phenolic resins for hardwoods share the B-stage characteristic of reliquefying briefly under heat and pressure to allow transfer and flow on the glue lines of a plywood panel. This liquefaction can occurs without water. This is unlike all but the most recently developed softwood phenolic resins.

5. Phenolic resins for hardwood have higher thermal softening points than many other conventionally prepared resins. This indicates a network which has more cross-links after final cure and also greater durability.

6. They have a 40-45% solids content and 150-600 cp of viscosity at 25°C.

In general, lower resin alkali content and lower molecular weight are associated with slower cure, which explain why softwood plywood adhesive resins are both more alkaline and more condensed. Adequate exterior-grade adhesion can be attained on softwood veneer if these considerably condensed phenolic resins, which also cure more quickly, are used. Conversely, the increased functionality of hardwood adhesive resins partially compensates for their inherently slower cure rate. Hardwood phenolic resins require about 30% longer press times for adequate cure.

Notwithstanding their good adhesive capability, phenolic resins for hardwood gluing carry one distinct disadvantage; they do not pre-press as well as softwood phenolic resins. Their lower condensation and longer flow are not assets. Repressing is important because it is done to minimise face veneer losses and to reduce precure times on hot plates. Therefore, other means can be employed to obtain the required

tackiness. Additives and adhesive formulations for this purpose are available. To increase the prepress capacity of low-alkali, long flow phenolic resins suitable for hardwood gluing, small amounts of starch or polyvinyl alcohol can be added to the resin glue mix just before use.

Finished resin viscosity is increased to allow for the thickening effect of these additives without reducing the average molecular weight of the phenolic resin. Water-soluble thickeners (such as hydroxyethyl cellulose, polyethylene glycols, and maleic anhydride copolymers) contribute to prepress tack. However, they cause a large increase in resin viscosity and the amount added must be small. Consequently, the benefit to repressing is limited. Most animal- and vegetable-based thickeners, such as gum arabic, are subject to hydrolysis in alkaline phenolic resins, and loss effectiveness in a matter of hours.

1.9.3 Additives used in PF resin chemistry

A number of additives and modifiers contribute useful properties to phenolic resins used for wood gluing. Multi-purpose additives are the aminoresins and urea-formaldehyde and melamine-formaldehyde polymers. These soluble not only urea and melamine plywood adhesive resins, but also dimethylol urea, trimethylol melamine, and hexamethylol melamine. When added in amounts from 5-15% of phenolic resin solids,

they improve resin tack and repressing, increase long assembly time tolerance, shorten pressing times, and enhance resin function-ality. This results in stronger bonds on wood veneers.

As long as they are used in limited quantities, they have a negligible effect on long-term phenolic bond durabi-lity. They appear to be well protected from hydrolytic degra-dation by the cured phenolic polymer network. The dispersion of the aminoresin molecules in the alkaline medium of the phenolic resin inhibits their curing reaction, which is acid catalysted. It causes them to function as methylolated cross-linking units for the phenol-formaldehyde polymer.

Formaldehyde in liquid or solution or solid form, and formaldehyde generating compounds, are also phenolic resin additives which improve functionality and decrease curing times. Paraformaldehyde is more frequently used, but hexamethylene-tetramine, formaldehyde/sodium-bisulfite complexes, tris(hydroxymethyl)nitromethane, and glyoxal are also used. Significant effects are obtained when 3-5% is added, based on phenolic resin solids. Further reduction is curing time are possible if 1-2% resorcinol is added, or resorcinol-acting natural extractive such as wattle-tannin extract. This should be mixed with paraformaldehyde and added to the liquid phenolic resins glue mix.

Formaldehyde additions which overcome the effect of phenolic extractive in certain hardwood species, which prevent proper cure or adhesion of phenol-formaldehyde resins. Free formaldehyde appears to react rapidly with those phenolic extractive before they can interfere with the phenolic resin curing mechanism. With certain wood species which are rich in extractive, this technique has been used to increase bond durability from interior-grade to true exterior-grade performance.

Natural phenolic compounds are used as both replacements for substantial portions of synthetic phenol in plywood adhesive resins, and as glue mix additives to improve performance; 4-6% is added, based on phenolic resin solids. They bring about improvements in assembly time tolerance and flow with no significant change in adhesion. Glue mix addi-tions of wattle extract with additional formaldehyde produce faster hot-pressing cycles. However, some assembly-time tolerance and pot-life has to be sacrificed in the process, but full exterior-grade durability is retained.

The lignin residues from wood pulp production are also a class of extractive which are currently receiving attention as phenolic resin additives. Substituted phenols, such as cresols and xylenols have been used as glue mix additives for phenolic adhesive resins to improve assembly time-tolerance. They are also used as solvents to remove

oleoresinous deposits on the surface of pitchy softwood veneers. They can be used as flow promoters in phenolic hardwood adhesives. The amount added should not exceed 3-4% of the phenolic resin solids content to avoid interference with the rate of resin curing.

Complexing additives commonly include the soluble salts of boron, chromium, zinc, cobalt, lead, manganese, magnesium, and others. Some of these compounds have been successful in reducing pressing times and improving prepress performance [10] when added to phenolic resin adhesives. Borax is widely used in North America to shorten the prepress cycle of pheno-lic plywood glues for softwoods. However, these compounds tend to increase the molecular weight of a phenolic resin by comp-lexing several molecules together their hydroxyl groups. The gain in the resin molecular weight and prepress tack is some-times accompanied by a reduction in assembly-time tolerance and the loss of the B- stage melt-flow behaviour. In hardwood gluing, this is sometimes not advantageous, and the addition of complexing salts should be approached with caution.

Mixed borate salts are very effective as a treatment for the preservation of wood products against fungi and most insects. The application of these borate-based treatments to green hardwood veneer inhibits bonding with phenolic adhesives after veneer drying. The boron salts,

which become localised in high concentration on the veneer surface, tend to gel the phenolic resin before it can reach the wood surface and bond to it. However, very dilute aqueous solutions of borates (i.e., 0.25%) applied to softwood veneers in their green state decrease their thermal degradation during high temperature drying and preserve their reactive sites for bonding with phenolic adhesives. Unfortunately, a borax solution of such a low concentration does not make green veneers mold- or insect-resistant.

1.9.4 Formulations of Plywood glue mixes

The gluing principles for the preparation of plywood adhesives glue mixers are:

1. To maintain phenolic solids in the mixed glue as high as possible (preferable in the range 30-40%)

2. To incorporate a cellulosic filler, such as a nut shell flour of 200 mesh of finer, in about 20-40% of phenolic solids. Non abrasive inorganic fillers may also be satisfactory.

3. Alternatively, to add about haif this amount of unrefined starchy material, such as wheat flour.

4. To add no alkali, or at the most only 1-2% to disperse and stabilise the starchy material.

5. To add only enough water to produce a glue viscosity which can be handled by the gluing equipment. The preferred viscosity range is 1500-2500 cp, measured at 25 °C.

6. To ensure proper wetting of the veneer by the glue film, a surface active agent should be added (about 0.1-0.25% on the resin solids)

1.9.5 Plywood Manufacturing variables

(a). Adhesive application

The double-roller spreader is the most frequently used plywood adhesive applicator worldwidely, but curtain coaters, extruders and spray applications are popular in some countries. Glue spreads must be uniform and controllable, in a range suitable for wood veneer. The exact weight depends on the veneer thickness and the properties of the species. The combination of thick and thin veneers inside the same panel construction should be avoided.

(b). Assembly Method

The assembly method for plywood involves the alternate lay-up of veneers spread with glue and those without glue. The sheet of veneers should be handled with reasonable care so they are not crack or break in the process. The pieces of veneer forming each panel should be referenced first and then placed on top of each other to avoid glue films being wiped off, which occurs if the plies are slid over each other. The handling of spread, unpressed panels should be minimised for the same reason.

(c). Assembly Time

Assembly-time manipulation is an important step in the process of gluing dense and difficult hardwood species successfully. This involves lengthening the assembly time to allow the liquid glue lines to lose water gradually, and become tacky, high-solids films before pressure is applied. Minimum top panel times of 15-30 min are recommended for hardwood veneers. A corresponding bottom panel assembly time of 45 min to 1 hr or more is recommended. Except for repressing the panel assemblies to make easier press loading possible and to minimize degradation, the glue lines should be allowed to dry out completely on most dense hardwood veneers. The inherent flow in properly formulated phenolic wood adhesives provides transfer, wetting, and full adhesion in the hot press.

(d). Prepressing

Because of their high concentration of resin solids, most phenolic wood repressing is recommended. Starchy materials in the resin or in the glue mix improve repressing and shorten the required stand time. A repressing cycle of 10 min at about 5-7 kg cm-2 is sufficient to develop temporary bonds between most wood veneers. These cold-press bonds generally hold for 1 hr or more. It is possible, to lay up and successfully manufacture plywood panels without repressing.

(e). Pressing Temperature

Alkaline phenol-formaldehyde adhesives do not bond satisfactorily under prolonged pressure an ambient temperature. They simply dry out and leave films of friable adhesive solids because no low-temperature cure mechanism is present. Phenolic adhesives have a definite minimum energy input requirement to cure. For highly advanced and functional softwood plywood resins, this minimum heat input level is 1 min at 100°C on the innermost glue lines of a plywood panel. For typical hardwood phenolic adhesives, the minimum heat input level for satisfactory cure is about 3 min at 100°C, or even longer, depending on the exact resin variables of functionality and flow [28]. Phenolic plywood adhesives require a much higher minimum heat input than do urea resin adhesives in order to cure. The temperature rise on the interior glue lines of a panel must also be more rapid. Some water must be present on the

glue lines to permit liquefaction, flow, and transfer before curing. This is important for softwood phenolic adhesives and to a lesser extent, for hardwood adhesives. Loss of water and drying out occurs more rapidly at intermediate pressing temperatures (where the result is a gradual rise in temperature on inner glue lines) for high-heat activated phenolic cure. Under these conditions, phenolic glue films dry out and develop inferior, water-sensitive bonds. Curing temperature for phenolic adhesives should remain above 125°C except for thin panels. Another practical benefit which can be derived from this minimum hot-press temperature limit is that the steam pressure required to maintain 125°C is generally sufficient to prevent waterlogging of the press platens. This in turn eliminates cold spots and insufficiency cured glue line areas. These tend to occur all too frequently at lower press temperatures when steam presses are used.

(f). Platen Pressure

High density veneers need extra pressure to make adequate contact on each glue line in a panel assembly. The minimum platen pressures for proper bonding for dense hardwoods and medium-density softwood are 14 and 12 kg cm^{-2}, respectively. For rough veneer surfaces or extremely dense wood species, a pressure of 16 kg cm^{-2} in the minimum required. The loss of panel thickness due to densification during hot pressing is no higher for heavy hardwoods than it is for softwoods pressed at 12 kg

cm^{-2} (e.g., 4-6%). High veneer moisture contents cause a rapid increase in press densification and permanent loss of panel thickness. Veneer moisture content should therefore be controlled within fairly close limits.

The hot press should reach full pressure in 1 min or less, preferably 30 sec, to minimise the effect of precure on outer glue lines. This is especially true for very thin, decorative face veneers. Hydraulic booster pumps are available to correct this deficiency and are worth the cost of their installation in terms of the consistent improvement in adhesion obtained.

(g). Panel Construction

It is not possible or practical to specially the optimum thickness to which veneers should be peeled for the best drying and gluing practice. However, extremes of thick and thin peel should be avoided, except for decorative application (where the panels have a thick core and very thin, decorative handling faces). The preferred thickness for easy drying, minimum hardening losses, and maximised strength should be between 2 and 4 mm. Above that range, veneer tends to become rough and deeply cracked, drying become too long, and chances of overdrying increases. If the veneer is less than 2 mm thick, handling losses increases substantially unless the veneer has been taped green. Thin

plies promote excessive blistering on adjacent glue lines when they are used in the interior of a panel assembly.

1.10. WOOD RELATED FACTORS

(a). Density and Porosity

The effect of density on adhesion is more physical than chemical. Dense, nonporous wood surfaces confine the liquefied adhesive to the immediate glue line for longer time under pressure. The cause of adhesive solids to move too much to areas of minimum contact or pressure, which results in poor bonding. Liquid glue lines on lower-density wood lose water into the wood more quickly and become viscous, high-solid films before heat and pressure are applied. In this form, they flow less and present a more concentrated layer of adhesive solids. This producer stronger, more uniform phenolic adhesive bonds. Conversely, excessively thin glue mixes used on softwood show not only a fast loss of water into the veneer, but also overpene-tration of the whole adhesive solution into it.

On exposure to water or weathering dense hardwoods develop stronger mechanical separating forces on the glue line than do softer species and loose bond durability. Because the extent of wood failure on dense wood surfaces tends to be shallow, bonds are more easily ruptured by these strong cross-grain expensive or warping forces.

Open-grain dense hardwoods are easier to glue than close-grained hardwoods but they pose one or two problems. The open resin canals at the surface siphon away considerable quanti-ties of liquid or liquefied adhesive as transfer and flow occur. Unless extra glue is applied not enough is left to bond the heavy lignified ridges of fibber between the canals.

(b). Extractive content

Most wood species contain various combination and appre-ciable quantities of natural latex or oleoresinous materials for wound healing, phenolic substances for hardwood protection, and polycaccharides growth or nutrient compounds in their sap. There substances, which become concentrated on the surfaces of wood veneer through drying, present both physical and chemical barriers to bonding. They form a surface layer which prevent the adhesive from reaching the wood structure. Some of these materials are chemical plastizers for phenolic resins and promote excessive flow. Others react directly with phenolic polymers to accelerate or retard cure rate. Collectively, they can seriously interfere with normal adhesive behaviour and bond development.

(c). Drying Conditions

The conditions of temperature, time and humidity under which hardwood

veneer and dries can have a profound effect on bonding. High temperature low humidity and long heat exposure all promote thermochemical modifications of wood surfaces, which destroy bonding sites and reduce adhesion. This is called overdrying and is indicated by a water-repellant veneer surface which normal adhesives will neither wet nor bond. Phenolic glue films cured against overdried veneer surfaces show little transfer.

(d). Freshness

There is a definite correlation between the age (the elapsed time between peeling or drying and actual assembly into plywood) of the veneer at the time of gluing and the level of adhesion. The older the veneer, the poorer the bond. The loss of wood failure after 6 months of storage can be as much as 15-20%. Two things apparently happen to veneer during a long storage time which alter or block bonding sites available for adhesion. One is a slow but steady series of reactions between atmospheric oxygen and the cellulose, lignin, and sap constituents in the wood surface. The net effect is a progressive loss of surface functionality and therefore adhesion. The other is a bacterial or fungal attack, which occurs if the veneer is stored green. Moldy wood not only bonds poorly bur also much weaker. If prolonged veneer storage is unavoidable dry it first.

(e). Surface Smoothness

A smooth surface is a necessity for high-density hardwood veneers. Where there is no surface contact, there can be no adhesion. The pressure in areas where contact does occur become so high that glue films which are normally satis-factory are squeezed off into no-contact areas, resulting in joint starvation. Use of alternately low- and high-density plies is more practical, but even this is not a good substitute for proper heating and peeling of the wood log. This can be avoided by good knife maintenance and lathe adjustment so that the veneer surfaces does become woolly and covered with torn fibbers or other wood debris.

(f). Thickness Control

Wood veneer should be uniformly thick for effective bonding. The roller spreaders used in plywood mills are equipped with hard-rubber covers to promote long wear and resistance to swell by fungicidal solution in the glue. Therefore, they do not readily accommodate roughness or variations in veneer thickness and cause a high percentage of rejection due to incomplete glue coverage. Therefore, a smooth and uniform veneer is a potentially important source of saving of both glue and wood. In the hot press variation in veneer thickness is definitely a hazard. Thin veneers tend to carry glue spreads and make low-pressure contact with adjacent ply. Both factors contribute to excessive panel blistering under normal gluing and hot-pressing conditions. Conversely,

thick veneers pick up light glue spreads and develop poor bonds due to dry-out.

(g). Surface Cleanliness

Veneer surfaces should be kept clean to promote the development of strong adhesive bonds. The presence of oil smears, muddy footprints, and sandy dust on the surfaces to be glued contribute to areas of poor adhesion and subsequent panel failure. The same is true of wood chips, broken knots, and slivers carried onto the glue lines by one or more of the ply in the panel assembly. Each chip or peace of knot can cause a low-pressure area of up to several square inches on the glue line.

1.11. GENERAL OBSERVATIONS ON PARTICLEBOARD MANUFACTURE

In the case of the application of phenolic adhesives to the manufacture of exterior-grade particleboard, the closest attention must be focused on the application of the resin rather than on its formulation. A good phenolic resin for plywood can be successfully used for the manufacture of particleboard once the different conditions of application have been understood. The pressing time of the board varies according to the type of adhesive, its reactivity, and the moisture content of the glued particles. In many cases a light water spray is applied to the two

surfaces of the board before pressing to shorten the pressing time. The light film of water covering the surface is vaporised when it comes in contact with the hot caul sheet of the press and migrate from the surfaces towards the core of the panel, causing a faster increasing in temperature and faster cure.

The water spray prevent precuring of the adhesive on the surface of the board during closure of the press before contact with the hot top caul sheet. The wood undergoes a partially irreversible plastic deformation during pressing, caused by the combined action of pressure and heat. Different products can be obtained by varying the type of pressing cycle of the board. Considerable variations in the properties of the final board can be obtained by varying the moisture content of surface and core layers, and by using faster resins to the core layer and slower reacting resins to the surface layers in the case of three layer boards. This can also be achieved by varying geometry and sizes of the wood chips, the density of the board, and so on.

Resols used for particleboard manufacture have been shown to begin curing at lower temperatures than those for novolak resins. Resols-glued particleboard show no bond formation at 120 ^{o}C. At 130°C the resol glued panels show internal bond strengths 0.55-0.7 MPa. The internal bond strength for the wet tests increases as the board core temperature

goes over 150°C during pressing. The normal temperature for 12- to 13-mm thick board glued with phenolic adhesive is 170 -200°C. The pressing time is 5 - 7.5 min.

CHAPTER TWO

INTERNAL BOND STRENGTH OF A PARTICLEBOARD IN RELATION TO THE ^{13}C NMR SPECTRAL DATA

DISCUSSION

2.1 OUTLINE

Although the technology for formulating phenol-formaldehyde resin adhesives for wood products manufacture is well established, it has for the most part been developed empirically. Consequently their are few publications available relating mathematically the basic properties of these resins to wood adhesion. Application of most analytical techniques to the determination of these PF resins' structure is not practical, although IR spectroscopy has had limited success [29]. Successful attempts have been made to apply ^{13}C NMR in this field. The object of this work is to throw some light on the present state of the subject, and in effect to statically relate the resin F:P molar ratio, the resin viscosity and ^{13}C NMR data to the particleboard bond qualities such as Internal Bond (I.B. dry), strength retention after an accelerating-aging test (I.B. wet) and its formaldehyde emission level.

In the first part of this study the PF resin structure in relation to the Internal Bond tensile strength of the particleboard is discussed and in the second part (Chapter three) the resins' structure in relation to the formaldehyde emission is discussed.

2.2 SYNTHESIS OF PF RESINS

Several PF resin synthesis methods were found in the literature [30,31,32]. The following procedure was chosen for this work; two sets of PF resins (A, B series) were prepared with the same final F:P molar ratio but with different synthesis approach. A- a single step addition of formaldehyde to phenol with F:P molar ratios 1.1:1, 1.3:1, 1.5:1, 1.8:1, 2.0:1, 2.2:1 (6 resins) and B- a multi step addition of formaldehyde to phenol in addition to the above 2.1:1 ratio (7 resins) in strong alkaline media respectively (See Chapter 4.2, Experimental).

Various resin properties were determined by standard methods, including nonvolatile resin solids, viscosity, pH etc., and ^{13}C NMR spectra were recorded. The viscosity of the resins was determined by Brookfield viscometer and the percent nonvolatiles was determined as the ratio of the residue of a known amount of resin (~1g) after 5 hrs at 100-105 °C to the weight of the liquid resin (expressed as a percentage). The results for the different resins viscosity and % solid content are given in Table 9.

Most resins had to be synthesised more than once during the course of study. Nieh and Sellers [33] found slight different values of the properties even for the same F:P molar ratio resins synthesised at different intervals, and reported that the scatter of the data might had

been due to the minor variations of the reaction procedures, in storage time etc.,

The A- series of resins had a relatively higher % solid content and viscosity values than the B- series. The reason is the usage of paraformaldehyde in the synthesis of the A- series resins and of formalin 37% solution for the B- series. Paraformaldehyde is a solid powder and gives higher viscosity and % solid content values.

Higher F:P molar ratio resins gave higher values for viscosity than at lower F:P molar ratio. For the A- series resins the same amount of solvent was used for the preparation of the whole set. When going from lower to higher F:P ranges the additional paraformaldehyde had to be dissolved in the same volume of solvent used. Therefore, even the initial reaction mixture at higher F:P molar ratio resins were more viscous than the lower F:P molar ratio resins. This effect was not applicable to the B- series. Here formaldehyde was added as a 37% aqueous solution. The addition of water has caused the viscosity to decrease, as well as the % resin solids content, although they underwent longer periods of reaction than the A- series resins. When polymerisation proceeded further, it caused the viscosity to increase.

Kelusky at al. [34] reported, based on their study of line spectra of labelled ^{2}H formaldehyde and ^{2}H phenol by ^{13}C solid-state CP MAS NMR and ^{2}H quadropole echo NMR techniques that some of the prepolymers are fairly mobile, while about 50% is already rigid at a local level on the NMR time scale as cross linking proceeds. An increase in spin lattice relaxation time become parallel with the increase in the degree of cross linking. At high F:P molar ratio (>2) some NMR spectra were not highly resolved. This factor may have contributed to this effect.

Mildly condensed liquid resols perform better in wood adhesion and Nieh & Sellers showed that I.B. strength decreased as molecular weight of the PF resin increases [33]. But very low molecular weight, (i.e., a higher percentage of monomeric) phenolic resols give poor perforce as condensation is inhibited; this type of resins would need to undergo more condensation to form an infinitely hardened networks.

2.3 PARTICLEBOARD

Particleboards were produced from the above set of resins and their physical properties were recorde The preparation conditions for all the boards were kept the sam Details in Chapter 4.3 & 4.5.1 Experimental).

Evaluation of the resins were carried out by performing an Internal Bond strength (I.B) test on particleboard (measured perpendicular to the surface of the board). The I.B. strength was measured on both dry specimens and specimens subjected to an accelerated aging wet-dry circle (2 hrs. boil and 16 hrs. dry), and recorded as dry and wet I.B. strength respectively (See details in Chapter 4.3 & 4.5.1 Experimental). The results obtained are given in table 1. Effects of some resin characteristics (F:P molar ratio, viscosity, ^{13}C NMR spectral data etc.,) on particleboard strength properties were tested statistically.

I.B. strength of a board even with the same resin is a function of its density. I.B. strength, F:P molar ratio, and the density of the boards can be combined by fitting an approximate non-linear multi-variable regression equation by Levenberg-Marquardt modelling [35].

The equation that fitted the experimental data the best for the A- and B- series resins, is shown below.

For the A- series (single formaldehyde addition step),

$$IB = 1.092 - 0.866P + 0.447P^2 - 0.165D^{-3.753}$$

This equation gave a standard deviation of 0.079 in the I.B range between 0.088 - 0.796 MPa.

For the B- series (multiple formaldehyde addition step),

$$IB = 1.395 - 1.561P + 0.688P^2 - 0.120D^{-3.514}$$

This equation gave an estimated standard deviation of 0.114 in the IB range between 0.07 - 0.994 MPa. (see table 1).

Where IB = Dry Internal Bond strength (MPa)

P = F:P molar ratio

D = Density (g cm^{-3})

The wet I.B. strength cannot be fitted onto a multi-variable equation relating density, and F:P molar ratio simultaneously due to the lack of sufficient number of experimental data points.

For simplicity, I.B. strength results of the boards can also be interpreted by fitting an approximate non linear regression equation, linking only the I.B. strength of a board to the F:P molar ratio of the resin used. Now both dry and wet I.B. Data can be considered. Considering dry I.B. data, the following set of equations can be obtained.

For the A- series resins

$$\ln IB = 2.093P - 4.834 \qquad r = 0.97$$

Similarly for the B- series

$$\ln IB = 2.016P - 4.455 \qquad r = 0.927$$

where IB = Dry Internal Bond strength (MPa)

P = F:P molar ratio

and r = the correlation coefficient (See APPENDIX 1 for definition.

Figures 1(a), 1(b) show the fit of the equations to the experimental data for the A- and B- series boards respectively. A correlation factor greater than 0.9 is considered to be acceptable. Even though the variation of the density factor is neglected in presenting the above equations, still a higher correlation coefficient could be obtained.

The wet I.B. data did not followed the same trend. But could be best fitted on to an exponential and logarithmic regression equations for the A- and B- series respectively. The variation of the density factor has come into operation here.

For the A- series

$$\ln IB = 5.363P - 11.513 \qquad r = 0.994$$

For the B- series

$$IB = \ln(2.159P - 2.755) \qquad r = 0.989$$

Where $IB > 0$ and $P > 0$;

IB = wet Internal Bond strength (MPa)

and P = F:P molar ratio

Figure 1(c), 1(d) show the fit of the equation to the experimental data for the A- and B- series of boards respectively.

The I.B. strength data are in the range of the German standards for the manufacture of particleboard [36]. The German standards suggested for a low density board (0.4 - 0.6 g cm^{-3}) tensile strength measured perpendicular to surface must be between 0.62 - 2.76 MPa.

In the A- series resins a gradual decrease in I.B. strength was observed varying from 1.1 to 1.5 F:P molar ratio, due to the decrease in the average density of the boards. For all the other boards there is

an increase in I.B. strength with the increase in F:P molar ratio, which is as expected.

This effect can be explained by considering heats of reaction, and viscosity (contact angle) of the resin [37].

(a) Heats of reaction were positively related to bond quality, and largely determined by the amount of heat required to remove water during cure (including the water present in liquid resin as well as water from the condensation reaction).

Higher molar ratio resins which have higher chemical reactivity will take less time to cure, tending to yield high heats of reaction, high rates of heat of absorption and stronger glue bonds.

(b) excess penetration is one of the most important cases of poor glue bonds and, greatest penetration can be expected from the resin with the lowest viscosity.

It has been shown that bond strength increases as glue line thickness increases and glueline thickness increases as viscosity (contact angle) increases. Therefore a highly viscous resin does not penetrate excessively and may give the best compromise of wetting, spreading

and penetration, yielding stronger bonds at higher F:P molar ratio. But if the viscosity is very high it tends to form impervious skins that may retard heat penetration and water removal ability tending to yield low cured resins resulting poor bonds.

Nieh and Sellers [33] found weight average molecular weight has an exponential relation with viscosity of a PF resin with time; and an increasing trend of I.B. versus the viscosity of different F:P molar ratio resins. If more experimental data points have been used they could have gain a more significant result.

Presence of free formaldehyde can be observed (δ = 83.73) by ^{13}C NMR spectra 1.8:1 $\leq$ F:P molar ratio resins (see spectra 4 to 7 and 11 to 15). Free formaldehyde facilitates the solvation of the resins' oligomers sufficiently to promote their migration out of the glueline into the wood prior to hot pressing. Such migration would leave immobile molecules behind in the glueline. Therefore the presence of free formaldehyde contributes to yield higher I.B. strength values at higher F:P molar resins.

The average I.B. strength results for the B- Series resins (multiple step addition of formaldehyde) is higher than that of the A-series resins (single step addition of formaldehyde). This is clearly visible for higher

molar ratio resins (compare 1.8:1A to 1.8:1B, 2.0:1A to 2.0:1B and 2.2:1A to 2.2:1B). But at lower molar ratio the effect is less pronounced due to the gradual decrease of the average densities of the boards in the A- series up to 1.5:1 F:P molar ratio.

This is because in the B- series step-wise addition of formaldehyde under the conditions used has facilitated the formation of a relatively less cross-link (low molecular weight) linear polymer (i.e, relatively higher number of functional groups capable of bond formation in the glueline) than the corresponding A- series.

Nieh and Sellers found no significant difference in the density of panels made with different PF resins and reports F:P molar ratio, resin viscosity and resin molecular weight have no effect on panel property. Furthermore they found longer hot press times (7 Vs. 5 min) and higher resin solids application rates (7% Vs. 5%) did not yielded significantly higher density panels, under the experiment conditions used [33]. However, with increase of F:P molar ratio a gradual increase in the average density of the boards was observed in this study.

With increasing F:P molar ratio, boards showed higher I.B. strength values, while at the same time showing higher resistance to the water

absorption and thickness swell test, giving lower % increase in the thickness swell values. The B- series resins performed better than the corresponding A- series but the difference noticed is not very pronounced (Table 10). Boards from both the series (A,B) of resins F:P $\geq$ 1.5 molar ratio showed lower resistance to the wet test and can be classified to be weak boards (Table 1). This could be explained as follows. The ^{13}C NMR results for the respective liquid resins showed that methylol to methylene species ratio is low. (i.e., < 1) indicating that proportionately much fewer reactive groups exist in these resins, mostly may be on higher molar mass fractions. Hence cause the I.B. strength to decrease at the wood-resin interface.

Wood is a very hygroscopic material and swells to a great extent when it is in contact with water. As it is also a very anisotropic material, internal stresses are build up when it is wetted, causing not only dimensional changes but also splits and other damages during swelling and shrinking, thus compromising its performance in a humid environment. Higher F:P molar ratio resins have better crosslinking capabilities and better adhesion to the wood substrate whereas lower F:P molar ratio resins develop relatively less cross-links, forming more porous structures on curing on the wood, speeding up water penetration and eventually lose their water repellency.

2.4 ^{13}C NMR SPECTROSCOPY

Potentially interesting functional groups in PF resins can be identified as follows [32, 38].

(a) Total methylene bridging species (Me)

(δ = 29.21-31.4 ppm) and (δ = 34.93-35.9) and

(δ = 39.67- 41.00 ppm)

(b) Total methylol species (Mo) (δ = 61.4-65.52 ppm)

(c) Total *ortho* plus *para* free sites in the phenolic ring (o+p) (δ = 115.4-116.0) and (δ = 119.9-120.9 ppm)

(d) Total *meta* free sites (δ = 127.4-132.9 ppm) plus all the blocked (already reacted) sites in the phenolic ring (δ = 127.6-133.9 ppm) (peaks in this range overlap with each other)

(e) Total methylene ether species (δ = 66.57, 67.10, 70.57, 70.77, 71.16, 87.3, 89.3, 89.6, 92.2, 92.9 ppm

(f) Free formaldehyde peak (δ = 83.73 ppm)

Only the (a)-(d) set of chemical groups contribute predominantly to the bond quality in the glue line and are discussed in this section. The

ether peaks, methylol peaks and free formaldehyde peak are instead important to the formaldehyde emission from the boards and discussed in the next Chapter 3.

Peak intensity data are scattered due to different spinning rate for different regions of the ^{13}C NMR spectrum. Therefore no quantitative results can be obtained directly from the raw spectra.

However considering peak intensity ratio of the above set of chemical groups, difference between the variation in synthesis parameters and the final resins' properties could be deduced and some quantitative considerations can be derived.

Tabulated results of peak ratios discussed here are given in table 3.

2.4.1 Mo/Me peak ratio

Condensation is the rate determination step in alkaline catalysed polymerization and the formation of methylolated phenols is the initial step. While reaction proceeds numerous potential branching points are build into the polymer structure. Not all methylols will be able to cross-link and form chain segments. Therefore an increase in Mo/Me peak ratio with the increase in F:P molar ratio can be expected for both series of resins.

Further Steiner [48] acetylated a series of phenolic resols that had variable F:P molar ratios (0.75 - 2.6) and studied by ^{1}H NMR spectroscopy and found that the methylol content of the resins increased with molar ratio up to 1.8 and then levelled off.

Kelusky at. al. [34] studied the curing of PF resins by CP MAS NMR and observed the increase in the number of cross-links with the increase in the Me/Mo ratio. Therefore the ratio of total methylol (Mo) to total methylene (Me) may be defined as the "potential" cross linking ratio for PF resins. A larger increase in Mo/Me peak ratio was observed for the B- series of resins than the A- series at higher molar range, (compare 1.8:1A to 1.8:1B and 2.0:1A and 2.0:1B in Table 3). But some discontinuity was shown at low molar range (1.1:1A to 1.1:1B and 1.3:1A to 1.3:1B). Fig 2 show the relationship between the calculated ratios for the different resins.

Therefore with increasing F:P molar ratio a gradual increase in the "potential" degree of crosslinking is indicated, while the individual values for the B- series is higher than that of the A- series. This explains why the B- series perform better than the A- series in wood adhesion.

Generally all the formulated resols were characterised to be mildly cross-linked, the "potential" degree of cross-linking was higher in formulations that had higher levels of formaldehyde present during condensation.

The enhanced "potential" degree of cross-linking pattern of resins can be explained on the basis of chemical reactivity. Additional formaldehyde catalyses the cross-linking reaction. As the amount of crosslinking increases with increasing formaldehyde concentration, "potentially reactive" sites becomes rapidly shielded from further reaction due to greater steric hindrance. Therefore higher levels of formaldehyde have caused a higher percentage of unreacted, sterically hindered methylols yielding a higher relative index of "potential" degree of cross-linking.

By regression analysis a set of exponential equations can be obtained to evaluate the variation of Mo/Me peak ratio of the resins with F:P molar ratio. But it is necessary to note that in obtaining the equations data were used up to 2.0:1 F:P molar ratio only, and further F:P 1.3:1A data was also eliminated.

For the A- series

$$\ln Y_1 = 0.560P + 0.844 \qquad r = 0.942$$

Similarly for the B- series

$$\ln Y_1 = 1.274P - 0.128 \qquad r = 0.996$$

Where Y_1 = Mo/Me peak ratio

P = F:P molar ratio

Figure 2(a), 2(b) give the variation of the peak ratio with the F:P molar ratio for the A, B series of resins respectively.

The significance is that a higher Mo/Me ratio can be obtained at a [illegible] molar ratio resin with the multiple-step addition than with [illegible] formaldehyde addition. This ratio is important when considering the adhesive properties of a resin in the glueline. This ratio might play an important part of the adhesion at the wood-adhesive boundary and also contribute to the adhesive forces in the cured state.

It is important to relate the peak ratios obtained by ^{13}C NMR studies to the physical properties of the particleboard. Therefore, to be able to evaluate the physical properties of a PF resin bonded particleboard, by considering only the ^{13}C NMR studies of the particular liquid resin before hardening. This has been done for Urea-formaldehyde (UF) resin [35]. UF resins-bonded particleboard are not resistant to water

attack. Therefore in PF resins it is possible to reach a step further, and predict the performance of a PF resin bonded particleboard after an accelerated ageing test (boil test) from the NMR data obtained from the liquid resin.

A linear regression equation can be presented to show the variation of dry I.B. Strength with the Mo/Me peak ratio as follows. [fig. 2(c), 2(d)].

For the A- series resins

$$IB = 0.156Y_1 - 0.680 \qquad r = 0.934$$

For the B- series

$$IB = 0.068Y_1 - 0.203 \qquad r = 0.998$$

Where IB = Dry Internal Bond strength (MPa)

and Y_1 = Mo/Me Peak ratio

An average increase of about 16% in the cross-linking capabilities (Mo/Me) for a resin synthesised by a single- step formaldehyde addition to that of multiple addition was observed. Properties like hydrolysis, water uptake and formaldehyde emission are influenced by the amount of methylol species present in the resin.

Similarly correlation analysis of F:P molar ratio with the wet I.B. strength also has carried out. At higher molar ratio the boards performed well in the wet accelerated durability tests although the variation of Mo/Me peak ratio is more irregular. Hence the correlation was poorer. The following set of equations was anyhow be obtained. [fig. 2(e), 2(f)].

For the A- series

$$IB = 0.317Y_1 - 1.717 \qquad r = 0.713$$

For the B- series

$$IB = -0.036Y_1 + 0.718 \qquad r = 0.474$$

Where IB = wet Internal Bond Strength (MPa)

Y_1 = Mo/Me Peak ratio

The wet I.B. strength (measured after 2 hrs. boil and 16 hrs. dry) can be correlated to the DINv100 I.B. strength (measured just after 2 hrs. boil) by the following equation proposed by A. Pizzi found from unpublished results (See Appendix 2).

DINv100 I.B strength = 0.2605 Wet I.B. strength + 0.0905

Therefore when Wet I.B. strength is known it is possible to evaluate the DINv100 according the above equation. Thus another set equations can be presented to evaluate the variation of the DINv100 I.B. strength with this peak ratio as follows.

For the A- series

$$IB = 0.092Y_1 - 0.495 \qquad r = 0.768$$

Similarly for the B- series

$$IB = -0.012Y_1 + 0.273 \qquad r = 0.360$$

Where IB = DINv100 Internal Bond Strength (MPa)

Y_1 = Mo/Me Peak ratio

Note that these two sets of equations have opposite signs for the gradient and cannot be used for any comparative purposes. But in general below 1.8:1 F:P molar ratio, resins (i.e., 6 < Mo/Me peak ratio) were not resistant to the wet tests.

Therefore a direct mathematical relationship between the internal bond strength versus Mo/Me peak ratio at low molar ratio (<2) can be only obtained for dry tested particleboard. This equation is then a function

also of other conditions of applications. The relationship would be different for other types of homologous series of PF resins.

Anyhow the important principle remains that there is an excellent correlation with NMR data and the actual dry I.B. strength of boards manufactured under the same conditions.

I.B. strength can also be correlated to NMR data by considering the ratios of other species as well. These ratios will be discussed one by one.

2.4.2 (o+p)/(m+B) peak ratio

The ratio of *ortho* plus *para* free sites (o+p) in the phenolic ring to the *meta* free sites plus all the blocked i.e., (*o* and *p* already reacted) sites in the phenolic rings (m+B) give an excellent correlation with wood adhesive performance.

With increases in F:P molar ratio a gradual decrease in the (o+p)/(m+B) peak ratio is observed (Y_2, Table 4). While reaction proceeds a gradual decrease in free *ortho* plus *para* sites (substituted by methylols, methylenes etc.,) can be expected with the corresponding increase in the blocked sites. The *meta* sites does not take part in the reaction but the chemical shifts of this group coincide

with the same range as blocked sites and both species have then to be considered together. Therefore, as overall effect, a decrease in the (o+p)/(m+B) species ratio with increasing reaction time can be expected. The same trend can be expected with the increase of F:P molar ratio: this is indeed observed experimentally (compare 1.1:1A - 1.1:1B to 2.2:2A - 2.2:1B, Table 3). Fig 3 shows the relationship between the calculated peak ratios for the different resins.

To explain the phenomena the following set of linear equations gave the best correlation coefficients by regression analysis for the two series of resins.

For the A- series

$$Y_2 = -0.578P + 1.260 \qquad r = 0.990$$

For the B- series

$$Y_2 = -0.646P + 1.489 \qquad r = 0.987$$

Where Y_2 = (o+p)/(m+B) peak ratio

P = F:P molar ratio

Figure 3(a), 3(b) shows the variation of peak intensity ratio with the F:P molar ratio for the A-, B- series of boards respectively.

(o+p)/(m+B) peak ratio gives an exponential relationship with the dry I.B. strength for both the series of resins as follows and figure 3(c), 3(d) shows the relationship between the dry I.B. strength with this peak ratio for the two series of resins.

For the A- series resins

$$\ln IB = -5.278\ Y_2 - 0.086 \qquad r = 0.988$$

Similarly for the B- series

$$\ln IB = -4.055\ Y_2 + 0.278 \qquad r = 0.986$$

where Y_2 = (o+p)/(m+B) peak ratio

IB = Dry Internal Bond Strength (MPa)

The percentage unreacted sites (Y_2) in the A- series varies from 66% to 2.3% with varying F:P molar ratio from 1.1:1 to 2.2:1 and whereas in the B- series this figures vary from 83.4% to 7.6% with the variation of the F:P molar ratio from 1.1:1 to 2.2:1 (Table 3). Therefore, although the final F:P ratio is the same for both the series and all the resins produced can be regarded as mildly crosslinked, multiple addition of formaldehyde to the phenol has influenced the formation of a relatively lower degree of polymerised (lower molecular weight) linear resin than that of single step addition. On curing lower

molecular weight resols produce more rigid networks, hence stronger bonds. This contributes the B- series resins to perform as a better wood adhesives than the corresponding A- series resins.

Thus, this peak ratio gave a linear relationship with the wet I.B. strength as follows. [fig. 3(e), 3(f)].

For the A- series

$$IB = -3.933Y_2 + 0.762 \qquad r = 0.996$$

For the B- series

$$IB = -2.541Y_2 + 0.909 \qquad r = 0.984$$

Where IB = wet Internal Bond strength (MPa)

Y_2 = (c+p)/(m+B) peak ratio

Similarly DINv100 I.B. strength can also be related to this peak ratio and another set of linear equations can be presented as follows.

For the A- series

$$IB = -1.578Y_2 + 0.317 \qquad r = 0.958$$

For the B- series

$$IB = -1.030Y_2 + 0.372 \qquad r = 0.929$$

Where IB = DINv100 Internal Bond strength (MPa)

Y_2 = (o+p)/(m+B) peak ratio

Again the B- series gives a higher gradient than that of the A- series in relation to the I.B. strength and consequently higher wet I.B. values for the B- series are obtained.

2.4.3 Mo/(o+p) peak ratio

The calculated ratio of total methylol groups to the total *ortho* plus *para* free sites in the phenolic ring versus F:P molar ratio for different resins is given in figure 4, (represented by A and B lines respectively).

A large increase in the Mo/(o+p) peak ratio can be observed in the A-series resins indicating a much higher methylol content present in this series of resin at higher F:P molar ratio. (compare 1.8:1A to 1.8:1B and 2.0:1A to 2.0:1B). A gradual increase in peak ratio with molar ratio was seen for the other resins in both series.

When formaldehyde concentration in the resins increases it facilitates the generation of more methylol groups. The methylol groups formed

may react with each other to form methylene ether linkages and at the same time can react with a free *ortho* or *para* site in a phenolic ring to form methylene bridges. As not all methylols will be able to cross-link, when the reaction proceeds a gradual increase in methylol groups and a corresponding gradual decrease in the *ortho* and *para* free sites on the phenolic aromatic ring can be expected. Therefore, the overall effect observed is an increase in Mo/(o+p) ratio with the F:P molar ratio.

The following set of exponential equations can be obtained by regression analysis to evaluate the variation of this peak ratio with the F:P molar ratio for both series of resins. [fig. 4(a),4(b)].

For the A- series

$$\ln Y_3 = 3.725P - 5.838 \qquad r = 0.967$$

Similarly an exponential equation can be presented for the B- series as well. But the same phenomena can be explained by a power regression equation with a higher correlation coefficient as follows.

$$\ln Y_3 = 2.717P - 4.919 \qquad r = 0.956$$

$$\ln Y_3 = 3.991 \ln P - 2.292 \qquad r = 0.974$$

Where Y_3 = Mo/(o+p) peak ratio

P = F:P Molar ratio

The higher methylol content considerably improves the glueline properties, indicated by the overall increase in Mo/(o+p) peak ratio with increasing F:P molar ratio. This effect has attributed to the higher I.B. values at higher F:P molar ratio.

Regression analysis explaining the phenomena relating the NMR peak ratio for the Mo/(o+p) to the dry I.B. strength test can be calculated. [Fig. 4(c), 4(d)].

For the A- series a linear equation can be presented. But the same phenomena could be best presented logarithmically.

$$IB = 0.039Y_3 + 0.160 \qquad r = 0.908$$

$$IB = \ln (0.070Y_3 + 1.123) \qquad r = 0.919$$

Similarly for the B- series

$$IB = 0.318Y_3 + 0.040 \qquad r = 0.985$$

Where IB > 0; and $Y_3 > 0$

Y_3 = Mo/(o+p) peak ratio

and IB = dry Internal Bond strength (MPa)

Correlation studies have been done for the wet I.B. strength with the variation of this species ratio as well.

In spite of the few experimental data points available in presenting the equations it may be possible to define a margin for a PF resin bonded particleboard to resist for the wet tests;. i.e., a particleboard to resist for the wet test, this peak ratio must be 2.5< for the A- series and 0.8< for the B- series respectively.

The following set of equations illustrate the wet I.B. strength as a function of peak ratio. [fig 4(e), 4(f)].

For the A- series

$IB = 0.030Y_3 + 0.117 \qquad r = 0.878$

Similarly for the B- series

$IB = 0.275Y_3 - 0.084 \qquad r = 0.970$

Where Y_3 = Mo/(o+p) peak ratio

IB = wet Internal Bond strength (MPa)

A much higher coefficient can be obtained for the resins with the step-wise addition of formaldehyde, therefore the B- series is more influenced by the variation of the Mo/(o+p) peak ratio.

Another set of equations can be presented to evaluate the variation of the DINv100 I.B. strength with this peak ratio as follows.

For the A- series

$$IB = 0.013Y_3 + 0.037 \quad r = 0.814$$

For the B- series

$$IB = 0.113Y_3 - 0.034 \quad r = 0.932$$

Where IB = DINv100 Internal Bond strength (MPa)

and Y_3 = Mo/(o+p) peak ratio

2.4.4 (o+p)/Me peak ratio

A gradual decrease in the *ortho* plus *para* free sites over the methylene bridging groups in the phenolic rings with increase in the

F:P molar ratio is observed. When formaldehyde reacts with phenol it initially generate mono-methylol and subsequently di- methylol phenol and so on. This causes a reduction in the *ortho* and *para* free sites in the phenolic nucleus. At the same time these methylol phenols interact with each other to form methylene ether bridges and also with other *ortho* and *para* free sites in the phenolic rings generating methylene bridges and leading to the formation of linear PF polymers.

Therefore, an increase in formaldehyde leads to greater reduction in the proportion of free *ortho* plus *para* sites in the phenolic rings and simultaneously leads to an increase in the number of methylene bridging groups. Thus as overall effect can expect is, a gradual decrease in the (o+p)/Me peak ratio; this is indeed observed experimentally.

Some discontinuity is observed in the 2.0:1A resin and 2.12:1B resin. Fig 5 shows the relationship between the calculated ratios for the different resins.

Regression analysis explaining this phenomena gave a set of linear equations relating the NMR peak ratio of (o+p)/Me to the F:P molar ratio as follows. [Fig. 5(a), 5(b)].

For the A- series resins

$$Y_4 = -17.633P + 37.295 \qquad r = 0.966$$

Similarly for the B- series resins

$$Y_4 = -16.151P + 38.120 \qquad r = 0.976$$

Where Y_4 = (o+p)/Me Peak ratio

P = F:P peak ratio

The particleboards' I.B strength also presents the same trend as the peak ratio and the following set of equations can be obtained to show the variation in I.B. strength as a function of this ^{13}C NM peak ratio. [fig. 5(c), 5(d)].

For the A- series resins

$$IB = -0.033Y_4 + 0.588 \qquad r = 0.841$$

Similarly for the B- series resins

$$IB = -0.048Y_4 + 0.924 \qquad r = 0.970$$

Where Y_4 = (o+p)/Me Peak ratio

IB = Dry Internal Bond strength (MPa)

Wet I.B. strength also gave a linear relationship with the variation of this peak ratio as follows. [fig. 5(e), 5(f)].

For the A- series resins

$$IB = -0.224Y_4 + 0.749 \qquad r = 0.891$$

Similarly for the B- series resins

$$IB = -0.058Y_4 + 0.748 \qquad r = 0.926$$

Where Y_4 = (o+p)/Me Peak ratio

IB = Wet Internal Bond strength (MPa)

Similarly another set of equations have been obtained to evaluate the variation of the DINv100 I.B. strength with this peak ratio and are given below.

For the A- series

$$IB = -0.024Y_4 + 0.202 \qquad r = 0.718$$

For the B- series

$$IB = -0.023Y_4 + 0.308 \qquad r = 0.885$$

Where IB = DINv100 Internal Bond strength (MPa)

and Y_4 = (o+p)/Me Peak ratio

2.4.5 (Mo+Me)/(o+p) peak ratio

When reaction proceeds an increase in methylol groups, methylene bridging groups, ether linkages and simultaneously the corresponding reduction in the *ortho* and *para* positions can be expected (Table 3).

Therefore, a gradual increase in (Mo+Me)/(o+p) peak ratio with F:P molar ratio is observed. This ratio can be considered as a combination of two of the peak ratios already discussed viz., Mo/(o+p) and (o+p)/Me. Mo/(o+p) ratio gave an exponential relation and although (o+p)/Me ratio gave the best correlation linearly, it also gave an exponential correlation factor of above 0.84 with F:P molar ratio. So their combination can be best describe exponentially.

If all the substituted functional groups viz., methylols, methylene ethers and the methylene bridges versus *ortho* and *para* free sites had been considered correlation coefficients, would be high. (But, on curing, methylene ethers break down forming methylol groups and formaldehyde. It has been seen from the ^{13}C NMR spectral analysis that these are relatively small number of methylene ether bridges present in the resins. Therefore even though the contribution from this

species to the I.B. strength is not considered it does not lead to a large error in the final result. This is however important to the boards formaldehyde emission and is discussed in the next Chapter.

At higher molar ratio the variability in this peak ratio for the A- series is very much higher than that of the B- series of resins (compare 2.2:1A to 2.2:1B Fig 6).

Peak ratio versus F:P molar ratio gave the following exponential equations. [fig. 6(a), 6(b)].

For the A- series

$$\ln Y_5 = 3.671P - 5.589 \qquad r = 0.965$$

similarly for the B- series

$$\ln Y_5 = 2.746P - 4.791 \qquad r = 0.903$$

Where Y_5 = (Mo + Me)/(o + p) Peak ratio

and P = F:P molar ratio

A logarithmic equation can be obtained that shows the variation of the dry I.B. strength with the variation of the peak ratio as follows. [Fig. 6(c), 6(d)].

For the A- series resins

$$IB = \ln(0.061Y_5 + 1.123) \qquad r = 0.918$$

Similarly for the B- series resins

$$IB = \ln(0.430Y_5 + 0.985) \qquad r = 0.974$$

Where $IB > 0$; and $Y_5 > 0$

Y_5 = (Mo+Me)/(o+p) Peak ratio

and IB = Dry Internal Bond strength (Mpa)

Similarly wet I.B. strengths can also be correlated to this peak ratio and the following set of equations can be obtained.

For the A- series resins

$$IB = 0.026Y_5 + 0.118 \qquad r = 0.876$$

Similarly for the B- series resins

$$IB = 0.205Y_5 - 0.019 \qquad r = 0.930$$

Where Y_5 = (Mo+Me)/(o+p) Peak ratio

and IB = Wet I.B. strength (MPa)

Fig 6(c), 6(d) shows the variation of wet I.B. strength of the boards with this peak ratio for the A-and B- series of resins respectively.

Similarly another set of equations can be presented to evaluate the variation of the DINv100 I.B. strength with this peak ratio as follows.

For the A- series

$$IB = 0.011Y_5 + 0.037 \quad r = 0.812$$

For the B- series

$$IB = 0.084Y_5 - 0.001 \quad r = 0.890$$

Where IB = DINv100 Internal Bond strength (MPa)

and Y_5 = (Mo+Me)/(o+p) Peak ratio

2.4.6 Mo/(m+B) peak ratio

An increase in Mo/(m+B) peak ratio is observed with the increase in F:P molar ratio for both series of resins. A mathematical expression can be presented correlating the variation of this peak ratio with the F:P molar ratio. It is important to note that in determining the equations some data points had to left out due to the large error. viz., those for the 1.8:1A resin and 2.2:1B resin respectively. Fig 7 shows

the variation of calculated ratios for the different resins and fig. 7(a), 7(b) shows the variation of this peak ratio for the individual resin.

For the A- series resins

$$\ln Y_6 = 0.948P - 2.892 \qquad r = 0.894$$

For the B- series resins

$$\ln Y_6 = 0.723P - 2.646 \qquad r = 0.746$$

Where Y_6 = Mo/(o+p) peak ratio

P = F:P molar ratio

Similarly I.B strength data also can be correlated to this peak ratio and the following set of equations can be obtained. [fig. 7(c), 7(d)].

For the A- series

$$IB = 1.850Y_6 - 0.212 \qquad r = 0.780$$

Similarly for the B- series

$$IB = 2.365Y_6 - 0.134 \qquad r = 0.592$$

Where IB = Dry Internal Bond strength data (MPa)

Y_6 = Mo/(m+B) peak ratio

The correlation is poor for both series. Methylol group represent just only one out of three possible substituted groups to the phenolic aromatic ring. (m+B) represents the total blocked species. Therefore this may be expected.

The regression analysis of the wet I.B. strength and DINv100 I.B. strength versus this peak ratio data are not reported here as the correlation was too poor. But still there was an increasing I.B. stre[illegible] tendencies with this peak ratio.

2.4.7 Me/(m+B) peak ratio

This peak ratio also presents the same tendency as the Mo/(m+B) peak ratio discussed before. With increasing in F:P molar ratio an increase in peak ratio can be expected. Fig 8 shows the variation of ratios for the different resin series.

The variation of the Me/(m+B) peak ratio has a relatively good correlation with the F:P molar ratio for the A- series, but the B- series gave a very poor correlation. Regression analysis of the peak ratio versus the molar ratio gave the following set of equations. [Fig. 8(a), 8(b)].

For the A- series

$Y_7 = 0.027P - 0.003$ $\quad r = 0.691$

Similarly using the whole set of data points for the B- series a linear equation can be presented. But if 2.12:1 F:P molar ratio point is eliminated this phenomena can be best represented exponentially.

$$Y_7 = 0.015P + 0.017 \qquad r = 0.251$$

$$\ln Y_7 = -0.365P - 2.791 \qquad r = 0.834$$

Where Y_7 = Me/(m+B) peak ratio

and P = F:P molar ratio

The dry I.B. strength versus this peak ratio gave the following set of equations by regression analysis. However the correlation is poor. [Fig. 8(c), 8(d)].

For the A- series

$$IB = 10.835Y_7 - 0.197 \qquad r = 0.607$$

For the B- series

$$IB = 4.330Y_7 + 0.241 \qquad r = 0.310$$

Where IB = dry Internal Bond strength (Mpa)

and Y_7 = Me/(m+B) peak ratio

Here again the regression analytical equations of peak ratio versus wet I.B. strength and DINv100 are not reported as the correlation is very poor. A clear indication that this NMR peak ratio cannot be used successfully. A polynomial regression equation could have been used to explain these phenomena with a higher correlation. But it is not a true reflection since the fitting of a polynomial equation is to adjust, to include all the experimental points without considering deviations that could be due to experimental error.

2.4.8 (o+p)/{(o+p)+(m+B) peak ratio

This is the extended case of (o+p)/(m+B) peak ratio discussed before and a similar trend can be expected. Variation in peak ratio with the molar ratio gave a higher precision than the (o+p)/(m+B) peak ratio for the A- series and fig 9 shows the relationship between the calculated ratios for the different resins. Following a set of linear equations gave the best coefficients with the experimental data for the individual series. [Fig. 9(a), 9(b)].

For the A- series

$$Y_8 = -0.329P + 0.751 \qquad r = 0.997$$

similarly for the B- series

$$Y_8 = -0.328P + 0.817 \qquad r = 0.990$$

Where Y_8 = (o+p)/{(o+p)+(m+B)} peak ratio

P = F:P molar ratio

When it comes to the I.B. strength the same trend in the correlation coefficient was observed. For the single-step formaldehyde addition series (A- series), an exponential relationship can be obtained by regression analysis [fig. 9(c)].

$$\ln IB = -7.258Y_8 - 0.015 \qquad r = 0.996$$

Similarly an exponential equation can also be presented to describe the phenomena for the multiple-formaldehyde addition resin series (B-series). [fig. 9(d)].

$$\ln IB = -5.681Y_8 + 0.392 \qquad r = 0.972$$

Where IB = Dry Internal Bond strength (MPa)

and Y_8 = (o+p)/{(o+p)+(m+B)} peak ratio

Wet I.B. strength data can be best represented by a set of linear equations. [fig. 9(e), 9(f)]

For the A- series

$$IB = -4.699Y_8 + 0.782 \qquad r = 0.992$$

Similarly for the B- series

$$IB = -3.088Y_8 + 0.930 \qquad r = 0.993$$

Where IB = Wet Internal Bond strength (MPa)

and $Y_8 = (o+p)/\{(o+p)+(m+B)\}$ peak ratio

As done before another set of equations can be presented to evaluate the variation of the DINv100 I.B. strength with this peak ratio as follows.

For the A- series

$$IB = -1.167Y_8 + 0.270 \qquad r = 0.904$$

Similarly for the B- series

$$IB = -1.270Y_8 + 0.384 \qquad r = 0.951$$

Where IB = DINv100 Internal Bond strength (MPa)

and $Y_8 = (o+p)/\{(o+p)+(m+B)\}$ peak ratio

2.4.9 Me/{(o+p)+(m+B)} peak ratio

This is the extended case of Me/(o+p) peak ratio discussed before. It shows an improvement over the previous case. Figure 10 give the relationship between the calculated ratios for the different resins. The variation of individual peak ratio gave the following set of linear equations and it is worth while to note that some data points had to be eliminated due to the large error (viz., 1.8:1A and 2.2:1B). [fig. 10(a), 10(b)].

For the A- series

$$\ln Y_9 = 0.990P - 5.102 \qquad r = 0.974$$

Similarly for the B- series

$$\ln Y_9 = 1.510P - 5.683 \qquad r = 0.917$$

where Y_9 = Me/(o+p)(m+B) peak ratio

and P = F:P Molar ratio

Dry I.B. strength data were also subjected to regression analysis and gave the following linear equations with the best correlation. [Fig. 10(c), 10(d)].

For the A- series

$$IB = 18.973Y_9 - 0.321 \qquad r = 0.988$$

Simllarly for the B- series

$$IB = 9.762Y_9 - 0.069 \qquad r = 0.933$$

where Y_9 = Me/(o+p)(m+B) peak ratio

and IB = Dry Internal Bond strength (MPa)

It can be seen from the figures 10(c) and 10(d) that experimental I.B. strength data in the A- series coinside well with the straight line; but in the B- series data are scattered and lie along both sides of the straight line although it gives a higher correlation coefficient.

Wet I.B strength data also gave a set of linear equations. To get a good approximate equation some data had to be eliminated viz., 1.8:1A. Here again in the B- series experimental data points are scattered equally along the straight line and still gave a good correlation. [fig. 10(e), 10(f)].

For the A- series

$$IB = 19.475Y_9 - 0.518 \qquad r = 0.955$$

For the B- series

$$IB = 7.854Y_9 - 0.090 \qquad r = 0.955$$

Where IB = wet Internal Bond strength (MPa)

and Y_9 = Me/{(o+p)+(m+B) peak ratio

The DINv100 I.B. strength data also gave the following a set of linear equations with the variation of this peak ratio as follows.

For the A- series

$$IB = 8.017Y_9 - 0.211 \qquad r = 0.915$$

For the B- series

$$IB = 2.826Y_9 - 0.009 \qquad r = 0.935$$

Where IB = DINv100 Internal Bond strength (MPa)

and Y_9 = Me/{(o+p)+(m+B) peak ratio

2.4.10 Mo/{(o+p)+(m+B) peak ratio

This peak ratio can be considered as the combination of Mo/(o+p) and Mo/(m+B) peak ratios discussed earlier. As previously discussed the individual peak ratio of the two groups gave exponential relations with the variation of F:P molar ratio. Therefore, can except an

exponential relation from the combination as well. Fig 11 shows the relationship between the calculated peak ratios for the different resins. By regression analysis following a set of exponential equations could be obtained to evaluate the variation of the peak ratio(s) with the F:P molar ratio for the two series. [fig. 11(a), 11(b)].

For A- series

$$\ln Y_{10} = 1.399P - 3.975 \qquad r = 0.995$$

For B- series

$$\ln Y_{10} = 1.471P - 4.209 \qquad r = 0.985$$

Where $Y_{10} = Mo/[(o+p)+(m+B)]$

and P = F:P molar ratio

Dry I.B. strength data gave a set of linear regression equations with this peak ratio as follows. [fig. 11(c), 11(d)].

For A- series

$$IB = 2.367Y_{10} - 0.196 \qquad r = 0.983$$

For B- series

$$IB = 2.880Y_{10} - 0.193 \qquad r = 0.992$$

Where $Y_{10} = Mo/[(o+p)+(m+B)]$

and IB = dry Internal Bond strength (MPa)

Similarly wet I.B. strength data can also be correlated to this peak ratio and following equations can be obtained. [fig. 11(e), 11(f)].

For A- series

$$IB = 3.645Y_{10} - 0.815 \qquad r = 0.964$$

For B- series

$$IB = 3.089Y_{10} - 0.482 \qquad r = 0.981$$

Where $Y_{10} = Mo/[(o+p)+(m+B)]$

and IB = wet Internal Bond strength (MPa)

Similarly another set of equations can be presented to evaluate the variation of the DINv100 I.B. strength with this peak ratio as follows.

For the A- series

$$IB = 1.038Y_{10} - 0.171 \qquad r = 0.900$$

For the B- series

$$IB = 1.828Y_{10} - 0.336 \qquad r = 0.991$$

where IB = DINv100 Internal Bond strength (MPa)

and $Y_{10} = Mo/[(o+p)+(m+B)]$

So far in this chapter contribution from individual species to the internal bond strengthes of particleboard have been considered and most species correlated well giving high coefficients of correlation. The same approach can be extended by combining more ratios of important species that have a major contribution for the performance of the resins. This is in order that single equations can be presented to evaluate the physical and chemical properties of a particleboard from the ^{13}C NMR spectra of a particular resin used for the manufacture. The results of each one of the earlier ten ratios studied were taken into consideration. Table 4,5 and 6 shows the NMR species ratio correlation coefficients to the I.B. strengths for the respective series of resins. It can be seen that many (but not all) of the species ratio correlated well with the I.B. strength results for both the A- and B- series. But it can be considered that some ratios are

repetition of parts of others e.g., Y_5 can be considered as a combination of Y_3, Y_4 and the same time Y_5 can be considered as a combination of Y_6, Y_7. Therefore in presenting single equations to evaluate the physical and chemical properties of a particleboard double counting of the species should not occur.

It also can be further deduced that ratios such as Mo/Me are likely to play an important role in the final I.B. strength of a board. From the correlation studies the (o + p)/(m + B) ratio also appears to play a major role to the I.B. strength. This makes sense, since an increase in free *ortho* plus *para* sites, relative to the total blocked sites in the phenolic ring means a PF resin with fewer reactive functional groups, i.e., a lower potential density of cross-linking contributing to poor wood adhesive performance.

Hence, it can be deduced that all the ^{13}C NMR species ratio data discussed earlier could be presented by combining only these two ratios together to formulate just one equation to evaluate the I.B. strengthes of a particleboard produced by a particular series of resin.

Therefore the two above mentioned species ratios can be related to the I.B. strength by taking the respective experimental data.

The following equation was obtained for the dry I.B. Strength of a particleboard prepared using the A- series resins,

$$IB = 0.069Y_1 - 0.486Y_2$$

with an estimated standard deviation = 0.053

Similarly for the B- series

$$IB = 0.052Y_1 - 0.192Y_2$$

gave an estimated standard deviation = 0.033

Where IB = Dry Internal Bond strength (MPa)

Y_1 = Mo/Me Peak ratio

Y_2 = (o+p)/(m+B) species ratio

The same hypothesis has been extended to formulate an equation to predict the wet I.B. strength of a particleboard from the ^{13}C NMR data of the relevant resin by just a single equation.

For the A- series resins the following equation was obtained.

$$IB = 0.032Y_1 - 0.293Y_2$$

with an estimated standard deviation = 0.061

Similarly for the B- series

$$IB = 0.025Y_1 - 0.154Y_2$$

gave an estimated standard deviation = 0.055

Where IB = Wet Internal Bond strength (MPa)

Y_1 = Mo/Me Peak ratio

Y_2 = (o+p)/(m+B) species ratio

In addition to that, another set of linear equations can be presented to evaluate the DINv100 I.B. strength of a particleboard by the combination of the same species ratio together.

For the A- series

$$IB = 0.034Y_1 - 0.585Y_2$$

with an estimated standard deviation = 0.077

Similarly for the B- series

$$IB = 0.035Y_1 - 0.671Y_2$$

gave an estimated standard deviation = 0.168

Where IB = DINv100 Internal Bond strength (MPa)

Y_1 = Mo/Me Peak ratio

Y_2 = (o+p)/(m+B) species ratio

It is worth while to note that the "potential" degree of cross-linking (Mo/Me) has a positive contribution and simultaneously the ratio of free *ortho* plus *para* sites in the phenolic ring to the *meta* free plus all the blocked (already reacted) sites has a negative contribution to the I.B. strength. Therefore a PF resin to yield a higher I.B. strength it must have a higher "potential" degree of cross-linking (mo/Me) and the same time a lower (o+p)/(m+B) ratio.

This will be a very interesting conclusion; since it gives an idea about the degree of polymerisation of a PF resin. When single-step addition of formaldehyde (A) series resins and multiple-step addition of formaldehyde to phenol (B) series resins are compared the A- series has produced relatively lower Mo/Me ratio than the corresponding B-series. The same time has a lower (o+p)/(m+B) ratio than the corresponding B- series. So as the overall effect B- series perform better in wood adhesion than the corresponding A- series.

To illustrate the same hypothesis in a different angle another linear equation can be presented by considering the contribution of individual species to the I.B. strength and this is more flexible than the previously discussed equation as it consider the contribution from each individual species separately.

The following equation was obtained for the dry I.B. strength of a particleboard using the A- series resins,

$$IB = -0.470Y_8 + 3.734Y_9 + 1.431Y_{10}$$

and the standard deviation = 0.041

Similarly for the B- series

$$IB = -0.389Y_8 + 2.543Y_9 + 1.874Y_{10}$$

gave a standard deviation = 0.024

Where IB = Dry Internal Bond strength (MPa)

Y_8 = (o+p)/{(o+p)+(m+B)} peak ratio

Y_9 = Me/{(o+p)+(m+B)} peak ratio

Y_{10} = Mo/{(o+p)+(m+B)} peak ratio

The wet I.B. strength data of a particleboard can also be represented using the same methodology as follows.

For the A- series

$$IB = -1.812Y_8 + 11.674Y_9 + 0.002Y_{10}$$

the standard deviation = 0.100

Similarly for the B- series

$$IB = -0.187Y_8 + 0.887Y_9 + 1.883Y_{10}$$

gave the standard deviation = 0.006

Where IB = wet Internal Bond strength (MPa)

Y_8 = (o+p)/{(o+p)+(m+B)} peak ratio

Y_9 = Me/{(o+p)+(m+B)} peak ratio

Y_{10} = Mo/{(o+p)+(m+B)} peak ratio

The DINv100 I.B. strength results can also be presented by the same manner as follows.

For the A- series

$$IB = -0.743Y_8 + 1.915Y_9 + 0.428Y_{10}$$

the standard deviation = 0.075

Similarly for the B- series

$$IB = -0.134Y_8 + 0.059Y_9 + 0.967Y_{10}$$

with the standard deviation = 0.030

Where IB = DINv100 Internal Bond strength (MPa)

Y_8 = (o+p)/{(o+p)+(m+B)} peak ratio

Y_9 = Me/{(o+p)+(m+B)} peak ratio

Y_{10} = Mo/{(o+p)+(m+B)} peak ratio

In all these equations Y_8 has a negative contribution, whereas Y_9 and Y_{10} have a positive contribution, to the I.B. strength. Therefore it concludes that the presence of free *ortho* and *para* sites relative to the total sites in the phenolic ring means an index of lower reactive functional groups contributing adversely to the wood adhesive performance.

The error in presenting these equations appear to be on the low side. Therefore it indicates that the equations are quite satisfactory. Thus it is possible to conclude that these equations cover almost all the major contributing factors to wood adhesive performance in PF resins. The coefficients of the equations are unique for each homologous series of resins. The equation would also change for resins synthesised and boards manufactured under different conditions.

But there is an important factor which then can be deduced is that in PF resin series that the physical properties of a hardened resin (such as I.B. strength) can be related to the ratio of species present in the

resin before cure. There are also other ratios that could be considered, but their significance would be very low.

Therefore the general equation describing both the strength of a hardened PF resin, and with particleboard backed with it should be

$$\text{I.B. strength} = a[(o+p)/\{(o+p)+(m+B)\}] + b[Me/\{(o+p)+(m+B)\}] + c[Mo/\{(o+p)+(m+B)\}]$$

where the coefficients a,b,c are independent characteristic variables for each type of resin series preparation used and for an I.B. dry or wet.

CHAPTER THREE

RELEASE OF FORMALDEHYDE BY PARTICLEBOARD

DISCUSSION

3.1. *OUTLINE*

The formaldehyde emission decay from wood products has been investigated by several scientists. Kazakevics [39] has investigated New Zealand particleboard, and concluded that there was a rapid decrease in the rate of formaldehyde emission over the first year of storage. Gammage and Matthews [40] have conducted fast decay, slow decay by FTM 2 and home studies on formaldehyde emission. Singh [41] and Anderson [42] have conducted some measurements of formaldehyde in houses according to house age. Ferg [35] also has done some studies in relation to formaldehyde emission. But all these studies seems to have done in relation to UF bonded wood products.

Therefore although formaldehyde emission is not of major importance in PF resins, emission from particleboard bonded with this resin being generally low, it is nonetheless of interest to see if correlation between ^{13}C NMR peak ratios and emission exist. Thus as in the previous Chapter a similar approach has been taken for the correlation of ^{13}C NMR peak ratios of different characteristic chemical groups in

the resin known or suppose to contribute to the formaldehyde emission from the particleboard bonded with it.

Reactions of formaldehyde with phenol form non-hydrolysable bonds and the cured resin is stable and does not break down; hence it does not release formaldehyde even under extreme conditions. Therefore in contrast to UF resins, formaldehyde loses its chemical identity in PF resins. Therefore the formaldehyde emission is always due to an incomplete reaction of phenol and formaldehyde or to an excess of formaldehyde or formaldehyde - donating agents (paraformaldehyde) in the adhesive formulations.

It has been reported that the formaldehyde levels associated with wood-products bonded with alkaline cured PF adhesives are in most cases extremely low [43]. During hot-pressing of the particleboard only part of the excess uncured formaldehyde is emitted. The residual formaldehyde remaining entrapped may be unable to disproportionate to methanol and formic acid by the cannizarro reaction.

Therefore in PF bonded wood products it is possible that the free formaldehyde can react with polysaccharides and other wood products etc.,. This formaldehyde can exist in a wide variety of states, including dissolved methylene glycol monomers and oligomers,

polysaccharide hemiformals and formals etc., and each of these state may be a potential source of formaldehyde emission.

This emission potential approaches to zero as the small amount of formaldehyde initially present in the particleboard is released. Moreover as the emission potential is very low testing of PF-bonded particleboard and plywood usually give values in the range of experimental error of the method or only a very little above [43].

3.2. *RESIN ANALYSIS*

^{13}C NMR spectra indicated that only F:P of $\leq$ 1.8 less than 100% of the charged formaldehyde has reacted in the resin, showing a free formaldehyde peak at δ = 83.73 ppm (see spectra 4,5,6,7 and 11,12,13,14,15 respectively). Therefore it can be assumed that low F:P molar ratio alkaline PF resins synthesised contain a very little or no residual free formaldehyde and NMR is not sensitive enough to indicate its existence.

As it has been stated earlier that most resins had to be synthesised more than once. While doing so even for the same F:P molar ratio resins spectra, some indicated the presence of the free formaldehyde peak but some did not; (compare spectra 6,7 in the A- series and 11, 12 in the B- series respectively).

Loss of free formaldehyde during the resin synthesis or the sample preparation stages can be given as the possible explanation for the observed formaldehyde loss in these resins indicated by the absence of the peak at δ = 83.73 ppm. In addition to this Gollob [44] has reported that some formaldehyde may has consumed in the cannizarro reaction which is favoured under the conditions of high alkalinity used in the synthesis.

The formaldehyde emission from the particleboards prepared with the different resins were extracted by using the desiccator method (See Experimental, 4.4 for details).

It has been reported that the reproducibility of the desiccator method is sometimes unsatisfactory due to the inhomogeneities in the specimens [41]. This could be avoided by testing about six specimens from one particleboard and averaging out the data.

Further it has been reported that the static conditions of the confinement in the desiccator method restrict spontaneous emission, while the inevitable time lag between emission and absorption mean that this method cannot be truly quantitative [43]. In this case of study, emission from the PF bonded particleboard being very low and the same time the test was carried at room temperature and the

testing period was quite long enough so that it can be assumed that all the free formaldehyde has been emitted from the particleboard.

For the standardization of the desiccator method variant, standard solutions were prepared by dissolving a known amount of formalin (37%) solution in distilled water.

Fluorometric Acetlyacetone method was used for the determination of the emission intensity of the standard formaldehyde solutions as well as the extracted formaldehyde solutions from the particleboards.

The fluorescence emission intensity of the standard solutions were determined and their results were plotted on a graph with a best curve fit (see Table 11 and Fig. 12 respectively).

The graph obeyed the Beers law at low formaldehyde concentrations, but deviated from the linearity at higher concentrations. This has been due to the self absorption of the sample in the high concentrated solutions.

The best fit polynomial equation for the standardised curve (fig. 12) can be given as follows.

$$Y = 44.994 + 243.877X - 116.379x^2 + 17.592X^3 \quad r = 0.996$$

The lower range of this curve can be best represented by the following linear equation and has been used for the calculations in this study.

$$Y = 283.919X + 38.084 \qquad r = 0.994$$

Where Y = Fluorescence Intensity

and X = Formaldehyde concentration ($\mu g/l$)

In this study all the readings obtained, were low enough to lie in the linear range of the polynomial curve obtained above and therefore further dilution of the solutions were not necessary.

One layer "core" only particleboards were produced. The formaldehyde emission from "core" only boards are usually higher than the three layer commercial boards. The emission levels obtained by the desiccator method were very low at microscopic level. This could have been further reduced if an additive (urea, di or tri methylol urea or melamine etc., 5 to 15 % of phenolic resin solids) had been used. The dispersion of the alkaline media of the phenolic resin inhibit their curing reaction and allows the additives to function as methylolated cross-linking units for the PF polymer.

All the particleboards were tested during the Winter at normal room temperature without any incubation due to some practical difficulties; hence eventually they were subjected to the temperature fluctuation during the total testing period of emission over the 24 hours (i.e., ~ +18, 19 °C during the day time and 0, -1 °C during night).

It has been reported that under normal conditions an increase in temperature of 5-8 °C doubles the formaldehyde concentration and an increase in relative humidity of 10% enhance the formaldehyde concentration level by 15-20% [43]. In this study the first factor has influenced. Therefore the obtained values from the desiccator method could have been higher it was possible to carried out the experiments under control conditions.

The results obtained by the disaccator method have been converted to the WKI method and reported as mg per 100g of particleboard according to a modified transformation equation found in the literature (see Table 12, 13 for the results and APPENDIX 3 for the modified transformation equations respectively) [35].

A lower formaldehyde emission level was obtained for the particleboards prepared with the multiple-step formaldehyde addition (B- series) to the single step formaldehyde addition (A- series)

(compare 1.1:1A to 1.1:B - 2.2:1A to 2.2:1B respectively in Table 12 and 13). The reason for this could be due to the fact that during the early stage of the reaction synthesis there is less free formaldehyde content in the reaction mixture when the resin is synthesised by the multiple step addition over the single step addition.

Experimental formaldehyde emission data converted to the WKI method can be correlated to the variation of the F:P molar ratio and are given below. [Fig 13(a), 13b)]. As it can be seen, the equations explain the phenomena well.

For the A- series

$$F = 0.007P + 2.297 \qquad r = 0.987$$

Similarly for the B- series

$$F = 0.002P + 2.301 \qquad r = 0.954$$

where F = Formaldehyde emission (mg/100g of board)

and P = F:P Molar Ratio

As mentioned earlier in PF resins only three species could possibly be considered as potentially contributing to the formaldehyde emission

from a particleboard bonded with it; viz., methylol species, ether species and free formaldehyde peak.

Therefore the experimental formaldehyde emission data converted to WKI method can be correlated to the each of the suspected emission source of peak ratios as follows.

3.2.1 Mo/{(o+p)+(m+B)} peak ratio

In PF resins the methylol group is attached to one of the carbons of the aromatic ring. Although C--C bonds are considered to be stable to hydrolysis, recently it has been shown by Myers that this group may not exclude as a "potential" formaldehyde emission source [45].

Even though the variation of this Y_{10} Peak ratio with the variation of the F:P molar ratio has been discussed previously it is repeated below. [Fig. 11(a), 11(b)].

For the A- Series

$$\ln Y_{10} = 1.399P - 3.975 \qquad r = 0.995$$

Similarly for the B- Series

$$\ln Y_{10} = 1.471P - 4.209 \qquad r = 0.985$$

Where P = F:P Molar ratio

and Y_{10} = Mo/{(o+p)+(m+B)} peak ratio

With increasing F:P molar a gradual increase in this peak ratio and the same time a gradual increase in the experimental formaldehyde emission is observed (Table 13, 15). The experimental formaldehyde emission data from the particleboard therefore can be best correlation linearly to the variation of this peak ratio as follows [fig 11(g), 11(h)].

For the A- series

$$F = 0.025Y_{10} + 2.303 \qquad r = 0.981$$

Similiarly for the B- series

$$F = 0.009Y_{10} + 2.303 \qquad r = 0.982$$

where F = Formaldehyde emission (mg/ 100g of board)

and Y_{10} = Mo/{(o+p)+(m+B)} peak ratio

3.2.2 Et/{(o+p)+(m+B)} peak ratio

Gollob [44] studied the acetate derivatives of PF resins by ^1H NMR varying F:P molar ratio and NaOH level and reported that ethers are present in high F:P formulations with little NaOH but decreases if NaOH increases, if F:P decreases or with reaction time.

In this study also with increasing F:P molar ratio a gradual increase in this peak ratio is observed. In the A- series the situation can be best described linearly after eliminating F:P of 1.3:1, 1.8:1, 2.0:1 data points due to large error [fig. 14(a)]. But in the B- series the variation of this peak ratio with F:P molar ratio can be best represented exponentially [fig. 14(b)].

For the A- Series

$$Y_{12} = 0.108P - 0.089 \qquad r = 0.999$$

Similarly for the B- Series

$$\ln Y_{12} = 4.200P - 11.271 \qquad r = 0.982$$

where P = F:P Molar Ratio

and Y_{12} = Et./{(o+p)+(m+B)} peak ratio

The experimental formaldehyde emission data from the particleboard by WKI method can also be correlated linearly to the variation of this peak ratio and are given below. [fig 14(c), 14(d)].

For the A- series

$$F = 0.073Y_{12} + 2.302 \qquad r = 0.997$$

Similarly for the B- series

$$F = 0.018Y_{12} + 2.304 \qquad r = 0.909$$

where F = Formaldehyde emission (mg/ 100g of board)

and Y_{12} = Et./{(o+p)+(m+B)} peak ratio

3.2.3 Free F/{(o+p)+(m+B)} peak ratio

As mentioned earlier the free formaldehyde peak was observed in the spectra ≤ 1.8:1 of F:P molar ratio resins only. But this peak was not observed in the 1.8:1A resin [Spectra 4, Table 15 (a)]. In the B- series 2.2:1B resin, free formaldehyde data point had to be omitted due to large error [Table 15 (b)]. Therefore in the A- series only 2 data sets and in the B- series only 3 data sets can be considered.

Therefore the variation of this peak ratio with the variation of F:P molar ratio for the two series can be best represented with the available few experimental data points as follows. [Fig. 15(a), 15(b)].

For the A- Series

$$Y_{11} = 0.260P - 0.495 \qquad r = 1$$

Similarly for the B- Series

$$\ln Y_{11} = 13.958P - 30.705 \qquad r = 0.917$$

where P = F:P Molar Ratio

and Y_{11} = Free Formaldehyde Peak/{(o+p)+(m+B)}

Free formaldehyde peak also can be correlated to the experimental formaldehyde emission data (converted to WKI method) as follows. [Fig. 15(c), 15(d)].

For the A- series

$$F = 0.040Y_{11} + 2.310 \qquad r = 1$$

Similarly for the B- series

$$F = 0.003Y_{11} + 2.305 \qquad r = 0.964$$

where F = Formaldehyde emission (mg/ 100g of board)

and Y_{11} = Free Formaldehyde Peak/{(o+p)+(m+B)}

Table 16 shows the ^{13}C NMR species ratios correlation to the experimental formaldehyde emiss... and Table 17 shows the ^{13}C NMR species ratio correlation to the ...ation of F:P molar ratio for the two series of resins respectively. Therefore the individual peak ratios

discussed earlier can be considered together to formulate a combined equation for a specific series of resins by taking the respective experimental data.

Therefore for the A- series the following equation can be obtained.

$$F = -39.3783Y_{10} + 38.2311Y_{11} + 105.0315Y_{12}$$

Standard deviation = 0.403 mg/100 g board. It is necessary to note that here linear regenerated formaldehyde emission data had to be used.

Similarly for the B- series

$$F = 17.893Y_{10} + 2.440Y_{11} - 43.866Y_{12}$$

with a standard deviation = 0.887 mg/100g board.

Where Y_{10} = Mo/{(o+p)+(m+B)}

Y_{11} = Free formaldehyde/{(o+p)+(m+B)}

Y_{12} = Ether/{(o+p)+(m+B)}

and F = formaldehyde emission in mg/100 g of particleboard by WKI method.

It is of interest to note the sign of the coefficients a, b and c in these equations. The a coefficient is negative for the A- series and positive for the B- series; this indicates that in the A- series a considerable amount of methylols lead to methylene ether bridges during hardening subtracting from the value of formaldehyde emission. In the B- series instead the amount of methylols leading to methylene ether on hardening is low. The finding is consistent with the processes of preparation of the two series of resins. In the B- series the proportion of methylols is much lower than in the A- series as expected. This behaviour is confirmed by the sign of the c coefficient. In the A- series part of the high proportion of methylene ether formed, reorganise readily to methylene linkages contributing significantly to hardened resin formaldehyde emission. This is not the case for the lower proportion of methylene ethers in the B- series. The sign of the b coefficient is always positive, indicating that free formaldehyde always contributes to formaldehyde emission.

Therefore the formaldehyde emission from a particleboard made by a typical PF resin can be given by a general equation as follows. The coefficients of the equations are unique to the particular formaldehyde emission determination method.

$$F = a[\{Mo/\{(o+p)+(m+B)\}\}]+b[\{\text{free } F/\{(o+p)+(m+B)\}\}]+$$

$$c[\{\text{Methylene ether}/\{(o+p)+(m+B)\}]$$

However these equations appear to be valid for a short period of time. Zinn at. al. have conducted a long-term study of formaldehyde emission from particleboard and made the following conclusions [46].

(a) Formaldehyde emission levels from particleboard can be expected to decrease over time.

(b) The rate at which emission levels decrease is not constant, but diminishes with time.

(c) Generally, formaldehyde emission levels decreased linearly with respect to the natural log time.

(d) Decay of panel emission levels with respect to time of the medium density particleboards was strongly related to the initial emission level. The higher the initial emission level the greater the initial rate of decay.

Therefore in concluding the equations presented here can be used in predicting some of the physical and chemical properties of the

hardened PF resin by studying the ^{13}C NMR peak ratios of certain species in the liquid PF resin.

CHAPTER FOUR

EXPERIMENTAL

4.1 MATERIALS

4.1.1 Phenol

This is one of the main materials used in this study. M.W. 94.11 g/mol; colourless solid; purity 99%; crystalline form rhombic needles; refractive index 1.5425 at 40.6 °C; density = 1.072 g/ml at 20°C; melting point 41 °C; boiling point 182 °C; infinitely soluble in water from 66 °C.

4.1.2 Paraformaldehyde

A light yellow solid with the characteristic irritating odour of formaldehyde. It is a mixture of polyoxymethylene glycols having the type of formula $HO(CH_2O)_nH$, where the value of n varies from approximately 8 to 100 corresponds to an HCHO content up to 99%. and the balance consisting of combined water.

It dissolves in water with hydration and depolymerisation to yield formaldehyde solution. The rate of dissolution increases with temperature but decreases with increasing molecular weight, depending on the pH of the solvent medium.

In the pH range 3-5 the rate at which paraformaldehyde dissolves in water reaches a minimum, but increases rapidly at lower or higher pH values. Paraformaldehyde reacts as chemically as formaldehyde at a rate determined by the rate of depolymerisation under condition of use. The reactivity decreases with increasing molecular weight. On ageing, the average molecular weight of a polymer sample tents to increase gradually. Brands of commercial paraformaldehyde can be divided according to reactivity as fast, medium and slow. The brand used in study was Schering-Kahlbaum and can be regarded as a slow reactivity powder.

4.1.3 Formaldehyde solution

Formaldehyde can be most conveniently used as an aqueous solution although itself is a gas. The formulation used is a 37% by mass formaldehyde and 12% by mass methanol. Solution density; 1L = 1.09 kg.

4.1.4. Methanol

M.W. 32.04; refractive index 1.332 at 14.5 °C; density = 0.796 g/ml at 15°C; boiling point 64.45 °C; technical grade methanol was used.

4.1.5 Sodium hydroxide

M.W. 40.0 g/mol ordinary analar grade sodium hydroxide pellets were used.

4.1.6 Acetylacetone

Formula $C_5H_8O_2$; M.W.100.12 g/mol; Melting point -23 °C; Boiling point 139 °C; flash point 30 °C; refractive index = 1.451 at 20 °C; density 1L = 0.97 kg. Merck grade Acetylacetone was used.

4.1.7 Ammonium acetate

Formula CH_3COONH_4; M.W. 77.08 g/mol; Bulk density ~ 410 kg/m^3; melting point 114 °C; Merck grade Ammonium acetate was used.

4.1.8 Acetic acid

Formula CH_3COOH; M.W. 60.05 g/mol; Melting point 10 °C; boiling point 118 °C; flash point 40 °C; viscosity at 20 °C 1.53; technical grade acetic acid was used.

4.2 RESIN SYNTHESIS

4.2.1 A- Series: A series of PF resins of F:P molar ratios 1:1.1; 1.3:1; 1.5:1; 1.8:1; 2.0:1; and 2.2:1 (6 resins) were prepared as follows (A-series): 94g of phenol and the relative amount of paraformaldehyde to obtain the F:P molar ratios indicated above were added to 40g of

water/methanol 80/20 solution. The flask was immersed in an oil bath at 40°C and the mixture was stirred with a magnetic stirrer bar. After stirring for 10 minutes 5.0 ml NaOH (33%) solution was added to the mixture and 10 minutes later another 5.0 ml NaOH (33%) solution was added. The mixture was stirred for another 10 minutes and the temperature of the oil bath was increased slowly so that the reaction mixture reached reflux temperature (94 °C) over a period of 30 minutes, and during this period two other amounts of 5 ml (33%) NaOH were added at 10 minute interval. The mixture was refluxed under magnetic stirring for one hour and then cooled to ambient temperature in an ice bath. Viscosity of the resin was recorded and stored. Before application, the pH of the resin was adjusted too.

4.2.2 B- Series: Another series of resins (B- series) was prepared by stepwise addition of one of the reagents, according to the following procedure; 100 parts by mass of phenol, in 66.8 parts water and 15.6 parts of a 40% sodium hydroxide water solution was heated for 1 hour under magnetic stirring and in a reaction vessel equipped with reflux condensers and stabilised to 70 °C. The required amounts of 37% formalin solution, to obtain the molar ratios in addition to the ratios indicated in the previous method 2.12, (7 resins) were added in a number of equal aliquot, over a period of two and half hours, at 10 minutes intervals, while maintaining the reaction under magnetic

stirring and at 70 °C. During the last half an hour period of formalin addition the temperature of the reaction mixture was increased to 77-80 °C. The reaction mixture was maintained at this temperature for a 6 hour period, under magnetic stirring. The reaction was halted then by rapidly cooling to ambient temperature in an ice bath, the viscosity was recorded, and stored for further use.

4.3. PREPARATION OF TEST SPECIMENS

4.3.1 Particleboard

Triplicate (*Pinus Radiata*) one-layer core-only particleboards 12 mm thick were made from the modified resins to determine the st.ength of the cured resin. A particleboard is composed of wood chips that are bonded under heat and pressure with a thermosetting adhesive. The following set of conditions were kept the same for each of the boards prepared. About 400g of Pine chips in order to obtain the optimum board density of 650 -700 gcm^{-3}, varying in size from 1 to 2 mm thick and 0.5 - 3.0 cm long were used for each board sample. 8% (w/w) PF solids content, glue particles moisture content of 12 - 16 % were maintained. The pH of the resins were made approximately to 12.5 by the addition of NaOH (35% w/w) solution. The wood chips were passed through a gluing machine in which the glue was evenly mixed onto the wood chips.

The glued wood chips were sprayed by hand evenly on a wooden frame to give a particleboard size of 26x21x1.2 cm^3 after pressing.

A light water spray was applied to the surfaces of the boards before pressing. The water spray helps to shorten the pressing time; the water on the surface vaporises when in contact with the hot caul sheet of the press and migrate in the core of the panel thus causing a faster increasing of temperature and consequently faster curing. The water spray also prevent precuring of the adhesive on the surface of the board during closing of the press before contact with the hot top caul sheet.

Different pressing procedures can be applied. In this research pressing time for each particleboard was of 7.5 minutes: 2 minutes at 23.5 kg cm^{-2}, 2.5 minutes at 12 kg cm^{-2} 3 minutes at 3 kg cm^{-2} at a pressing temperature of 190 ^{o}C. The boards were left for two weeks before analysis.

The particleboards were subjected to a series of I.B. tensile-strength tests. (i) when dry - I.B. dry (ii) after subjected to an accelerated ageing durability test - I.B. wet (2h boiling followed by 16h drying at 105 ^{o}C (tested dried) [47]. The Internal Bond (I.B) tensile strength was measured using Haunsfield tensiometer. The tension was applied

perpendicular to the surface of the board giving a reading in kilo newton, later converted to MPa. the American standard specification. The original thickness of the particleboard and thickness after swelling and water absorption was also recorded. This is a good indication for the weather resistance as an exterior grade particleboard.

4.4. FORMALDEHYDE RELEASE BY PARTICLEBOARD.

Desiccator method [35,43] was used for the determination of the formaldehyde released by the particleboards made with PF resins. A 200 ml glass vessel filled with 100 ml distilled water was placed inside a two litre desiccator.

The particleboard specimens were cut, (25 mm x 25 mm x thickness), weighed and suspended over the water by a porcelain desiccator plate. The released formaldehyde was supposed to dissolve in distilled water. The desiccators were kept at room temperature for 24 hours (eventually they were subjected to the temperature fluctuation during the total period of emission i.e., ~ +18 to +19 during the day time and ~0 to -1 during night.) An average of 6 samples (two samples per time) per board were analyzed.

Fluorometric Acetylacetone method (with Hantzsch reagent) was used for the determination of formaldehyde content present in distilled water.

The standard solutions for the calibration curve were prepared by dissolving a known amount of formaldehyde in distilled water and diluting to the required concentrations.

10 ml of the sample or the standard solution and 10 ml of the *Hantzsch reagent* were mixed, and heated to 60 °C for 15 minutes (pH = 5.5 to 6.5). After cooling, the fluorescence of the solution was measured using a Parkin Elmer LS-5 Luminescence Spectrophotometer. Excitation took place at 410 nm and emission measured at 510 nm.

The results of the standard solutions were plotted on a graph and used for the determination of formaldehyde absorbed by the water from the particleboard in the desiccator (Table 10, 11).

Hantzsch Reagent

0.4 ml of Acetlyacetone, 0.6 ml of Acetic acid and 30.8 g of Ammonium Acetate were dissolved in distilled water and diluted to 200 ml. The reagent was prepared daily when needed prior to analysis.

4.5. TESTING METHODS

4.5.1 Viscosity

Viscosity of the resin is measured in centipoises with a Brookfield viscometer - model LVT. This is important in the case of particleboard preparation step when the resin is sprained into wood chips.

4.5.2 ^{13}C NMR Spectroscopy

^{13}C NMR spectra of the liquid resins were obtained on a AC200 (200 MHZ) spectrometer. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ for NMR control. $(CH_3)_3Si(CH_2)_3SO_3Na$ was [illegible] in D_2O, run separately, and the shifts for the four signals were [illegible]. About 1ml of liquid 50 % solid resin sample was placed in an NMR tube and diluted with about 0.4 ml deuterium oxide added directly to the sample.

4.5.3 Particleboard

4.5.3.1 Internal Bond tensile strength

The prepared particleboards were cut into small specimens (50 mm x 50 mm x thickness) and glued with a hot-melt thermoplastic adhesive to two metallic slabs and breaking stress was measured with a Hounsfield Tensiometer. This test was applied to the dry sample as and those that underwent an accelerated ageing durability (2 hr boil and 16 hr dry circle - tested dry) test [47]. In each case five

specimens were tested and the final value was obtained by averaging the results obtained.

4.5.3.2 Accelerated Ageing test

The particleboard samples were immersed in a steel water bath of boiling water and subjected to a two hour boil test. After exposure to the boiling test, the change in thickness was measure and recorded as a percentage. Then followed by a 16 hours dry at 105 °C. After exposure to the boiling test, the change in thickness was measure and recorded as a percentage. After cooling, the samples were ready for testing.

APPENDIX 1

The correlation between the physical properties (F:P molar ratio, I.B. strengths and formaldehyde emission) of resins and the particleboards prepared has been done by considering a linear regression equation: $Y = MX + B$, and the correlation coefficient r has been defined as follows, where 'X' is the dependent variable and 'Y' is the independent variable respectively.

$$r = (n\Sigma XY - \Sigma X\Sigma Y)/\sqrt{\{n\Sigma X^2 - (\Sigma X)^2\}\{n\Sigma Y^2 - (\Sigma Y)^2\}}$$

APPENDIX 2

The wet I.B. strength (I.B. strength of specimens after 2 hrs boil and 16 hrs dry - measured dry) can be correlated to the DINv100 I.B. strength (I.B. strength of specimens just after 2 hrs boil - measured wet) according to the following equation from unpublished results:

$$I.B._{DINv100} = 0.2605\ I.B._{wet} + 0.0905 \quad (i)$$

$$\text{And } I.B._{DINv100} < I.B._{wet} \quad (ii)$$

The condition (ii) should be valid for all the times at standard particleboard densities. At low wet I.B. ranges to satisfy this condition the above equation (i) can be modified as follows;

$$I.B._{DINv100} = 0.2605\ I.B._{wet}$$

APPENDIX 3: Reconstructed equation(s) to correlate the WKI method results and the Desiccator method results. (Data from Freg's Thesis)

Desiccator Method mg/100 g of Board	Desiccator Method µg/100 g of Board	WKI method mg/100 g of Board	WKI method µg/100 g of Board
0.33	330	4.0	4000
1.50	1500	8.2	8200
2.11	2100	11.0	11000
3.01	3010	14.6	14600
8.67	8670	38.2	38200

Correlation of Desiccator method & WKI method in milligram scale.

$D = 0.242W - 0.554$ $r = 0.999$

$W = 4.132D + 2.292$ $r = 0.999$

Where D = Desiccator method (mg F/100 g of board)
W = WKI method (mg F/100 g of board)

Correlation of Desiccator method & WKI method in microgram scale.

$D = 0.242W - 556.390$ $r = 0.999$

$W = 4.131D + 2303.20$ $r = 0.999$

Where D = Desiccator method (µg F/100 g of board)
W = WKI method (µg F/100 g of board)

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Table 1. Internal bond strength results for the particleboards prepared with the different Phenol-formaldehyde resins (Average Surface Area = 24.6 cm^3)

(a) A- Series Dry Test Results

Resin Sample	Density/$cm^{-3}g$	I.B. Strength /M.Pa
1.1	0.716	0.124
1.3	0.702	0.116
1.5	0.690	0.088
1.8	0.684	0.294
2.0	0.692	0.545
2.2	0.730	0.796

(b) B- Series Dry Test Results

Resin Sample	Density /$cm^{-3}g$	I.B. Strength /MPa
1.1	0.665	0.07
1.5	0.688	0.132
1.8	0.707	0.392
2.0	0.745	0.768
2.12	0.698	0.795
2.2	0.750	0.944

(c) A- Series Wet Test Results

Resin Sample	Density/$cm^{-3}g$	I.B. Strength/I.B.
1.8	0.689	0.081
2.0	0.695	0.290
2.2	0.748	0.692

(d) B- Series Wet Test Results

Resin Sample	Density /$cm^{-3}g$	I.B. Strength /MPa
1.8	0.627	0.105
2.0	0.720	0.492
2.12	0.680	0.620
2.2	0.739	0.648

Notation for the ^{13}C NMR Peak intensity data assignments for different PF resins for the I.B. Strength correlation

Mo = Total methylol species (peaks from 61.4 to 65.32 ppm)

Me = Total methylene bridging species (peaks from 29.21 to 41.00 ppm)

(o) = Total *ortho* free sites of the phenolic ring (peaks from 115.4 to 116.0 ppm)

(p) = Total *para* free sites of the phenolic ring (peaks from 119.9 to 120.9 ppm)

(m+B) = *meta* free positions & all blocked positions of the phenolic ring (peaks from 127.4 to 133.9 ppm)

Table 2: Selected average ^{13}C NMR peak intensity data assignments for different PF resins for the I.B. Strength correlation

A- Series

F/P molar ratio	Me groups 29.21 - 41.00 ppm	Mo groups 61.4 - 65.32 ppm	*ortho* free sites in phenolic ring 115.4 - 116.0 ppm	*para* free sites in phenolic ring 119.9 - 120.9	(m+B) sites in the phenolic ring 127.4 - 133.9 ppm
1.1	4.533	21.087	61.293	23.059	130.066
1.3	3.870	21.796	46.318	16.054	121.601
1.5	9.877	48.715	71.061	20.050	257.608
1.8	7.556	45.503	14.293	3.885	102.580
2.0	3.840	28.699	8.636	1.107	87.287
2.2	6.392	42.626	2.337	----	101.406

B- Series

F/P molar ratio	Me groups 29.21 - 41.00 ppm	Mo groups 61.4 - 65.32 ppm	*ortho* free sites in phenolic ring 115.4 - 116.0 ppm	*para* free sites in phenolic ring 119.9 - 120.9	(m+B) sites in the phenolic ring 127.4 - 133.9 ppm
1.1	4.01	15.043	56.502	21.046	92.964
1.3	5.814	27.659	71.605	23.856	146.773
1.5	3.202	17.195	39.658	10.821	115.788
1.8	3.498	29.743	28.106	6.451	123.480
2.0	4.496	51.465	29.612	3.562	149.558
2.12	1.965	7.233	2.749	-----	19.776
2.2	2.804	18.803	5.771	1.345	93.782

Notation for the ^{13}C NMR Peak intensity ratio data chart for the I.B. Strength correlation

$y_1 = Mo/Me$

$y_2 = (o+p)/(m+B)$

$y_3 = Mo/(o+p)$

$y_4 = (o+p)/Me$

$y_5 = (Me+Mo)/(o+p)$

$y_6 = Mo/(m+B)$

$y_7 = Me/(o+B)$

$y_8 = (o+p)/\{(o+p)+(m+B)\}$

$y_9 = Me/\{(o+p)+(m+B)\}$

$y_{10} = Mo/\{(o+p)+(m+B)\}$

Table 3: Average ^{13}C NMR Peak Intensity Ratio data chart

A- Series

F/P	1.1	1.3	1.5	1.8	2.0	2.2
y_1	4.654	5.632	4.932	6.022	7.474	6.669
y_2	0.660	0.513	0.354	0.177	0.112	0.023
y_3	0.252	0.350	0.535	2.503	2.946	18.240
y_4	18.558	16.117	9.225	2.406	2.537	0.366
y_5	0.306	0.412	0.643	2.919	3.340	20.975
y_6	0.167	0.179	0.189	0.444	0.329	0.420
y_7	0.036	0.032	0.039	0.074	0.044	0.063
y_8	0.376	0.339	0.261	0.151	0.100	0.023
y_9	0.019	0.021	0.028	0.063	0.040	0.062
y_{10}	0.089	0.119	0.140	0.255	0.296	0.411

B- Series

F/P	1.1	1.3	1.5	1.8	2.0	2.12	2.2
y_1	3.751	4.757	5.370	8.393	11.447	3.681	6.706
y_2	0.834	0.650	0.436	0.297	0.222	0.139	0.076
y_3	0.194	0.290	0.341	0.850	1.551	2.631	2.642
y_4	19.340	16.419	15.765	9.877	7.379	1.399	2.538
y_5	0.246	0.351	0.404	0.951	1.687	3.346	3.036
y_6	0.162	0.189	0.149	0.249	0.344	0.366	0.201
y_7	0.043	0.040	0.028	0.030	0.030	0.099	0.030
y_8	0.455	0.394	0.304	0.256	0.182	0.122	0.071
y_9	0.024	0.024	0.019	0.026	0.025	0.087	0.028
y_{10}	0.088	0.114	0.103	0.204	0.282	0.321	0.186

Table 4 : Table correlating ^{13}C NMR peak intensity ratio data to the internal bond strength dry test

	NMR species ratio	correlati-on for the A-series	correlati-on for the B-series
y_1	Mo/Me	0.934	0.998
y_2	(o+p)/(m+B)	0.988	0.986
y_3	Mo/(o+p)	0.919	0.985
y_4	(o+p)/Me	0.841	0.970
y_5	(Me+Mo)/(o+p)	0.918	0.974
y_6	Mo/(m+B)	0.780	0.592
y_7	Me/(m+B)	0.607	0.310
y_8	(o+p)/{(o+p)+(m+B)}	0.996	0.972
y_9	Me/{(o+p)+(m+B)}	0.988	0.933
y_{10}	Mo/{(o+p)+(m+B)}	0.983	0.992

Table 5 : Table correlating ^{13}C NMR peak intensity ratio data to the Internal bond strength wet test

	NMR species ratio	correlati-on for the A series	correlati-on for the B-series
y_1	Mo/Me	0.713	0.474
y_2	(o+p)/(m+B)	0.996	0.984
y_3	Mo/(o+p)	0.878	0.970
y_4	(o+p)/Me	0.891	0.926
y_5	(Me+Mo)/(o+p)	0.876	0.930
y_6	Mo/(m+B)	very low	very low
y_7	Me/(m+B)	very low	very low
y_8	(o+p)/{(o+p)+(m+B)	0.992	0.993
y_9	Me/{(o+p)+(m+B)	0.955	0.955
y_{10}	Mo/{(o+p)+(m+B)	0.964	0.981

Table 6 : Table correlating ^{13}C NMR peak intensity ratio data to the Internal bond strength DNIv100 test

	NMR species ratio	correlati-on for the A series	correlati-on for the B series
y_1	Mo/Me	0.768	0.360
y_2	(o+p)/(m+B)	0.876	0.929
y_3	Mo/(o+p)	0.814	0.932
y_4	(o+p)/Me	0.718	0.885
y_5	(Me+Mo)/(o+p)	0.812	0.890
y_6	Mo/(m+B)	very low	very low
y_7	Me/(m+B)	very low	very low
y_8	(o+p)/{(o+p)+(m+B)	0.904	0.951
y_9	Me/{(o+p)+(m+B)	0.915	0.
y_{10}	Mo/{(o+p)+(m+B)	0.900	0.991

Table 7. Table correlating ^{13}C NMR peak intensity ratio data to the F:P molar ratio

	NMR species ratio	correlation for the A-series	correlation for the B-series
y_1	Mo/Me	0.942	0.996
y_2	(o+p)/(m+B)	0.990	0.987
y_3	Mo/(o+p)	0.967	0.974
y_4	(o+p)/Me	0.966	0.976
y_5	(Me+Mr)/(o+p)	0.965	0.903
y_6	Mo/(m+B)	0.894	0.746
y_7	Me/(m+B)	0.691	0.834
y_8	(o+p)/{(o+p)+(m+B)	0.997	0.990
y_9	Me/{(o+p)+(m+B)	0.974	0.917
y_{10}	Mo/{(o+p)+(m+B)	0.995	0.985

Table 8. ^{13}C NMR assignments for the phenol formaldehyde resins

Functional group	Relative Position	Chemical shift [ppm] [32]	Chemical shift [ppm] [38]
Methylene bridges			
Ph-$\underline{C}H_2$-Ph	*ortho-ortho*	29.21	30.8 - 31.4
	ortho-para	34.93	35.5 - 35.9
	para-para	39.67	41.0
Methynol species			
$\underline{C}H_3OH$		50.70	
$\underline{C}H_3O$-CH_2OH		56.29	
Methylol species			
Ph-$\underline{C}H_2OH$	*ortho*	61.4-61.5	
Ph-$(\underline{C}H_2OH)_2$	*di-ortho*	61.6-62.3	
Ph-$\underline{C}H_2OH$	*para*	65.52	
Ether species			
Ph-$\underline{C}H_2OCH_2OH$	*ortho*	66.57	
Ph-$\underline{C}H_2OCH_2OCH_2OH$ & Ph-$(\underline{C}H_2OCH_2OH)_2$	*ortho di-ortho*	67.10	
Ph-$\underline{C}H_2OCH_2OH$	*para*	70.57	
Ph-$\underline{C}H_2OCH_2OCH_2OH$	*para*	71.16	
Ph-$\underline{C}H_2O\underline{C}H_2$-Ph		70.77	
HO$\underline{C}H_2OH$		83.73	
HO$\underline{C}H_2OCH_2OH$		87.29	

Ph-$CH_2OCH_2O\underline{C}H_2OH$ Ph-$CH_2OCH_2O\underline{C}H_2OH$	*ortho* *para*	87.3	
Ph-$CH_2O\underline{C}H_2OH$	*para*	89.27	
Ph-$CH_2O\underline{C}H_2OH$	*ortho*	89.59	
CH_3O-$\underline{C}H_2OH$		91.3	
Ph-$CH_2O\underline{C}H_2OCH_2OH$	*para*	92.2	
Ph-$CH_2O\underline{C}H_2OCH_2OH$	*ortho*	92.87	
	ortho free sites on the Phenolic ring		115.4-116.0
	para free sites on the phenolic ring		119.9-120.9
	meta free sites on the phenolic ring		127.4-132.9
	Blocked sites on the phenolic ring		127.6-133.9

Table 9 : Solid content and viscosity Data chart

F:P Molar ratio	A- Series % Solid content	Viscosity	B- Series % Solid content	Viscosity
1.1	58.88	190	39.34	35
1.3	60.19	290	41.46	60
1.5	62.76	796	42.12	
1.8	63.71	1430	43.22	
2.0	64.11	7300	44.14	1172
2.12			44.20	very high
2.2	64.35	very high	44.5	very high

Table 10: Results for the average thickness swell and Water absorption test

F:P Molar ratio	A-Series Avera. wet thickness mm	A-Series Avera. % increase in thickness	B-Series Avera. wet thickness mm	B-series Avera. % increase in thickness
1.8	14.4	26.32	14.31	25.53
2.0	14.2	24.56	14.19	24.47
2.12			14.12	23.86
2.2	13.87	21.67	13.9	21.93

Table 11. Fluorescence Intensity and Formaldehyde Concentration for the standard solutions

Fluorescence Intensity	Formaldehyde Concentration μgl^{-1}
245	3.700
212	1.850
178	0.925
165	0.740
139	0.463
106	0.247
92	0.185
63	0.074
35	0.000

Table 12. The average results for the formaldehyde emission test from the particleboards by the desiccator method

(a) A- Series

Resin sample	Average wt of aboard /g	Average intensity of a board	Formaldehyde Concentration μg^{-1}l	μg of F per 100g of board
2.2	9.90	107	0.2427	2.4518
2.0	8.71	86	0.1688	1.9376
1.8	8.86	81	0.1512	1.7061
1.5	8.53	61	0.0807	0.9462
1.3	7.88	59	0.0737	0.9349
1.1	8.82	47	0.0314	0.3560

(b) B- Series

Resin sample	Average wt of a board /g	Average intensity of a board	Formalde-hyde Concentrat ion $\mu g\ l^{-1}$	μg of F per 100g of board
2.2	9.73	72	0.1195	1.2277
2.12	8.44	55	0.0596	0.7059
2.0	9.56	52	0.0490	0.5127
1.8	8.78	49	0.0385	0.4379
1.5	8.58	43	0.0173	0.2017
1.1	7.84	40	0.0085	0.1090

Table 13: Converted Formaldehyde emission data according to the WKI mothod (See APPENDIX 3).

A - Series

F:P Molar Ratio	Desiccator method μg/100 g of Board	WKI method μg/100g of Board	WKI method mg/100g of Board
2.2	2.4518	2313.328	2.3133
2.0	1.9376	2311.204	2.3112
1.8	1.7061	2310.248	2.3102
1.5	0.9462	2307.109	2.3071
1.3	0.9349	2307.062	2.3071
1.1	0.3560	2304.671	2.3047

B - Series

F:P Molar Ratio	Desiccator method µg/100 g of Board	WKI method µg/100g of Board	WKI method µg/100g of Board
2.2	1.2277	2308.272	2.3083
2.12	0.7059	2306.116	2.3061
2.0	0.5127	2305.318	2.3053
1.8	0.4370	2305.005	2.3050
1.5	0.2017	2304.033	2.3040
1.1	0.1090	2303.650	2.3037

Selected peak ratios for the formaldehyde emission correlation

Free F = free formaldehyde peak at 83.73 ppm

Et = Total ether species (peaks from 87.29 to 92.87 ppm

Mo = Total metholol species (peaks from 61.4 to 65.52 ppm

(o+p)+(m+B) = Total *ortho*, *para* and *meta* free positions puls blocked positions on the phenolic ring (peaks from (115.4 - 116.0), (119.9-120.9) and (127.4 - 133.9) ppm

Table 14: Selected average ^{13}C NMR peak intensity data assignments for different PF resins for the formaldehyde emission correlation

(a) A- Series

F:P Molar ratio	free F	Ether groups	(o+p)+(m+B)
1.1		5.469	180.491
1.3		4.399	183.973
1.5		2.047	52.755
1.8			120.758
2.0	2.425	3.230	97.03
2.2	7.953	15.384	103.743

(b) B- Series

F:P Molar ratio	free F	Ether groups	(o+p)+(m+B)
1.1			170.234
1.3			242.234
1.5		0.717	166.267
1.8	1.400	3.189	207.955
2.0	0.979	14.996	193.608
2.12	8.418	21.784	22.523
2.2	1.345	13.930	100.898

Notation for the ^{13}C NMR Peak intensity ratio data chart for the experimental formaldehyde emission data correlation

y_{10} = Mo/{(o+p)+(m+B)}
y_{11} = Free F/{(o+p)+(m+B)}
y_{12} = Et /{(o+p)+(m+B)}

Table 15: Experimental formaldehyde emission data (by WKI method) and peak intensity ratio assignments for the formaldehyde emission correlation.

(a) A- Series

F:P Molar Ratio	Experimen. Formaldeh. emission mg/100g of board	y_{10}	y_{11}	y_{12}
1.1	2.3047	0.0889		0.0303
1.3	2.3071	0.1185		0.0239
1.5	2.3071	0.1397		0.0709
1.8	2.3102	0.2552		0.0129
2.0	2.3112	0.2958	0.025	0.0480
2.2	2.3133	0.4109	0.077	0.1483

(b) B- Series

F:P Molar Ratio	Experimen. Formaldeh. emission mg/100g of board	Y_{10}	Y_{11}	Y_{12}
1.1	2.3037	0.0882		
1.3		0.1782		
1.5	2.3040	0.1034		0.0043
1.8	2.3050	0.2035	0.0067	0.0128
2.0	2.3053	0.2816	0.0053	0.0647
2.12	2.3061	0.3211	0.3283	0.0970
2.2	2.3083	0.1863	0.0133	0.1381

Table 16 : Table correlating ^{13}C NMR species intensity ratio to the experimental formaldehyde emission data by WKI method.

	NMR species ratio	correlation for the A series	correlation for the B series
y_{10}	Mo/{(o+p)+(m+B)}	0.981	0.982
y_{11}	Free F/{(o+p)+(m+B)}	1	0.964
y_{12}	Et/{(o+p)+(m+B)}	0.997	0.909

Table 17 : Table correlating suspected emission source of ^{13}C NMR species intensity ratio to the F:P molar ratio

	NMR species ratio	correlation for the A series	correlation for the B series
y_{10}	Mo/{(o+p)+(m+B)}	0.995	0.985
y_{11}	Free F/{(o+p)+(m+B)}	1	0.917
y_{12}	Et/{(o+p)+(m+B)}	0.999	0.982

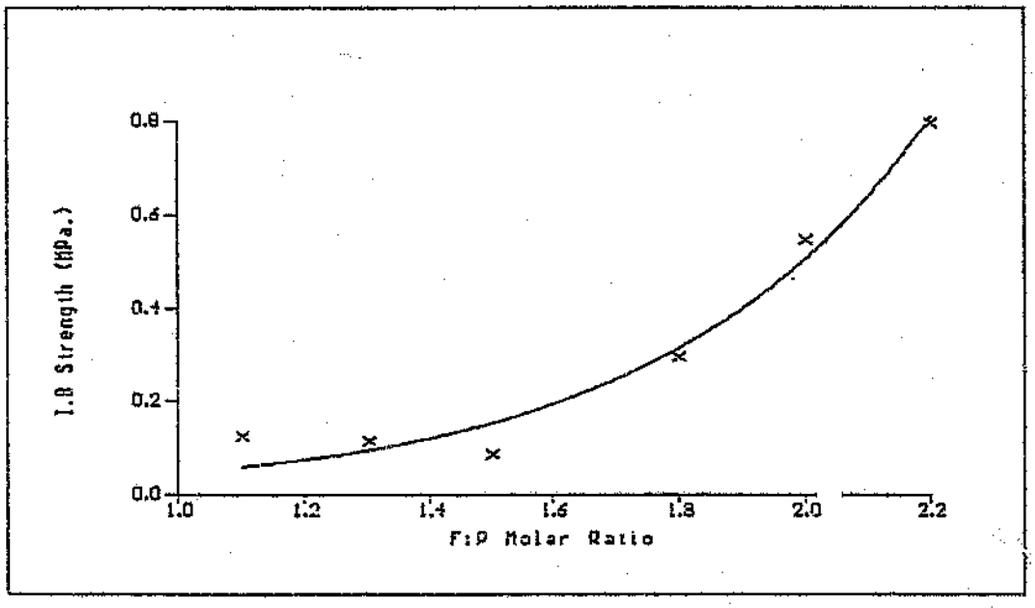


Fig. 1(a): I.B. Strength results for the Dry test made with the A- series resins.

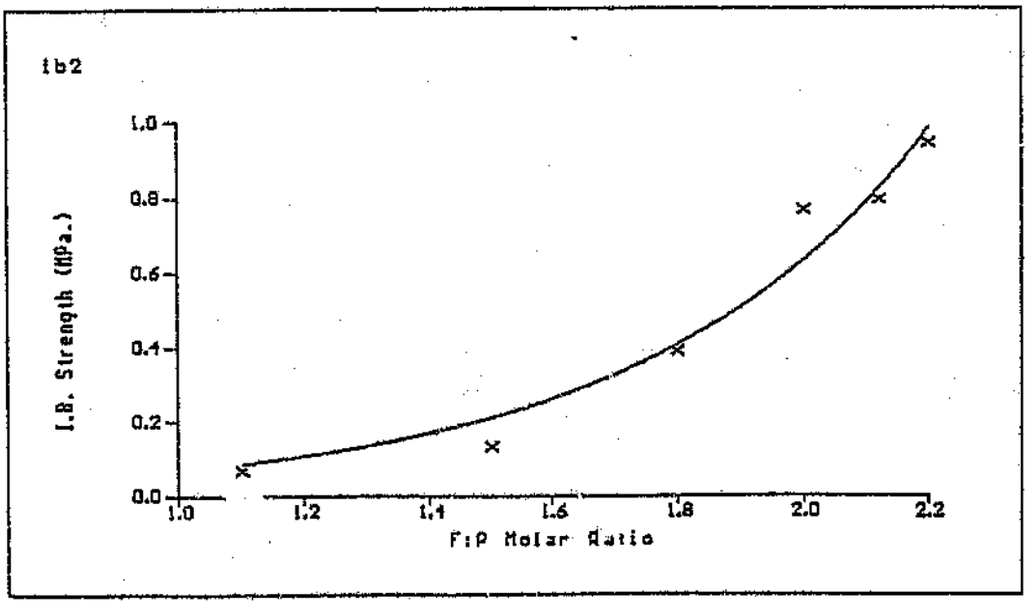


Fig. 1(b): I.B. Strength results for the Dry test made with the B- series resins.

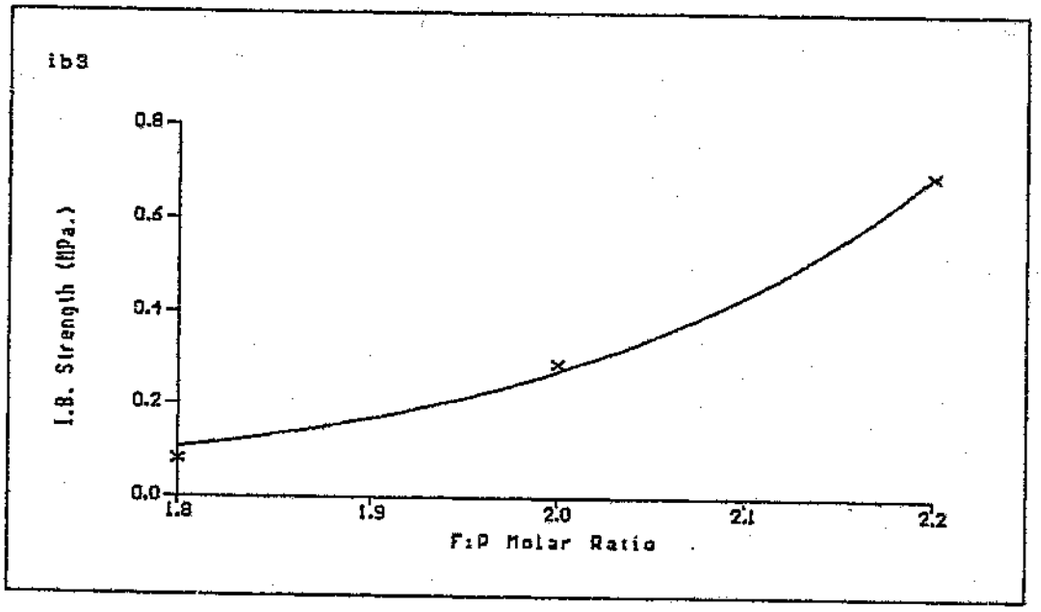


Fig. 1(c): I.B. Strength results for the Wet test made with the A- series resins.

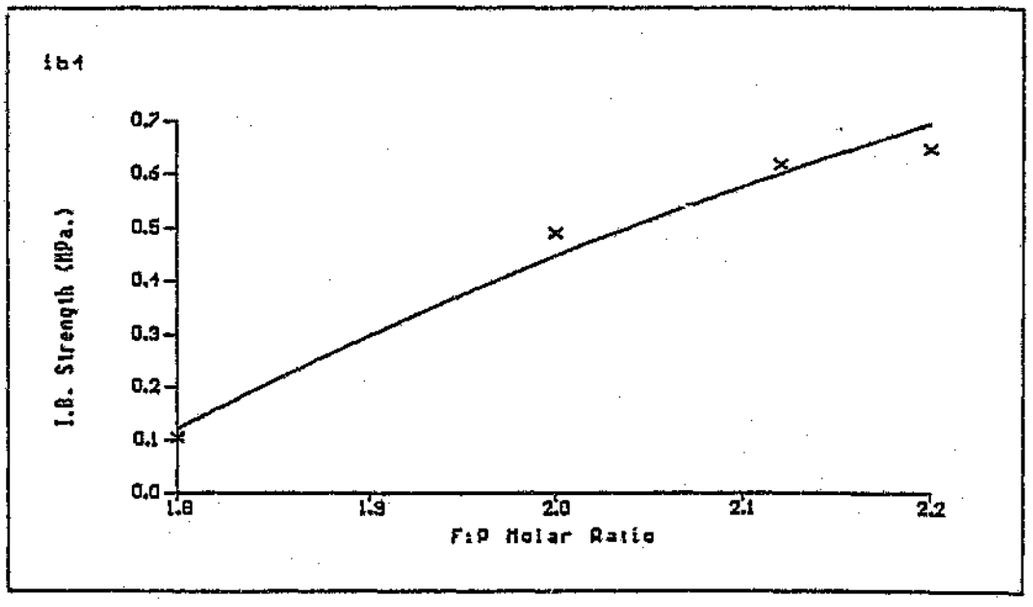


Fig. 1(d): I.B. Strength results for the Wet test made with the B- series resins.

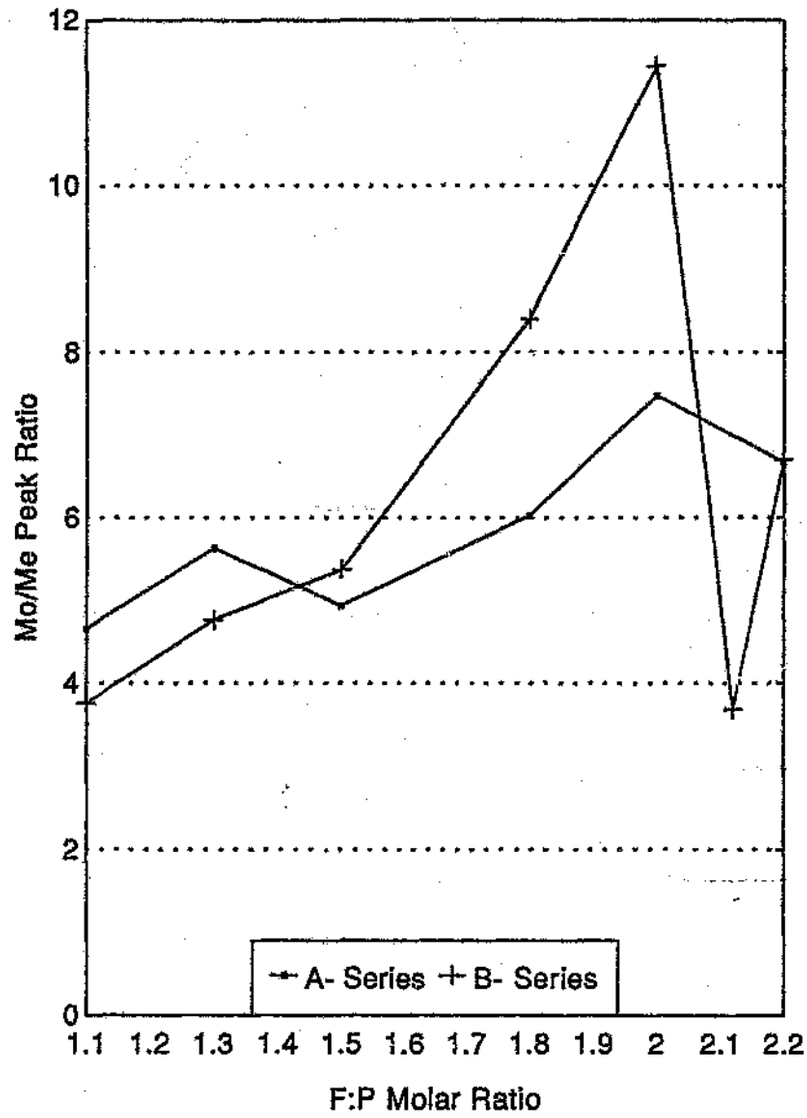


Fig. 2. Calculated ^{13}C NMR peak ratios for the Mo/Me species for the A- and B- series of resins

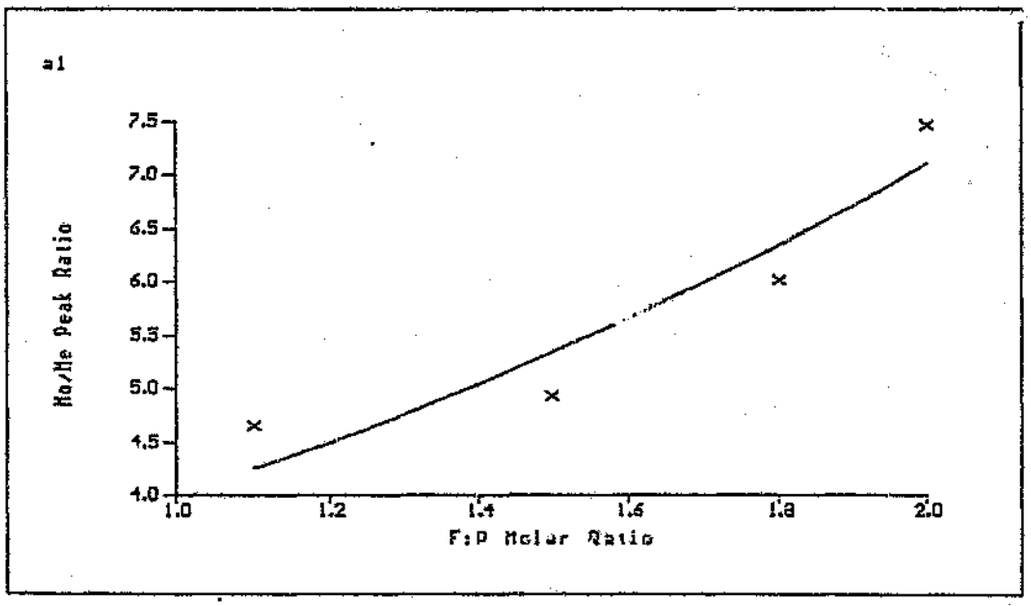


Fig. 2(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/Me species for the A- series resins.

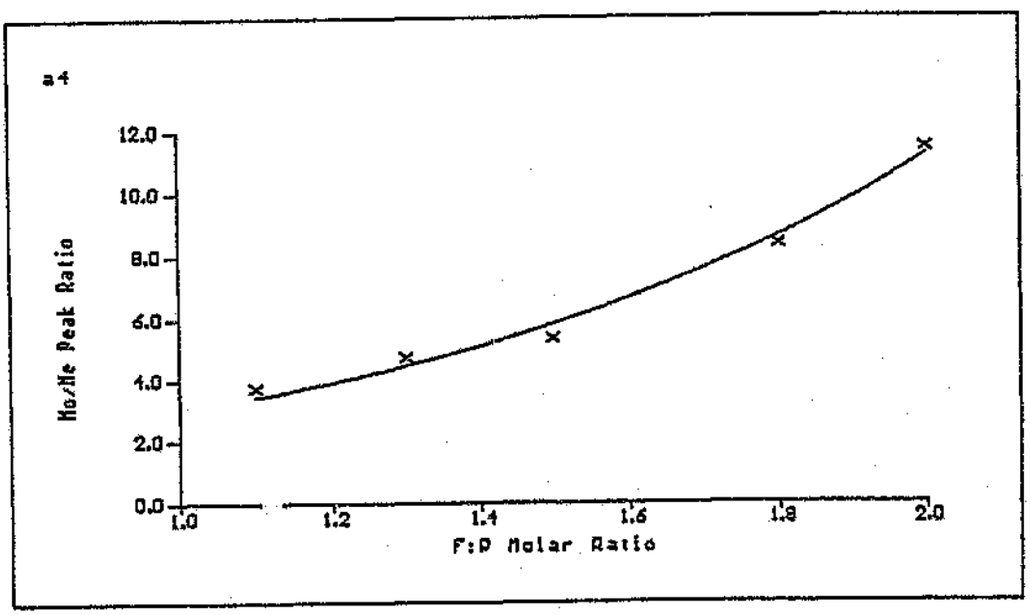


Fig. 2(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/Me species for the B- series resins.

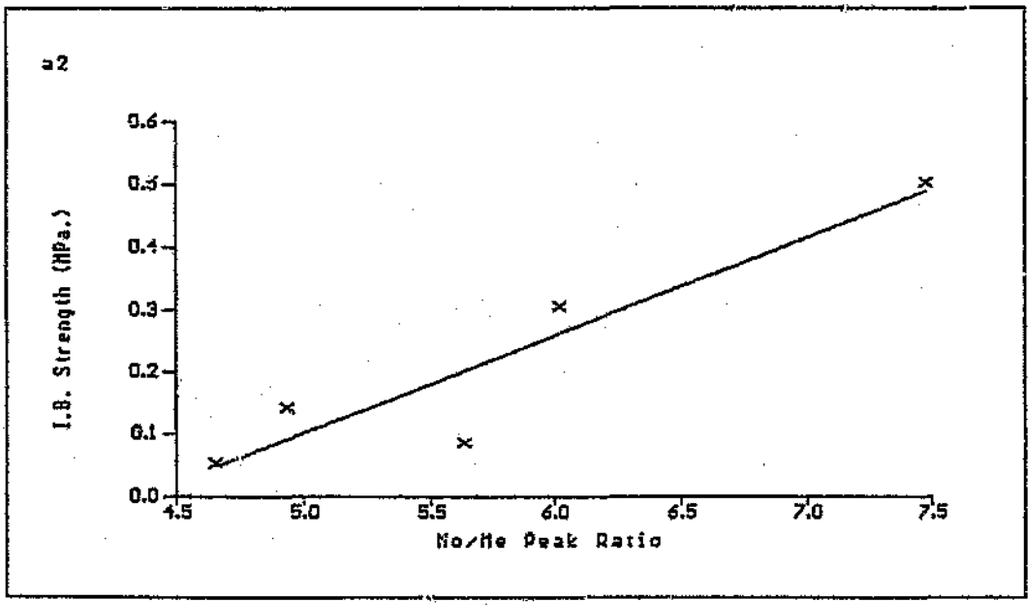


Fig. 2(c): ^{13}C NMR peak ratio for the Mo/Me species to the I.B. strength Dry test for the A- series resins.

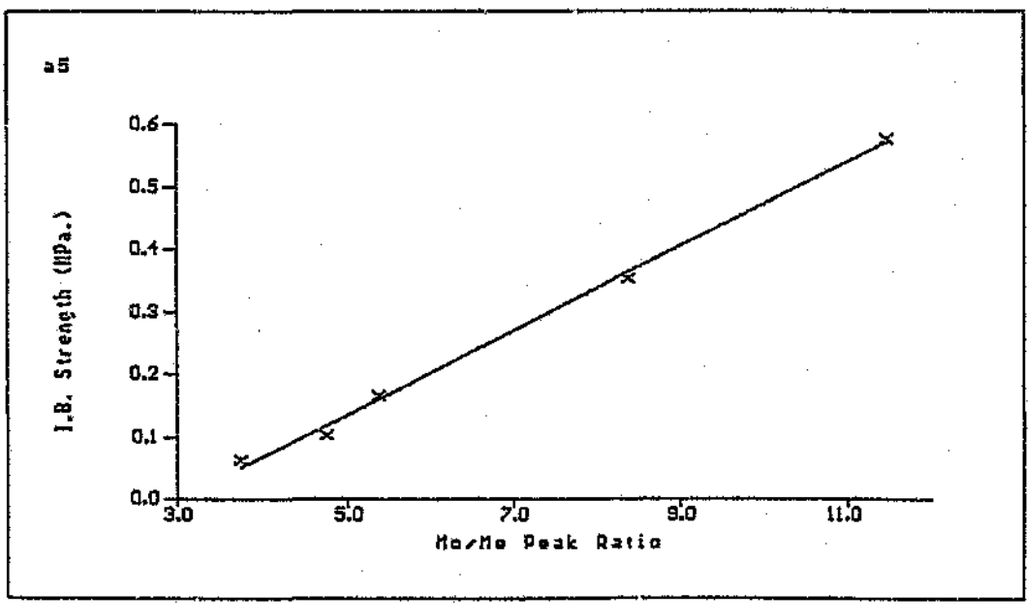


Fig. 2(d): ^{13}C NMR peak ratio for the Mo/Me species to the I.B. strength Dry test for the B- series resins.

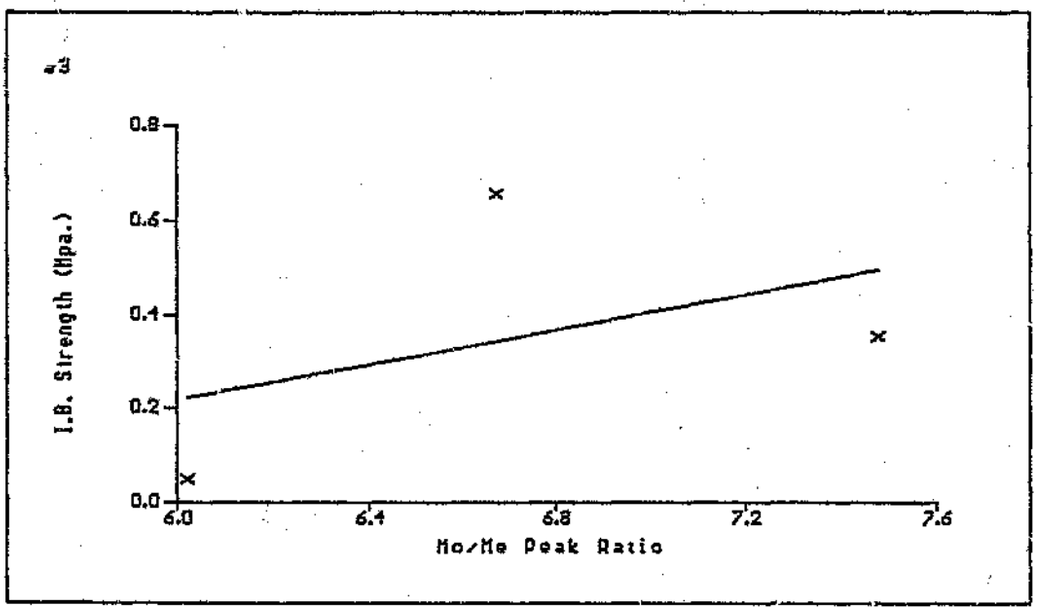


Fig. 2(e): ^{13}C NMR peak ratio for the Mo/Me species to the I.B. strength Wet test for the A- series resins.

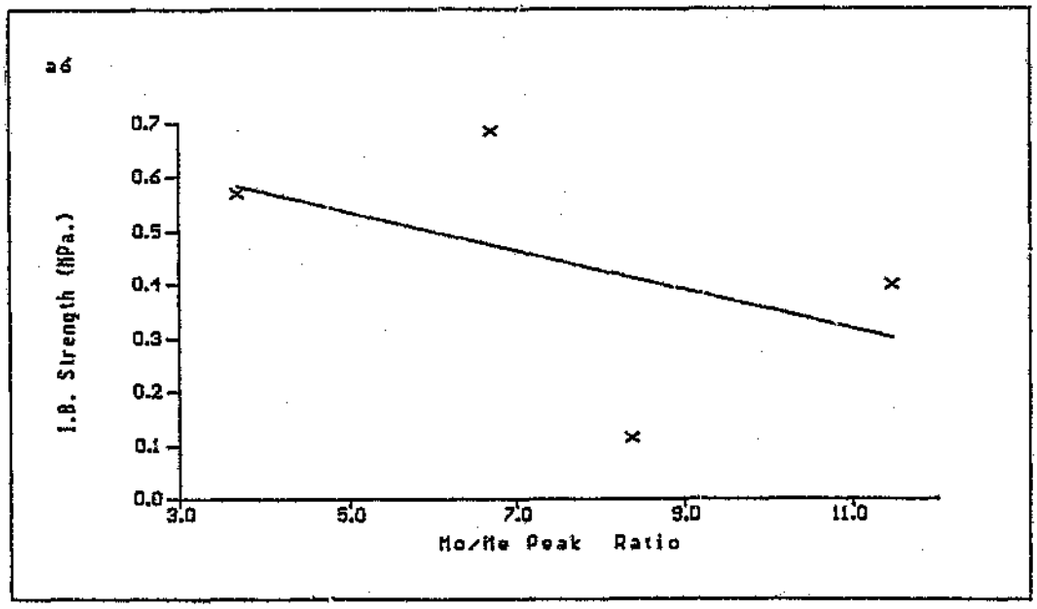


Fig. 2(f): ^{13}C NMR peak ratio for the Mo/Me species to the I.B. strength Wet test for the B- series resins.

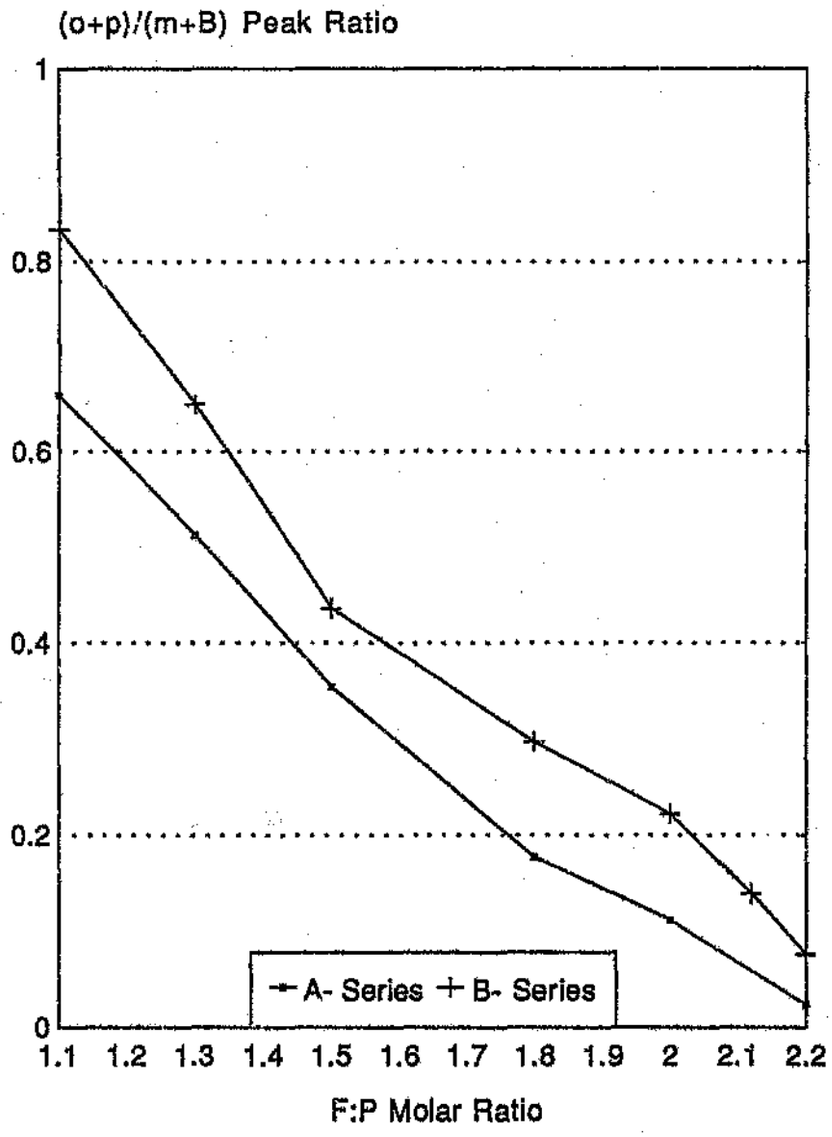


Fig. 3: Calculated ^{13}C NMR Peak ratios for the (o+p)/(m+B) species for the A- and B- series resins

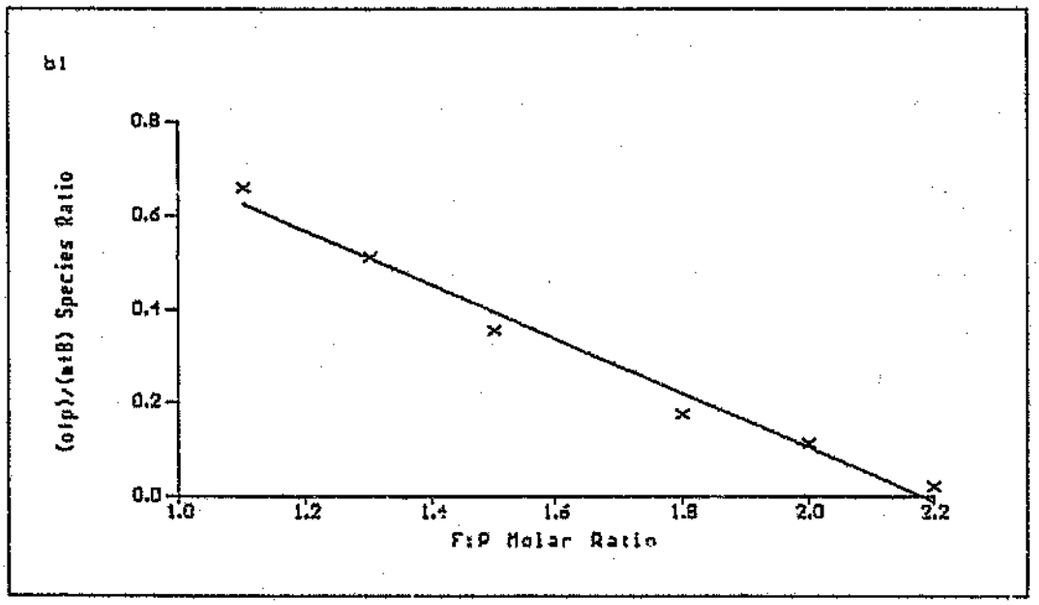


Fig. 3(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the (o+p)/(m+B) species for the A- series resins.

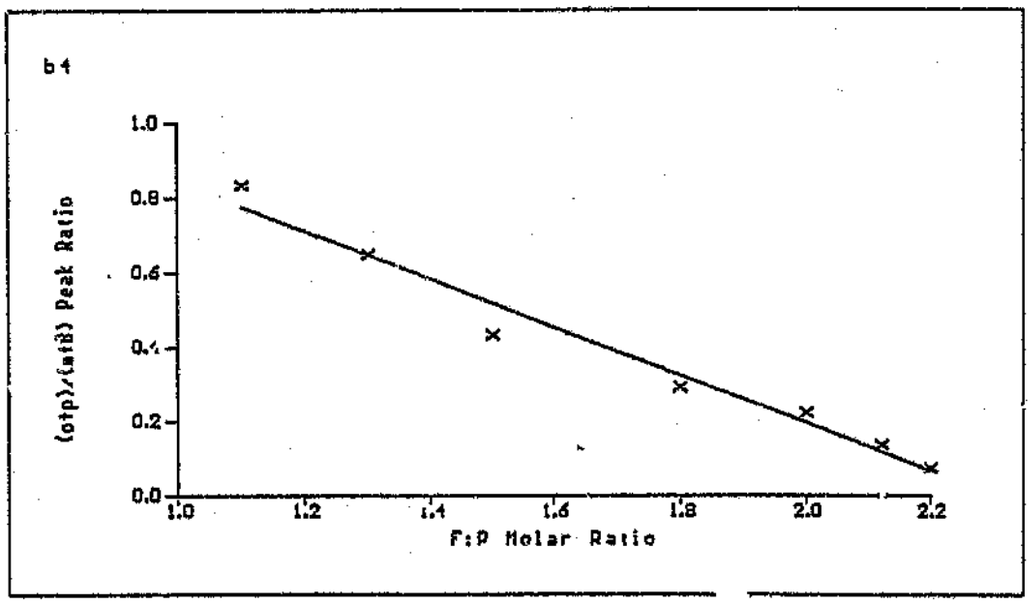


Fig. 3(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the (o+p)/(m+B) species for the B- series resins.

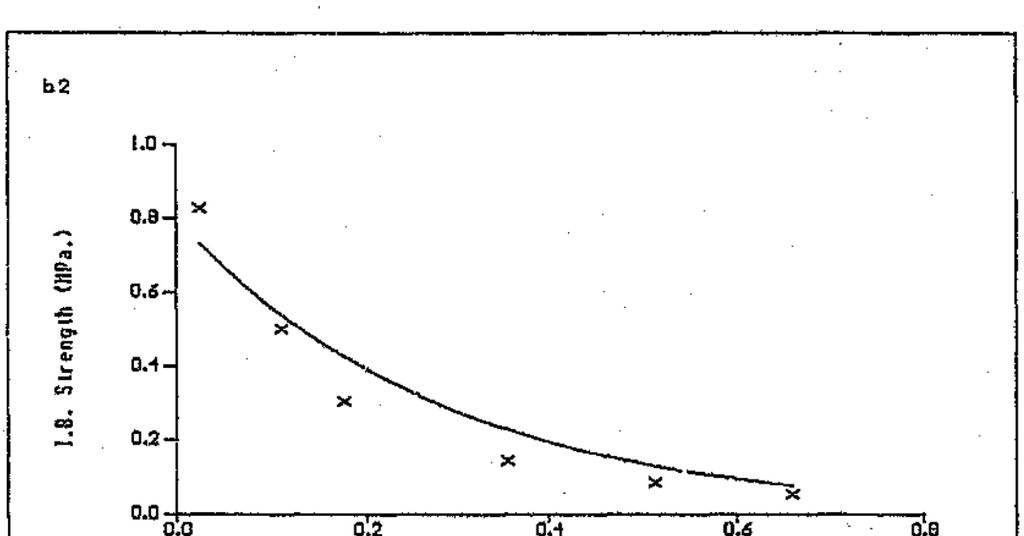


Fig. 3(c): ^{13}C NMR peak ratio for the (o+p)/(m+B) species to the I.B. strength Dry test for the A-series resins.

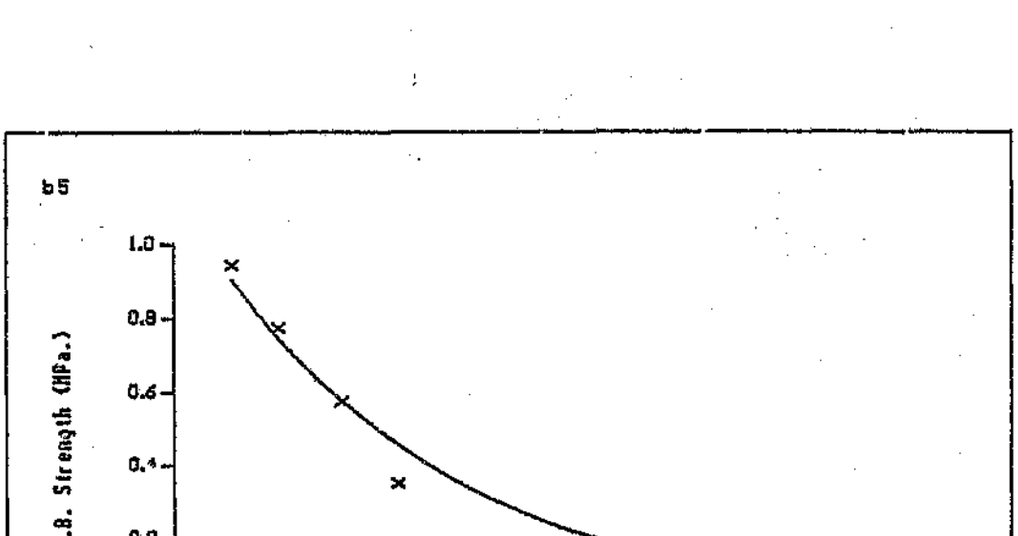


Fig. 3(d): ^{13}C NMR peak ratio for the (o+p)/(m+B) species to the I.B. strength Dry test for the B-series resins.

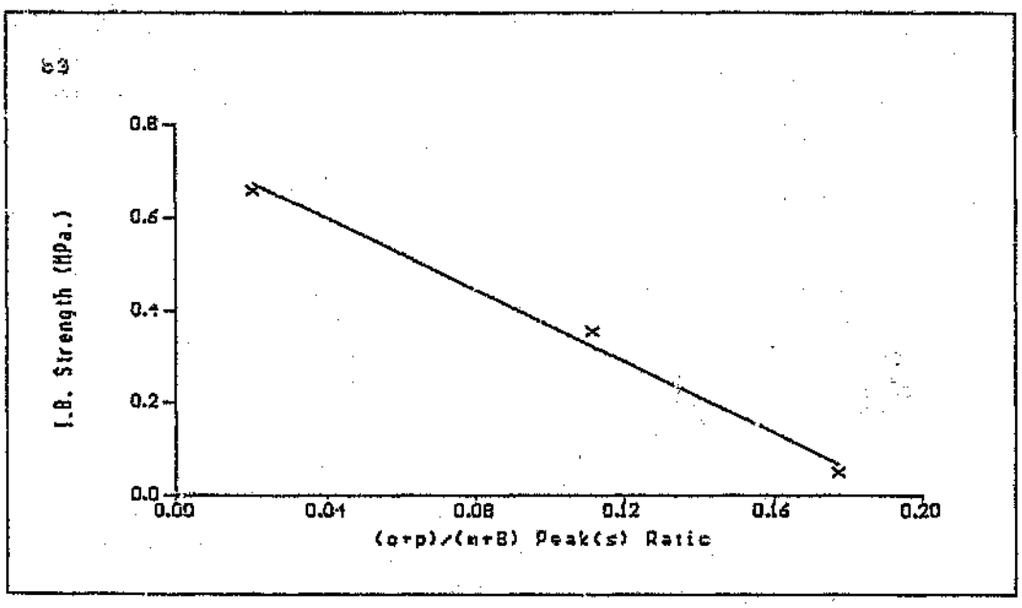


Fig. 3(e): ^{13}C NMR peak ratio for the (o+p)/(m+B) species to the I.B. strength Wet test for the A-series resins.

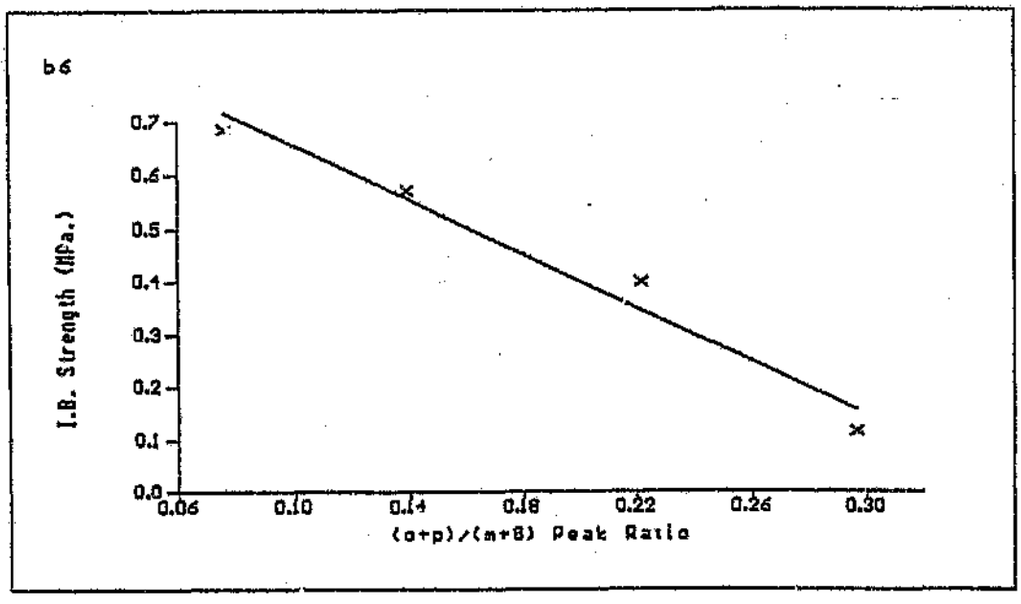


Fig. 3(f): ^{13}C NMR peak ratio for the (c+p)/(m+B) species to the I.B. strength Wet test for the B-series resins.

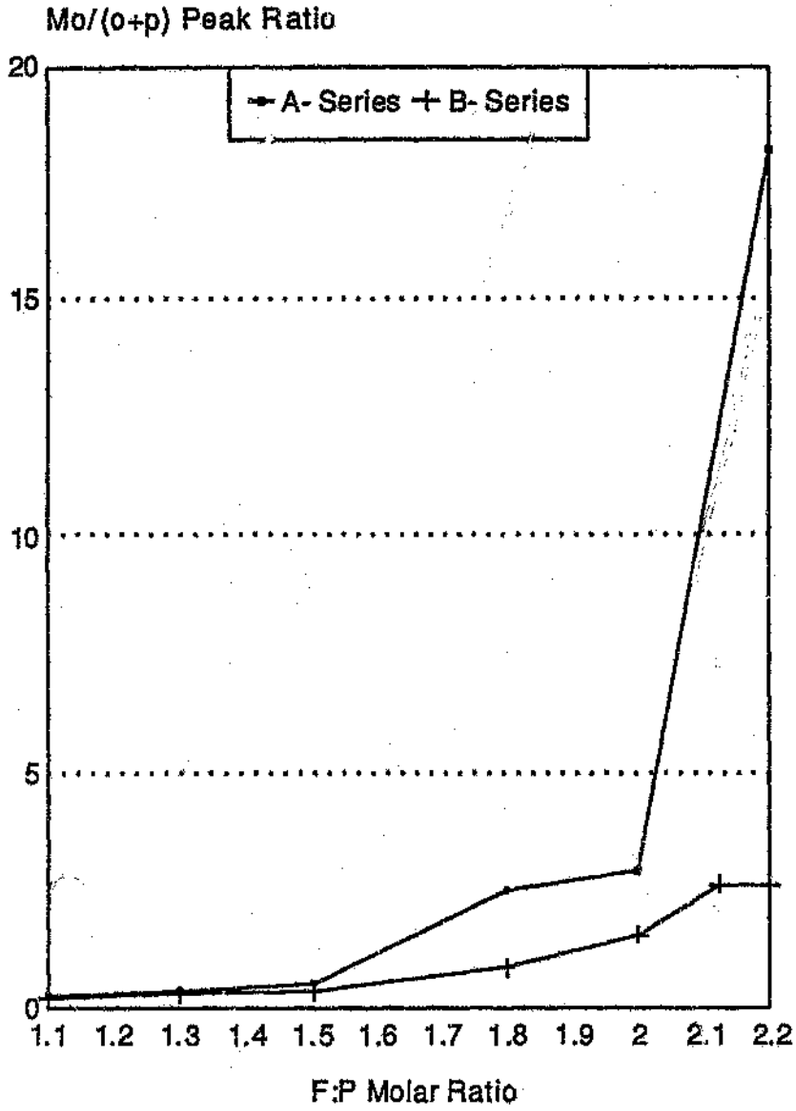


Fig. 4. Calculated ^{13}C NMR Peak ratios for the Mo/(o+p) Species for the A- and B- series of resins

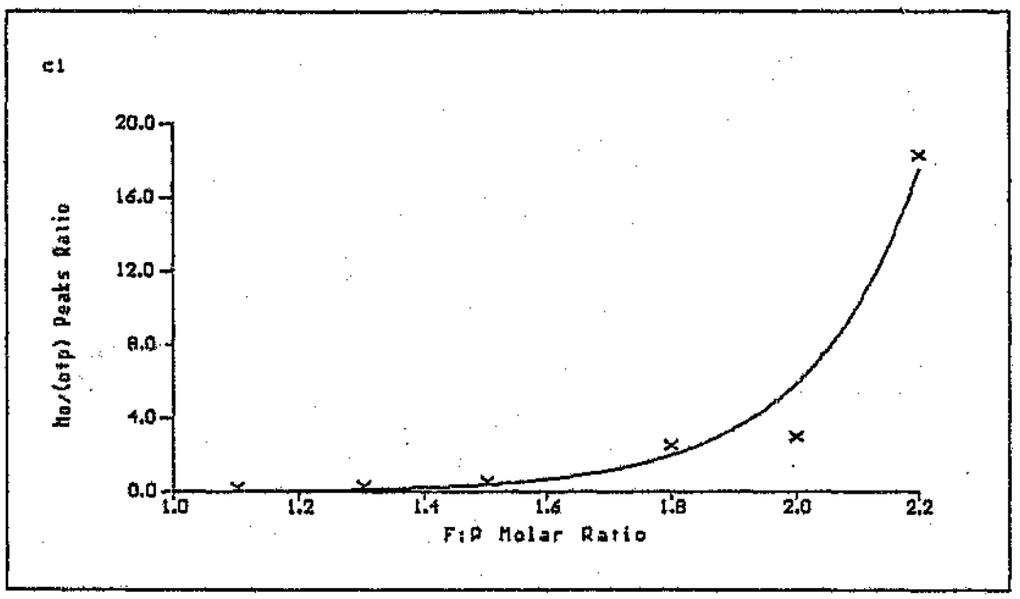


Fig. 4(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/(o+p) species for the A- series resins.

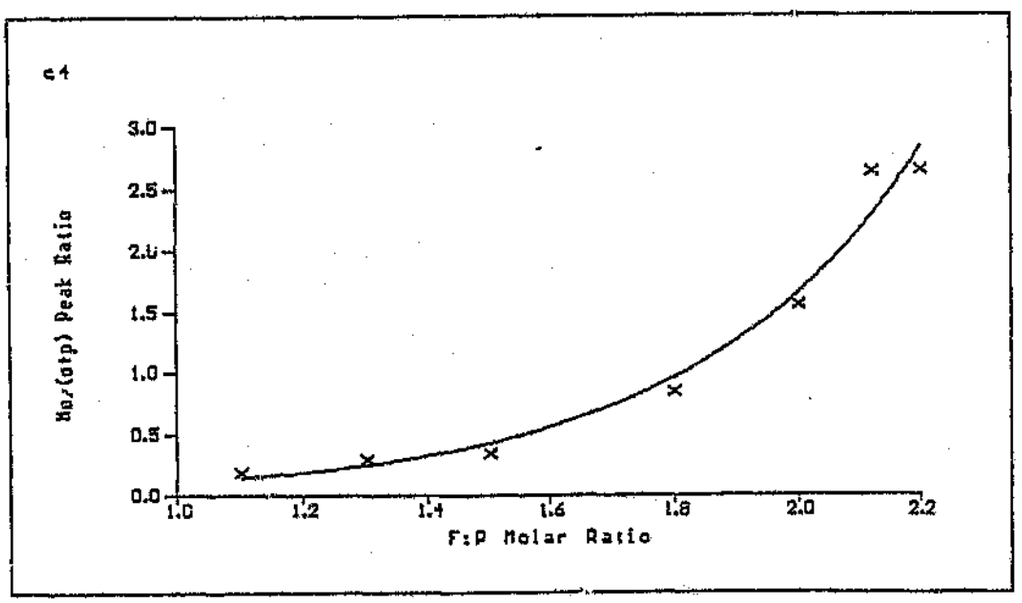


Fig. 4(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/(o+p) species for the B- series resins.

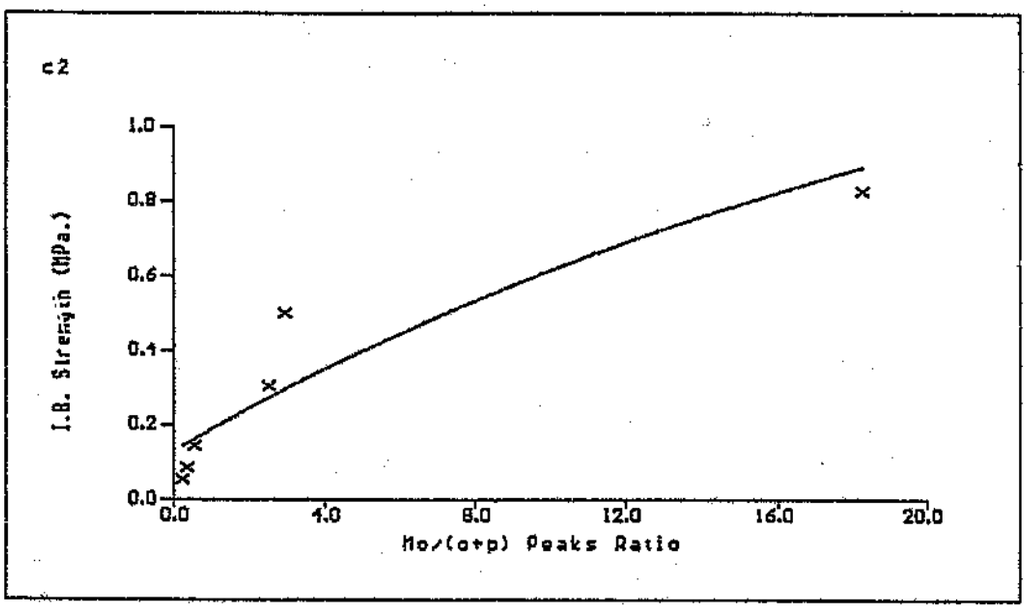


Fig. 4(c): ^{13}C NMR peak ratio for the Mo/(o+p) species to the I.B. strength Dry test for the A- series resins.

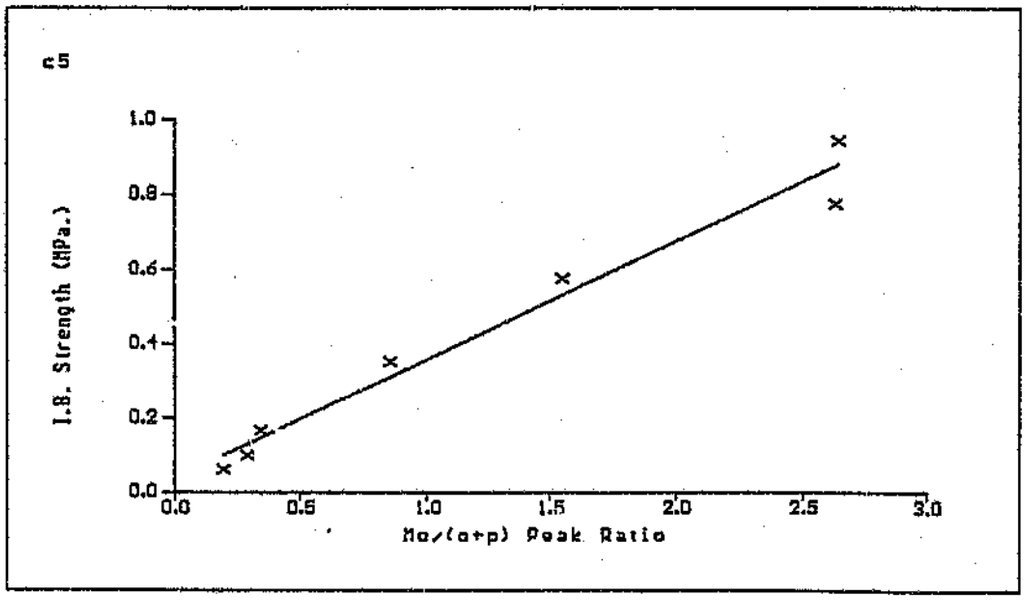


Fig. 4(d): ^{13}C NMR peak ratio for the Mo/(o+p) species to the I.B. strength Dry test for the B- series resins.

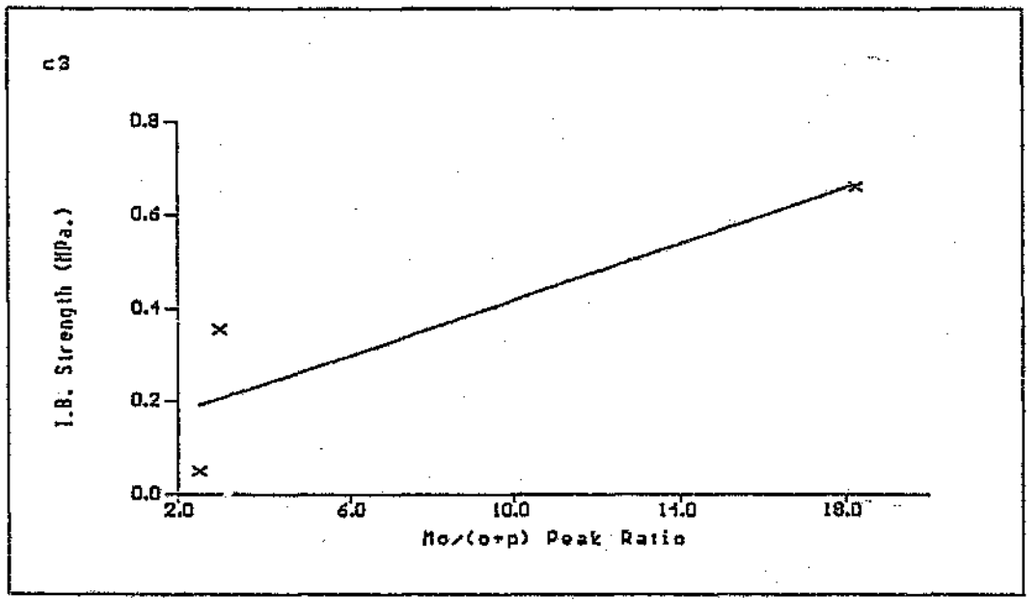


Fig. 4(e): ^{13}C NMR peak ratio for the Mo/(o+p) species to the I.B. strength Wet test for the A- series resins.

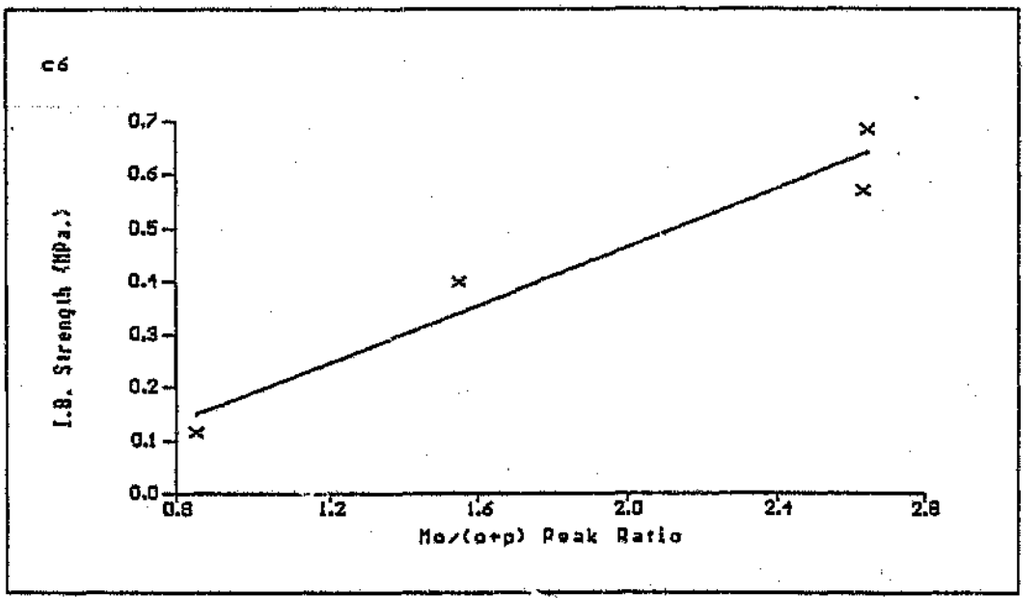


Fig. 4(f): ^{13}C NMR peak ratio for the Mo/(o+p) species to the I.B. strength Wet test for the B- series resins.

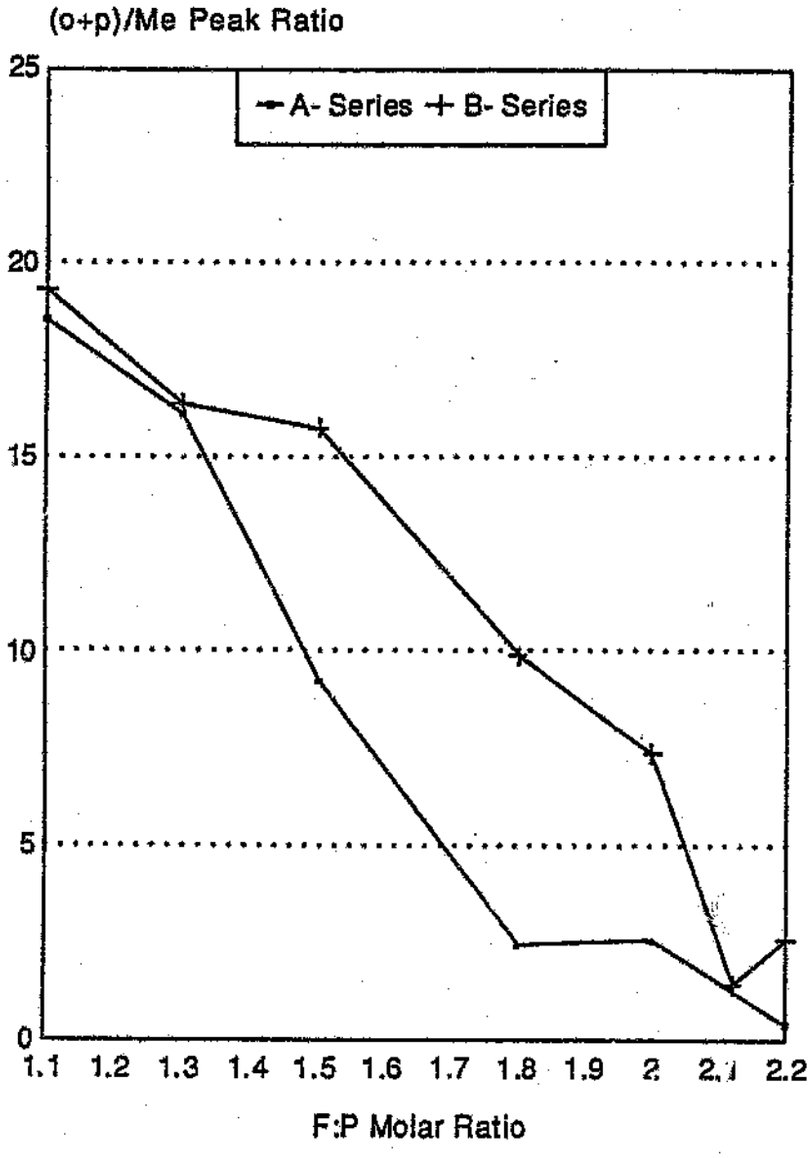


Fig 5: Calculated ^{13}C NMR peak ratios for the (o+p)/(m+B) species for the A- and B- series of resins.

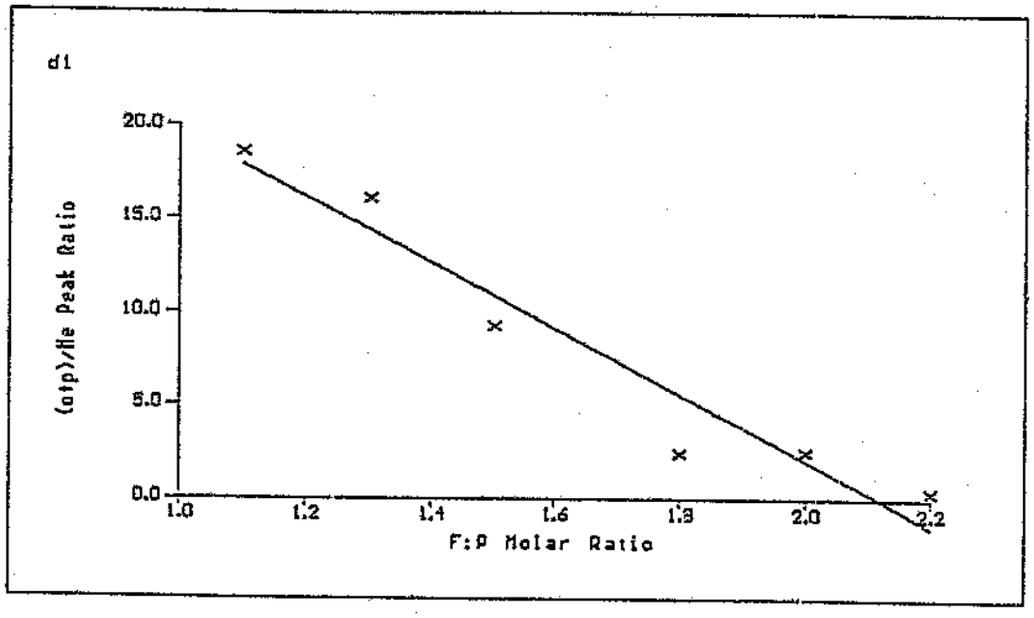


Fig. 5(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the (o+p)/Me species for the A- series resins.

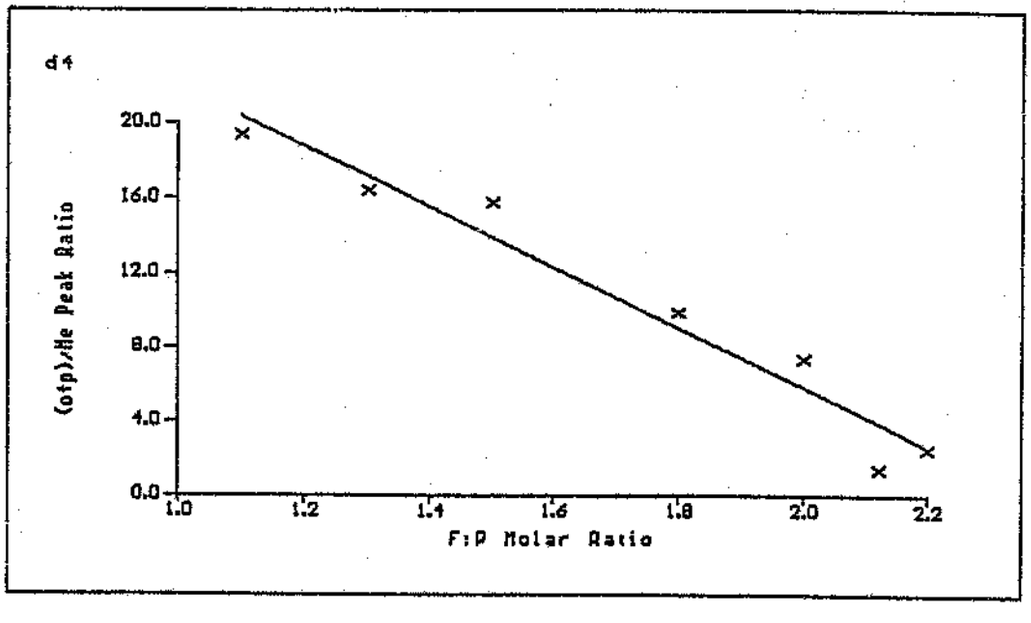


Fig. 5(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the (o+p)/Me species for the B- series resins.

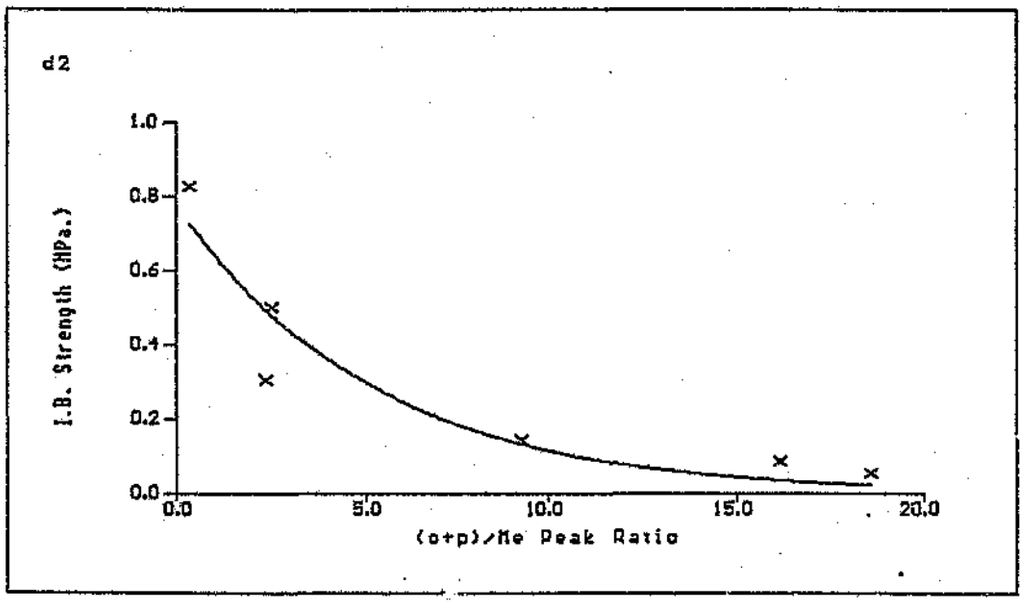


Fig. 5(c): ^{13}C NMR peak ratio for the (o+p)/Me species to the I.B. strength Dry test for the A- series resins.

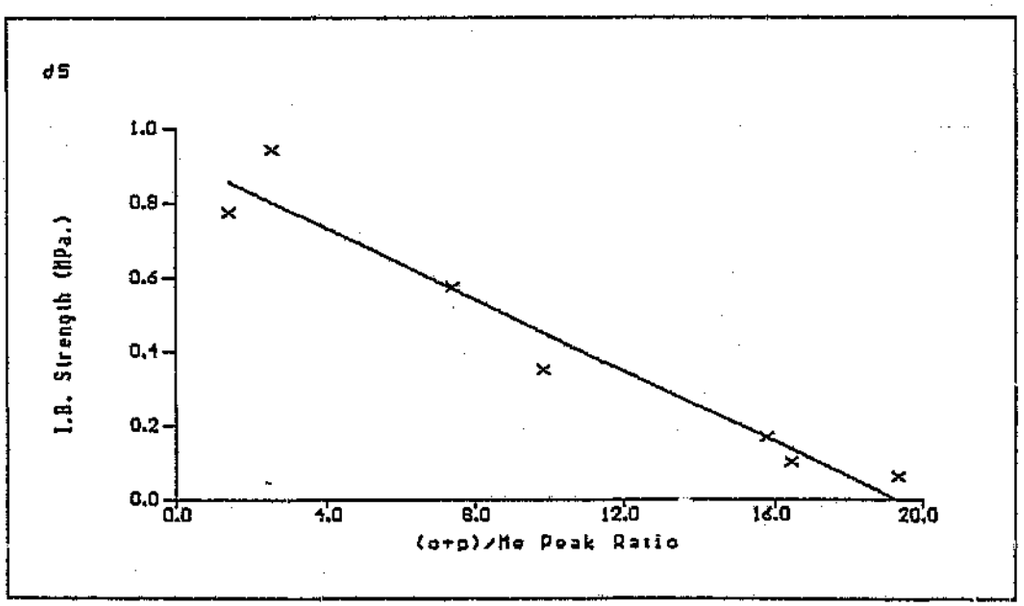


Fig. 5(d): ^{13}C NMR peak ratio for the (o+p)/Me species to the I.B. strength Dry test for the B- series resins.

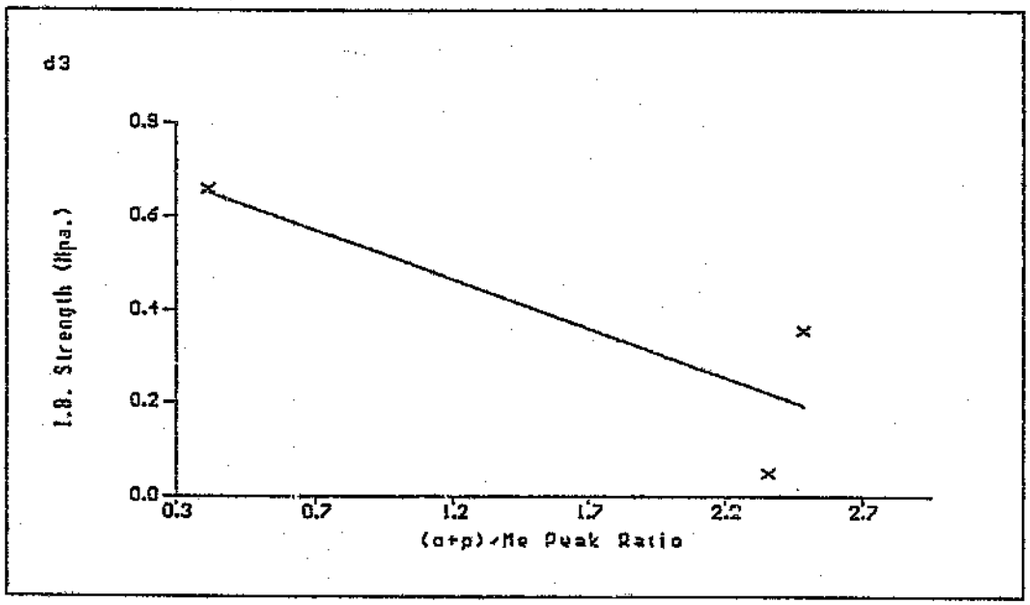


Fig. 5(e): ^{13}C NMR peak ratio for the (o+p)/Me species to the I.B. strength Wet test for the A- series resins.

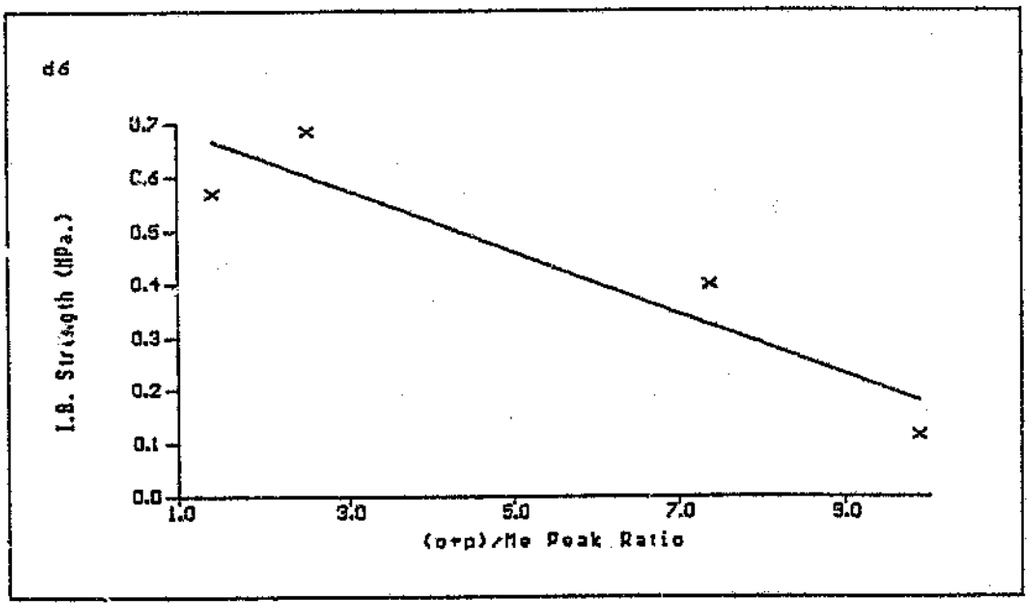


Fig. 5(f): ^{13}C NMR peak ratio for the (o+p)/Me species to the I.B. strength Wet test for the B- series resins.

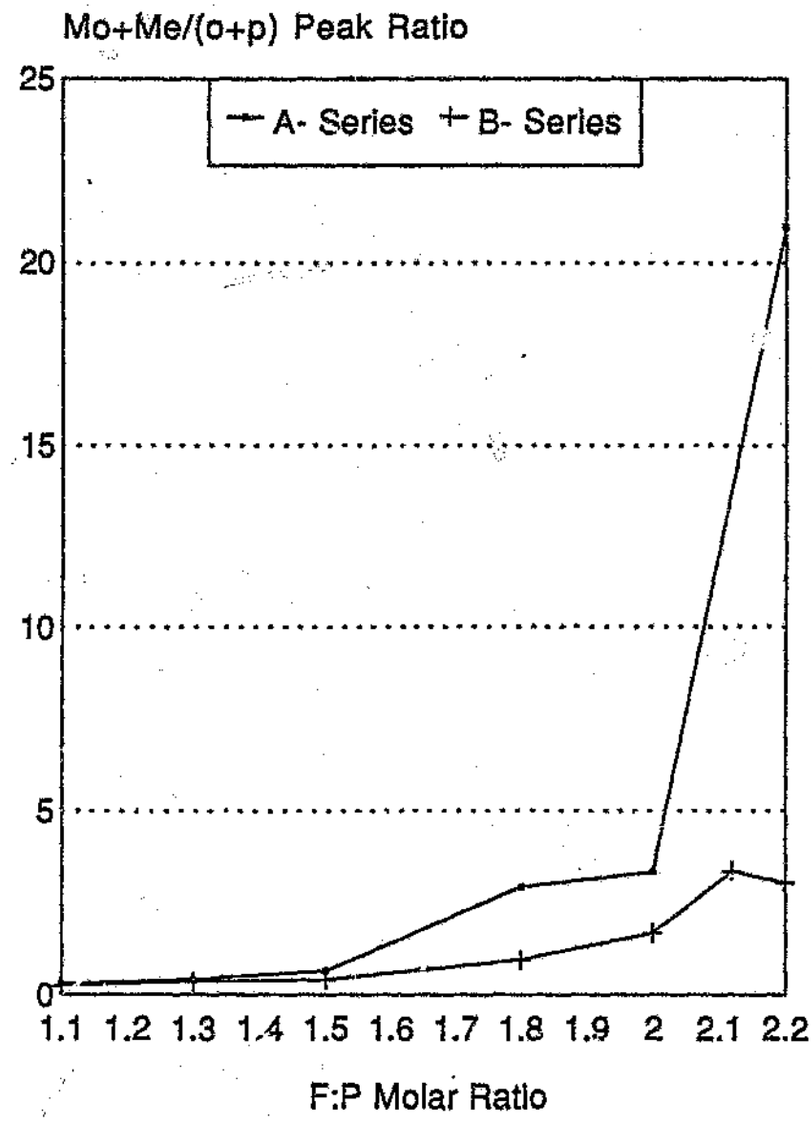


Fig 6: Calculated ^{13}C NMR peak ratios for the Mo+Me/(m+B) species for the A- and B- series of resins.

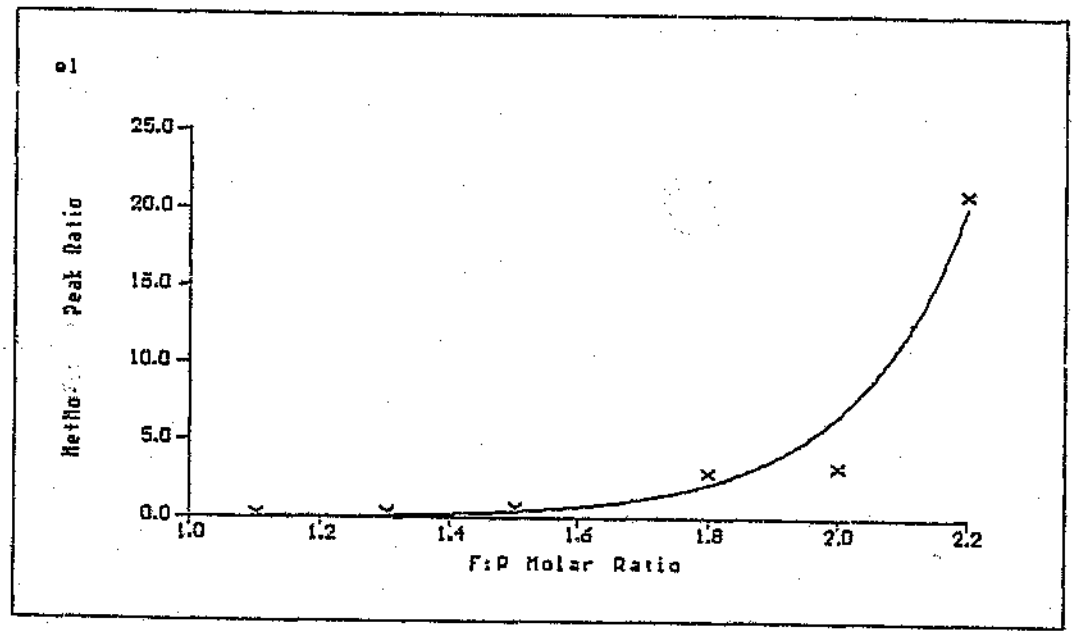


Fig. 6(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo+Me/(o+p) species for the A- series resins.

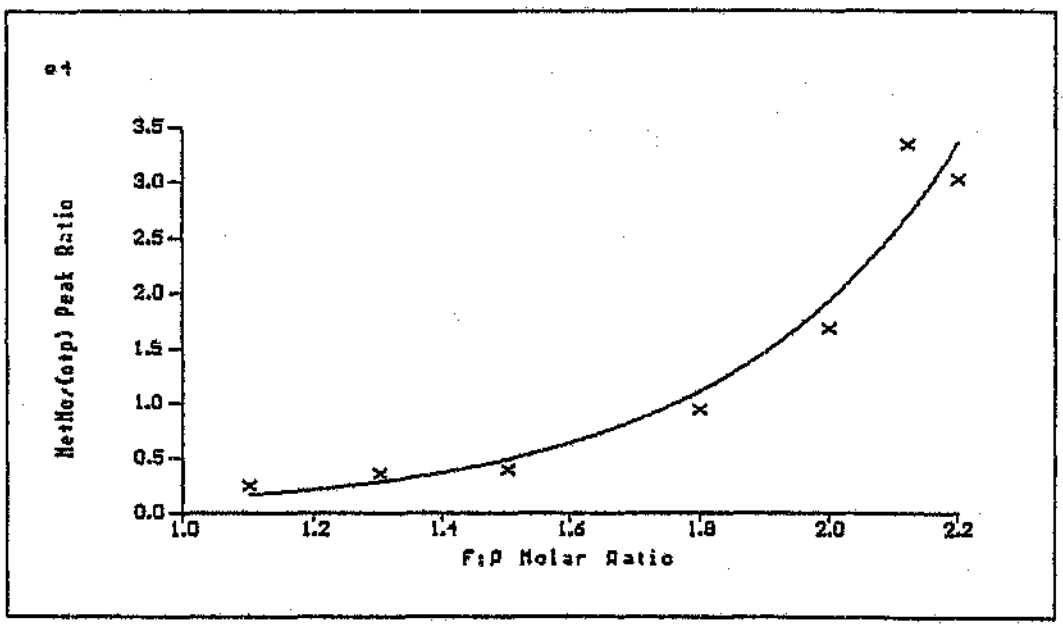


Fig. 6(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Me+Mo/(o+p) species for the B- series resins.

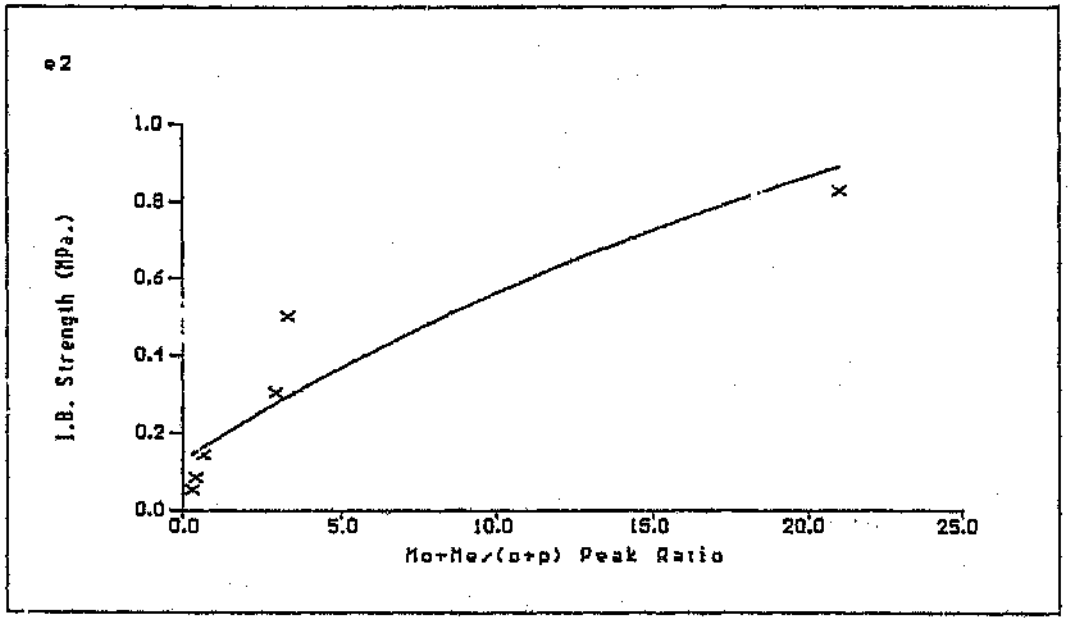


Fig. 6(c): ^{13}C NMR peak ratio for the Me+Mo/(o+p) species to the I.B. strength Dry test for the A-series resins.

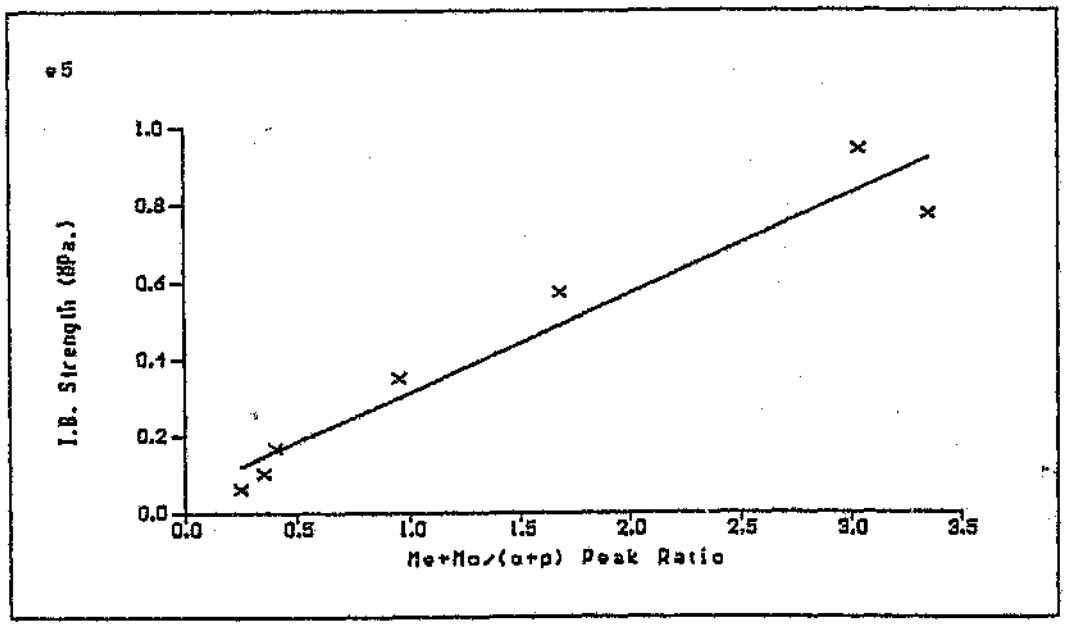


Fig. 6(d): ^{13}C NMR peak ratio for the Me+Mo/(o+p) species to the I.B. strength Dry test for the B-series resins.

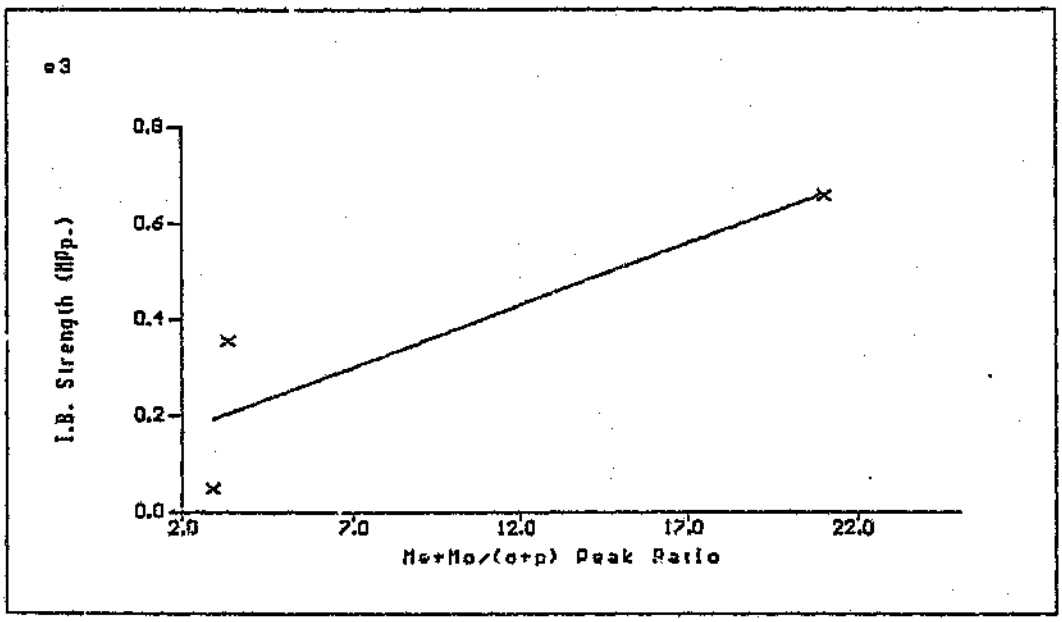


Fig. 6(e): ^{13}C NMR peak ratio for the Me+Mo/(o+p) species to the I.B. strength Wet test for the A-series resins.

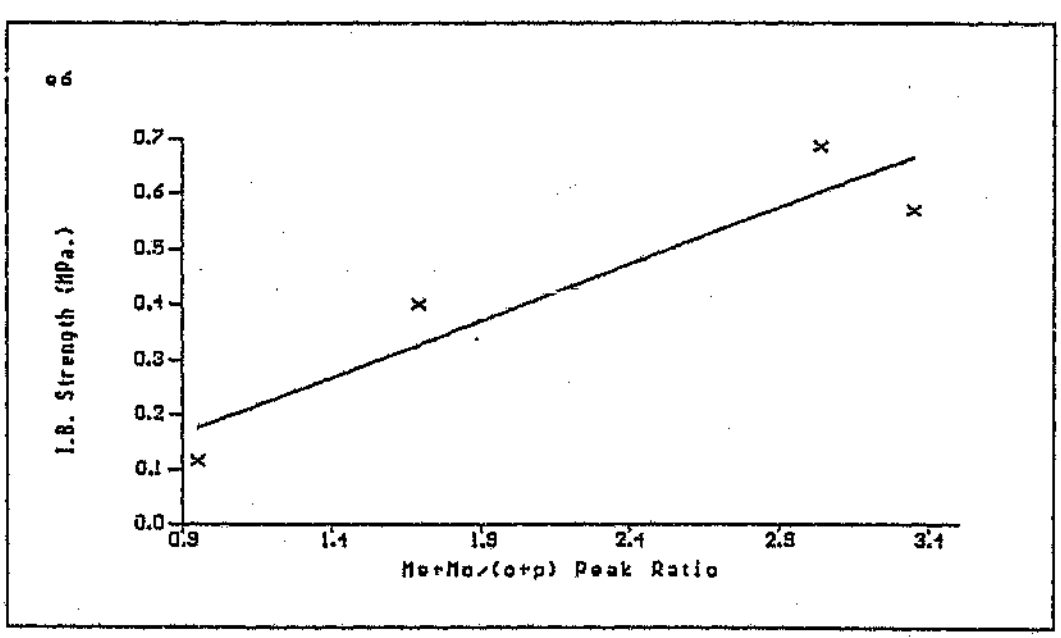


Fig. 6(f): ^{13}C NMR peak ratio for the Me+Mo/(o+p) species to the I.B. strength Wet test for the B-series resins.

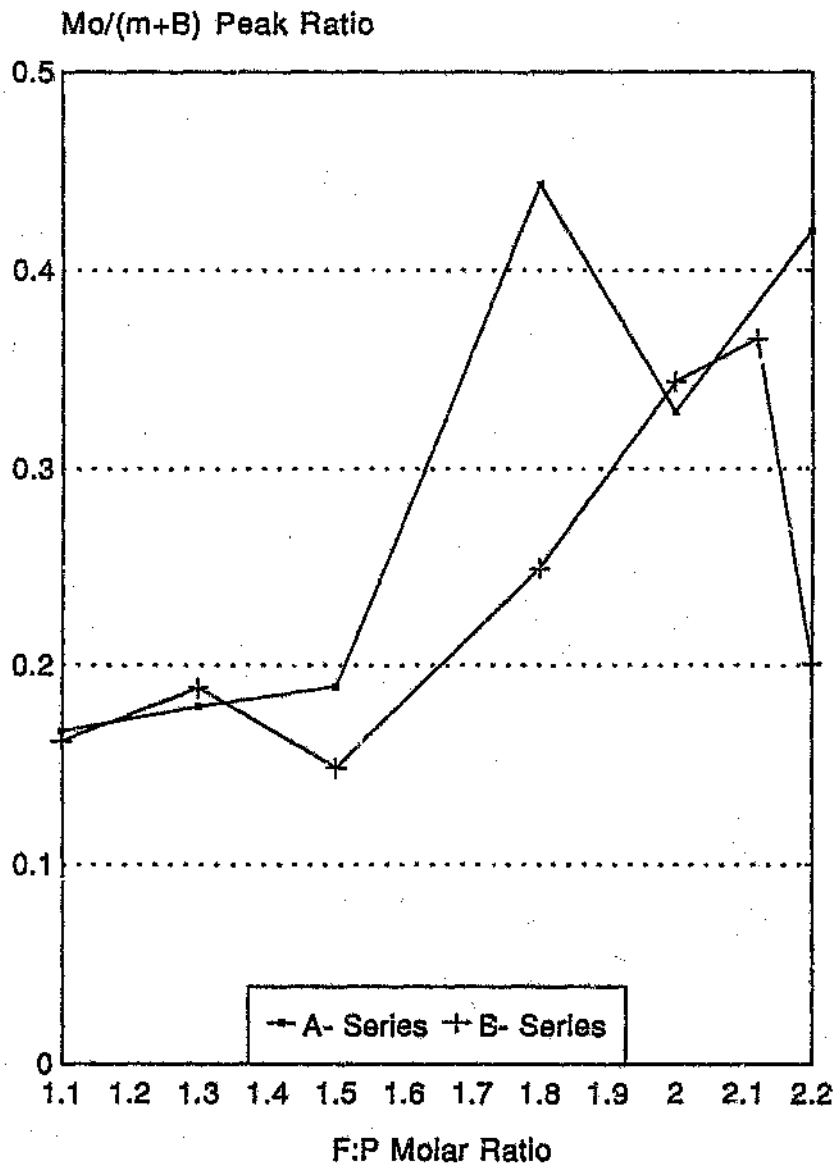


Fig 7: Calculated ^{13}C NMR peak ratios for the Mo/(m+B) species for the A- and B- series of resins

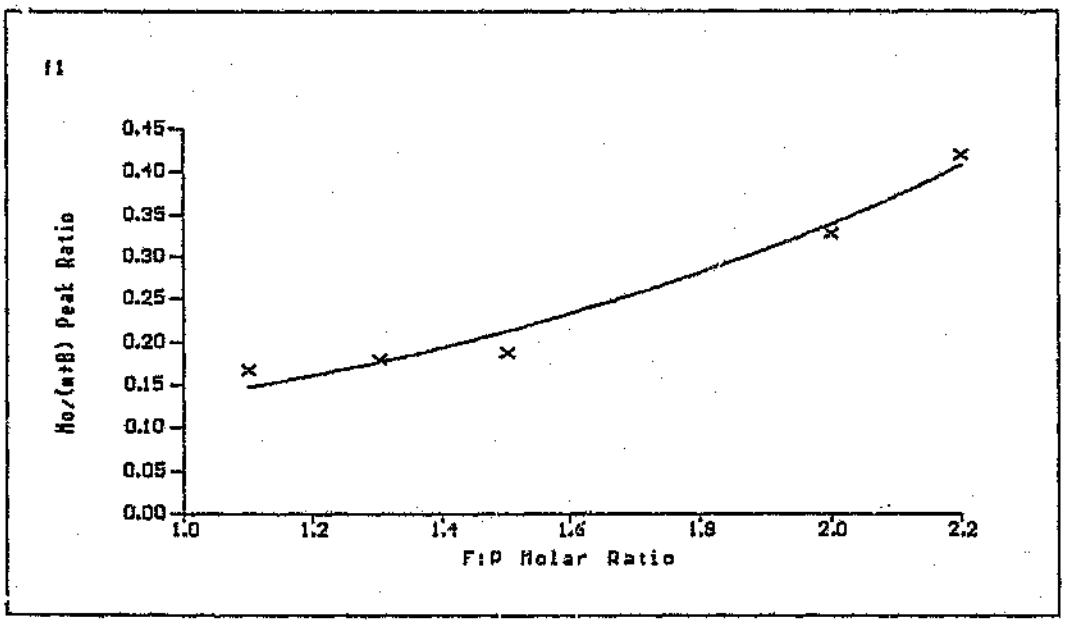


Fig. 7(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/(m+B) species for the A- series resins.

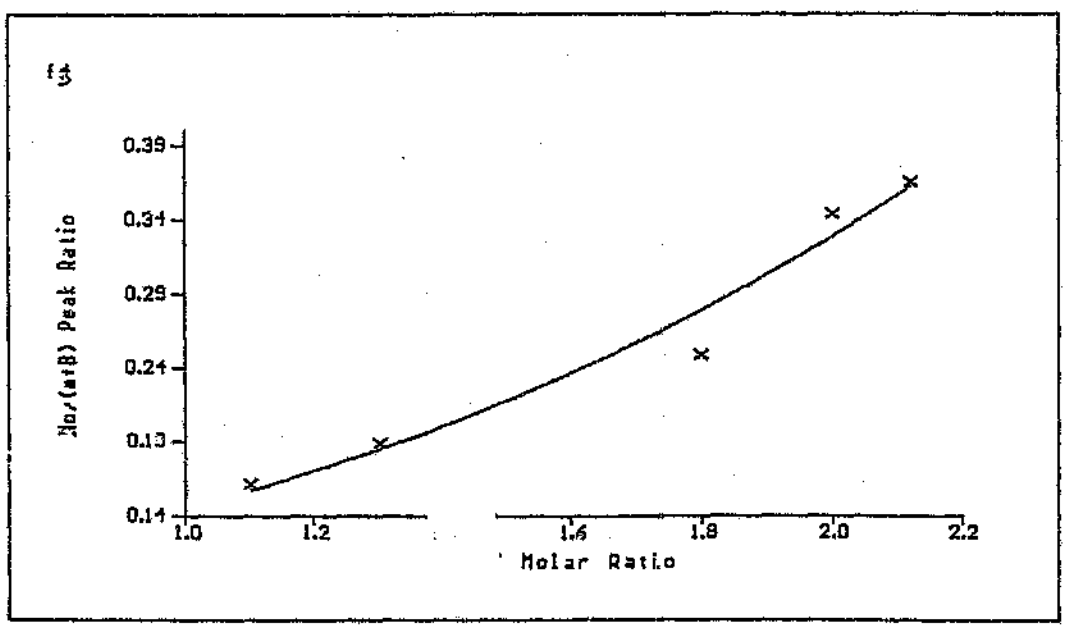


Fig. 7(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/(m+B) species for the B- series resins.

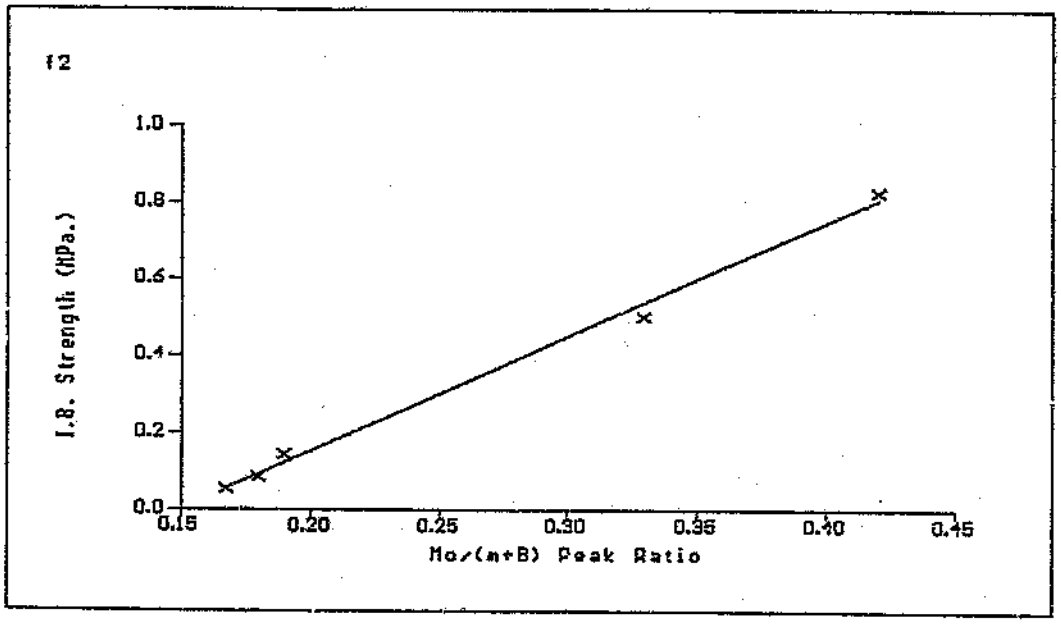


Fig. 7(c): ^{13}C NMR peak ratio for the Mo/(m+B) species to the I.B. strength Dry test for the A- series resins.

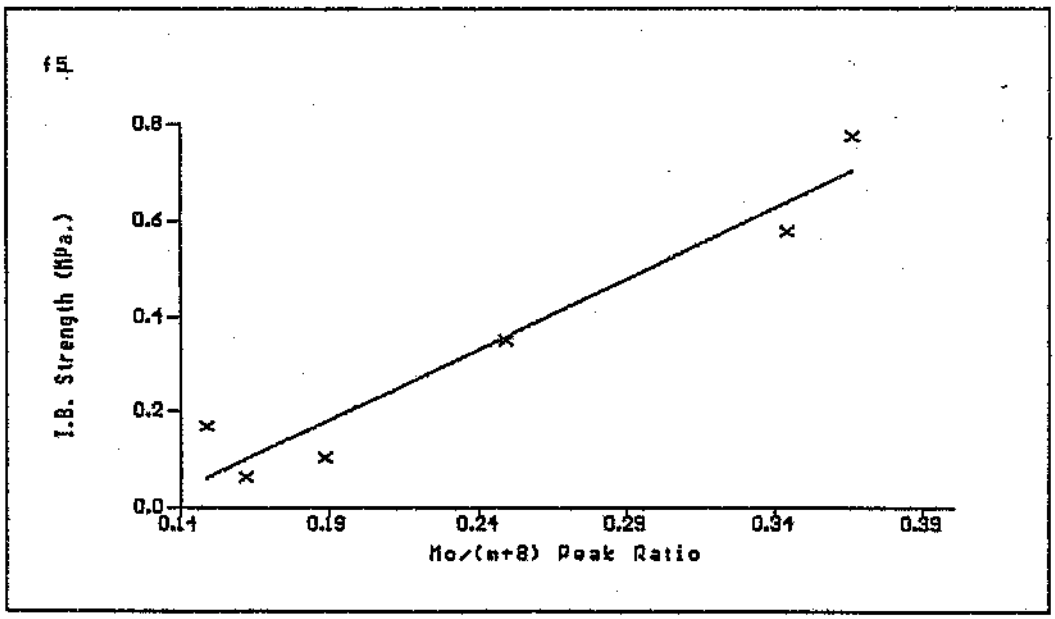


Fig. 7(d): ^{13}C NMR peak ratio for the Mo/(m+B) species to the I.B. strength Dry test for the B- series resins.

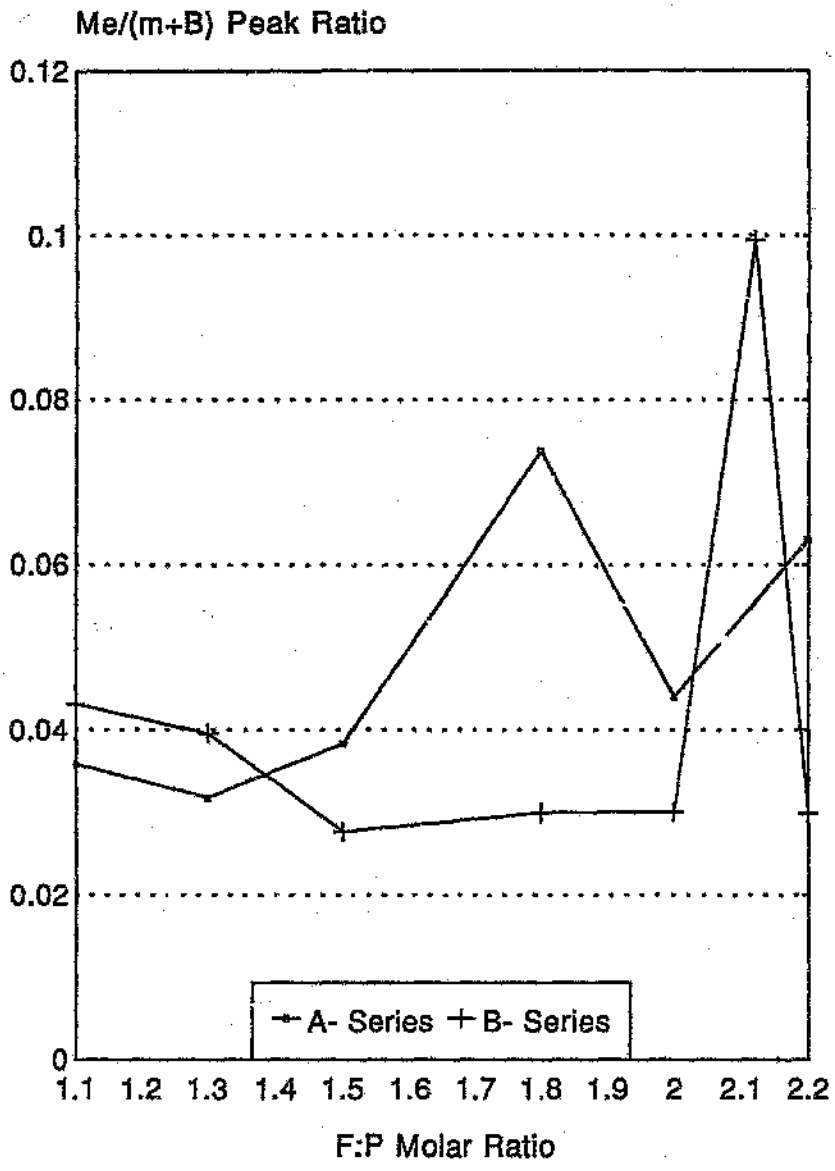


Fig 8: Calculated ^{13}C NMR peak ratios for the Me/(m+B) spesies for the A- and B- series of resins

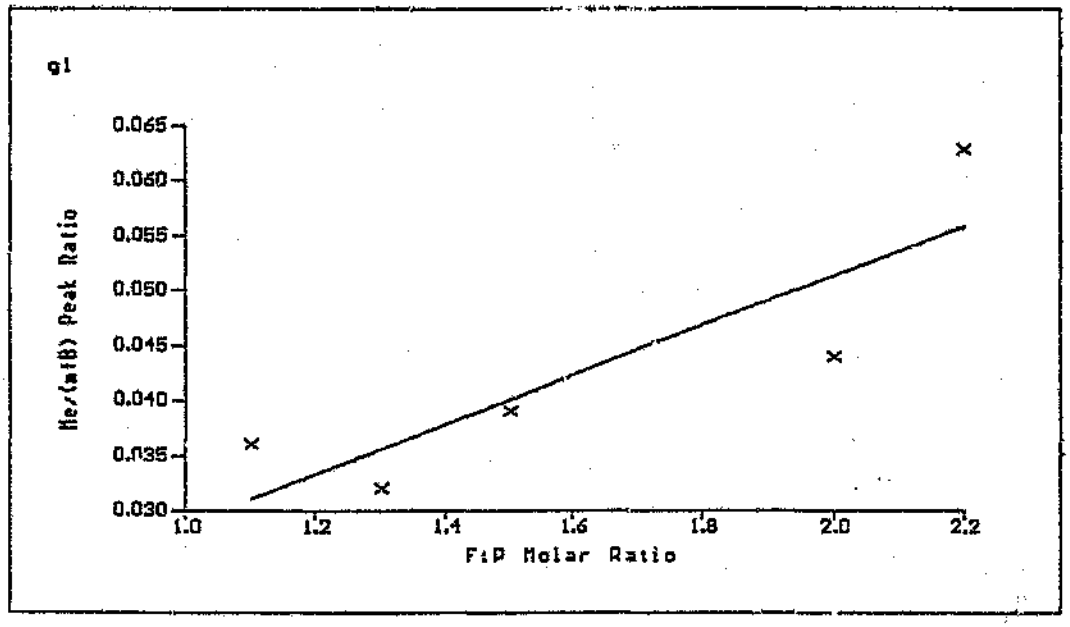


Fig. 8(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Me/(m+B) species for the A- series resins.

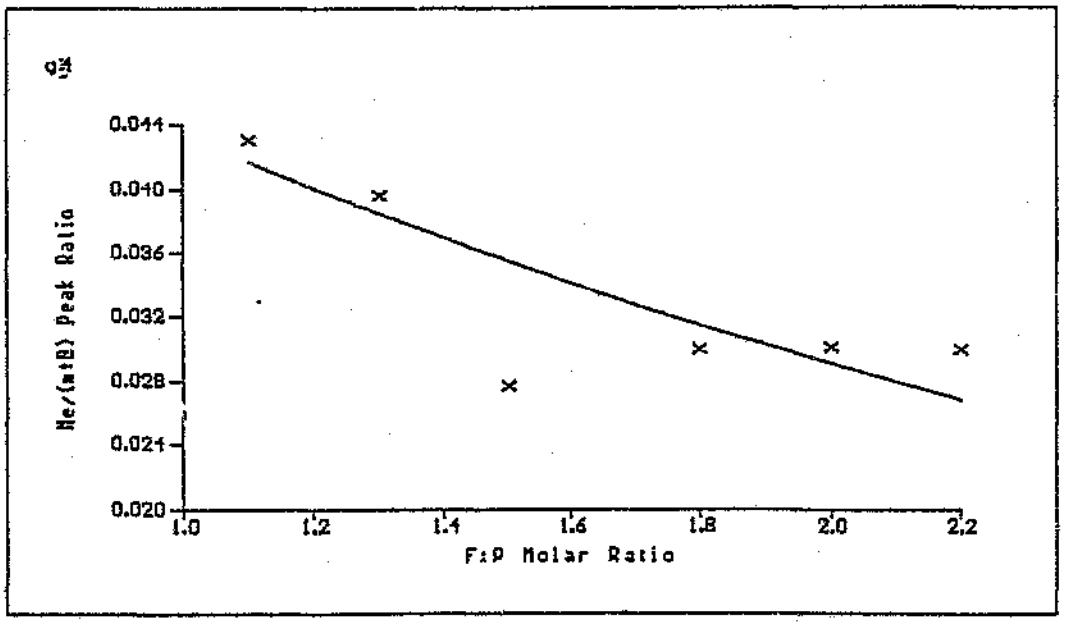


Fig. 8(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Me/(m+B) species for the B- series resins.

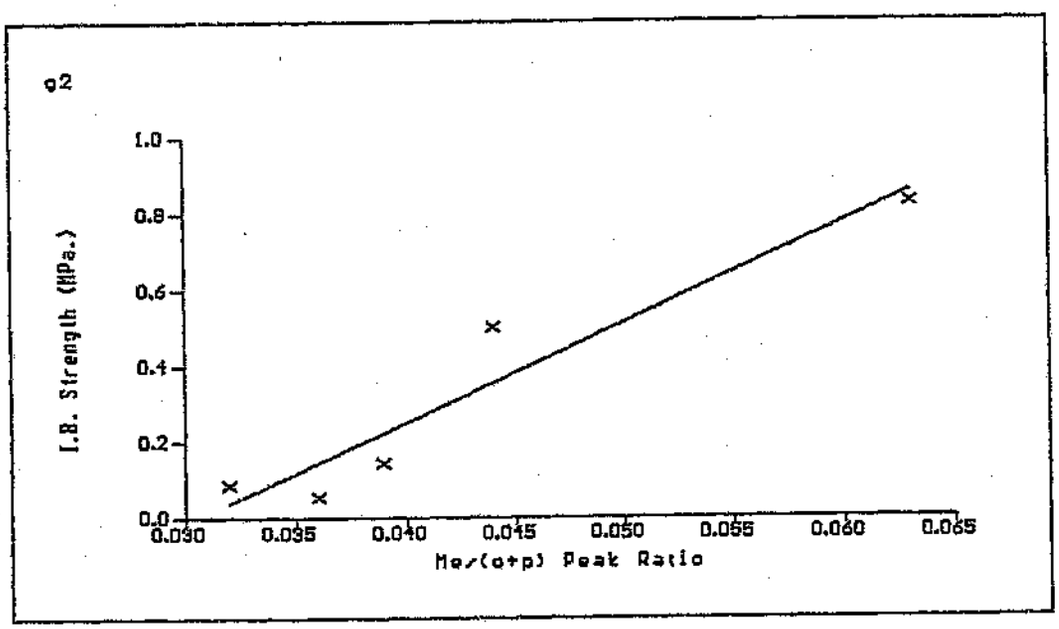


Fig. 8(c): ^{13}C NMR peak ratio for the Me/(m+B) species to the I.B. strength Dry test for the A- series resins.

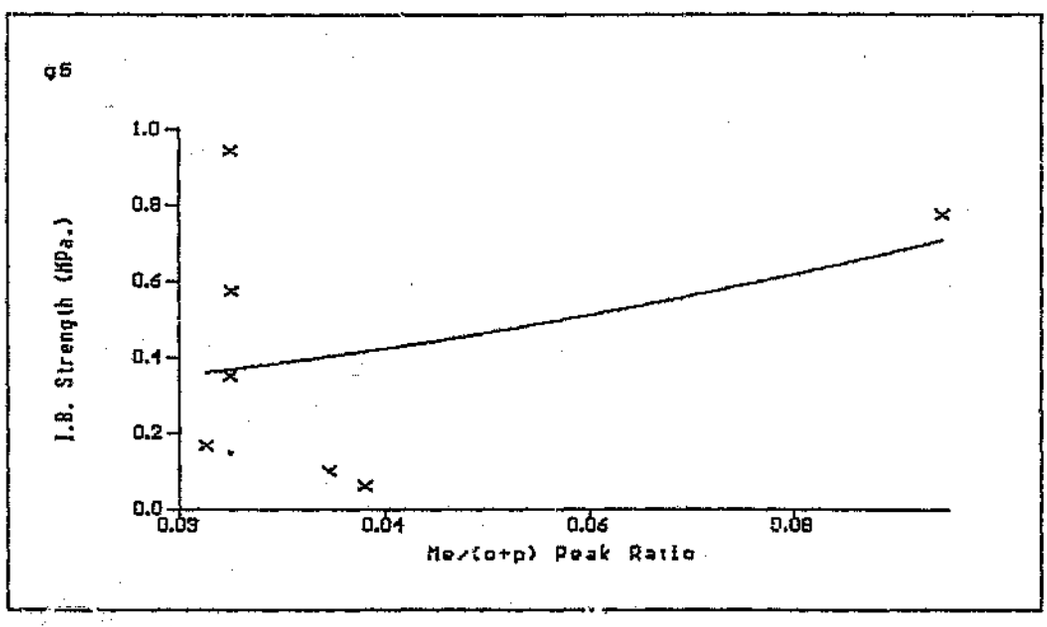


Fig. 8(d): ^{13}C NMR peak ratio for the Me/(m+B) species to the I.B. strength Dry test for the B- series resins.

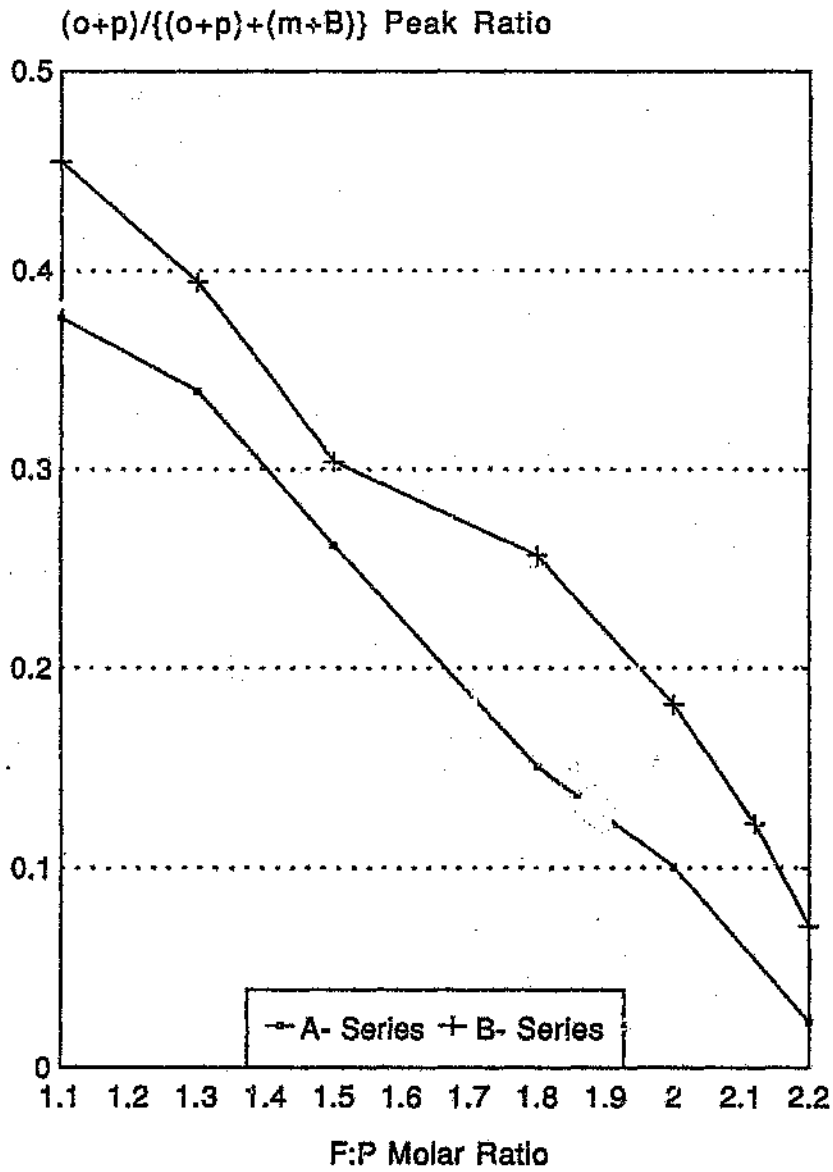


Fig 9: Calculated ^{13}C NMR peak ratios for the (o+p)/{(o+p)+(m+B)} species for the A- and B- series of resins.

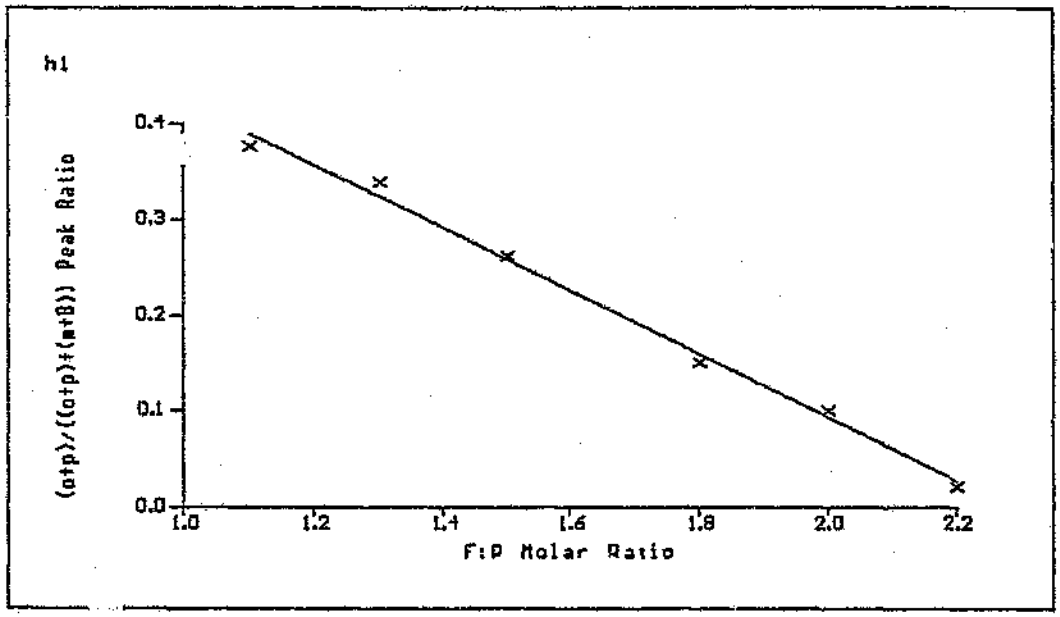


Fig. 9(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the {o+p)/{(o+p)+(m+B)} species for the A-series resins.

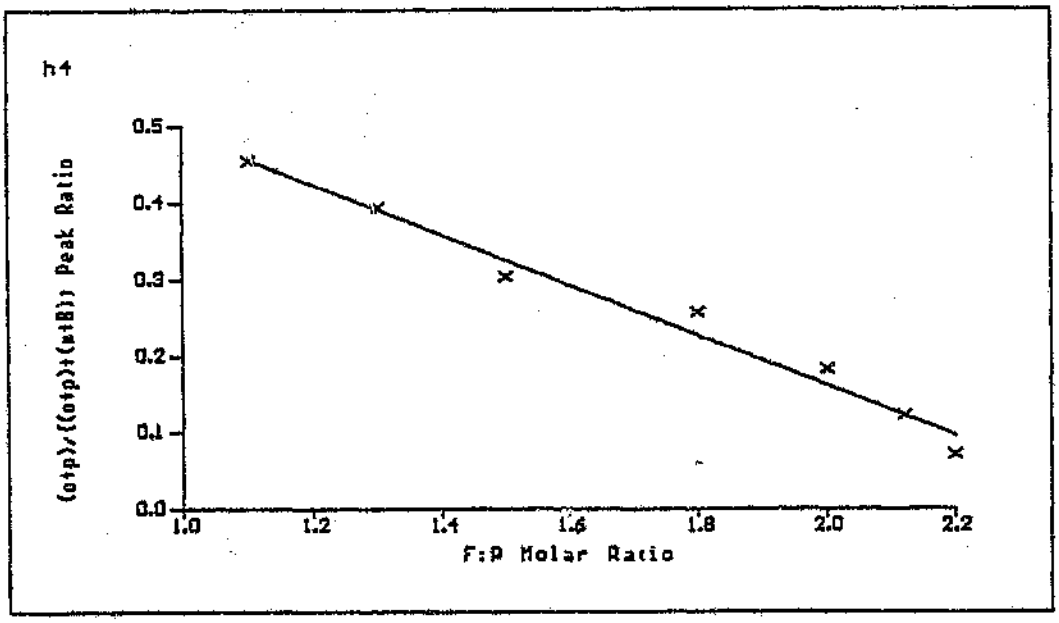


Fig. 9(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the (o+p)/{(o+p)+(m+B)} species for the B-series resins.

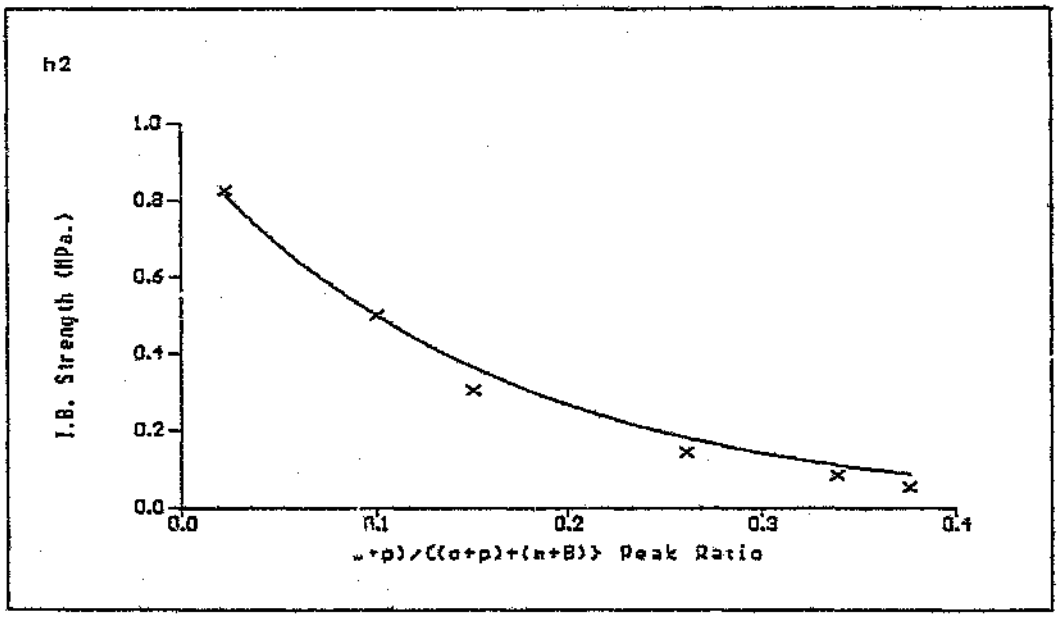


Fig. 9(c): ^{13}C NMR peak ratio for the (o+p)/{(o+p)+(m+B)} species to the I.B. strength Dry test for the A- series resins.

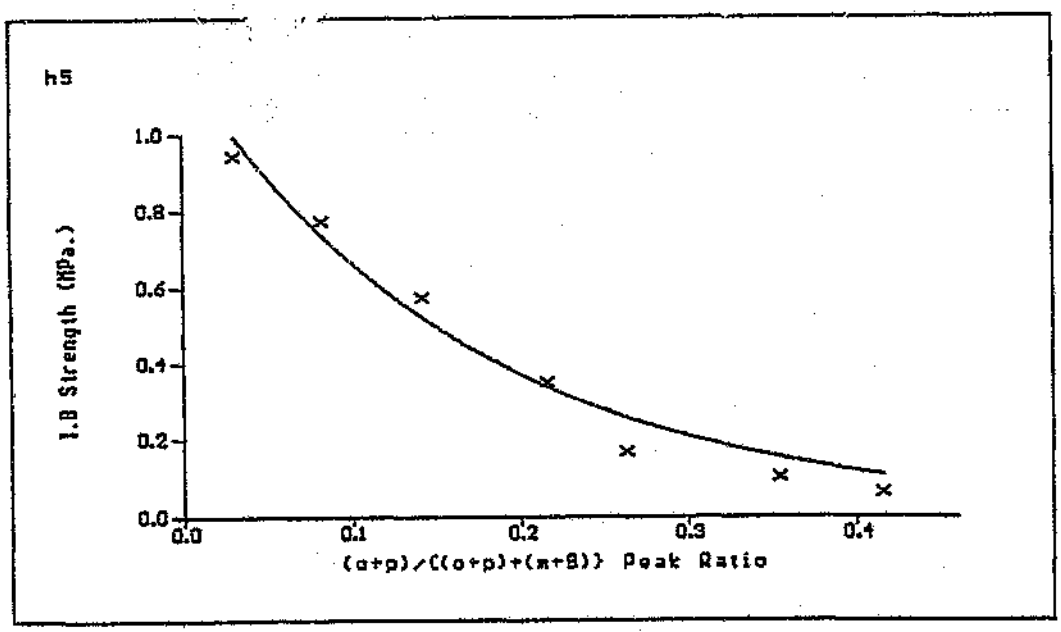


Fig. 9(d): ^{13}C NMR peak ratio for the (o+p)/{(o+p)+(m+B)} species to the I.B. strength Dry test for the B- series resins.

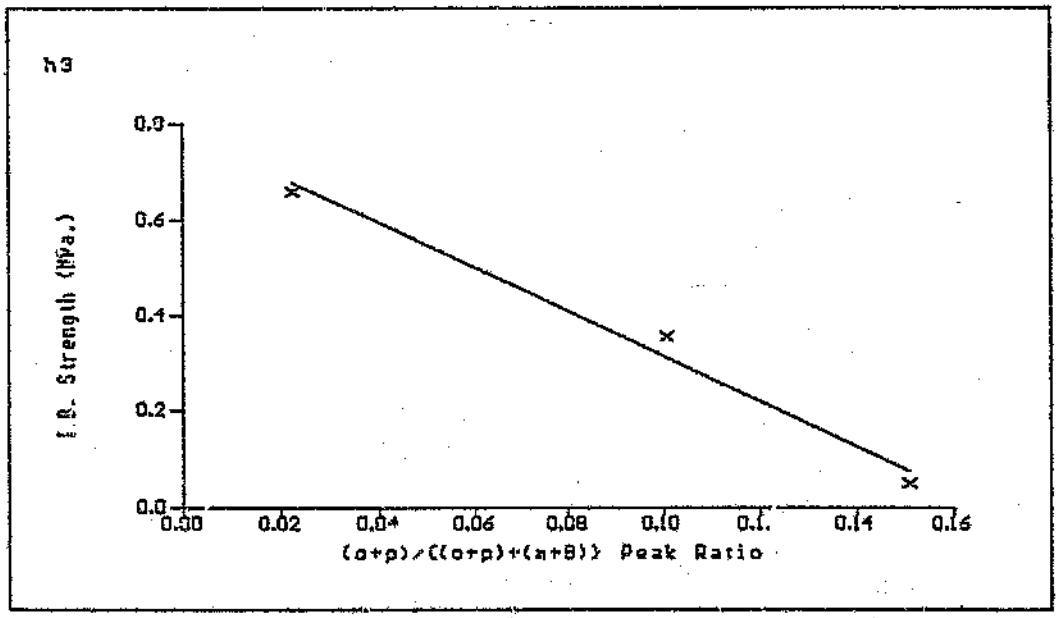


Fig. 9(e): ^{13}C NMR peak ratio for the (o+p)/{(o+p)+(m+B)} species to the I.B. strength Wet test for the A- series resins.

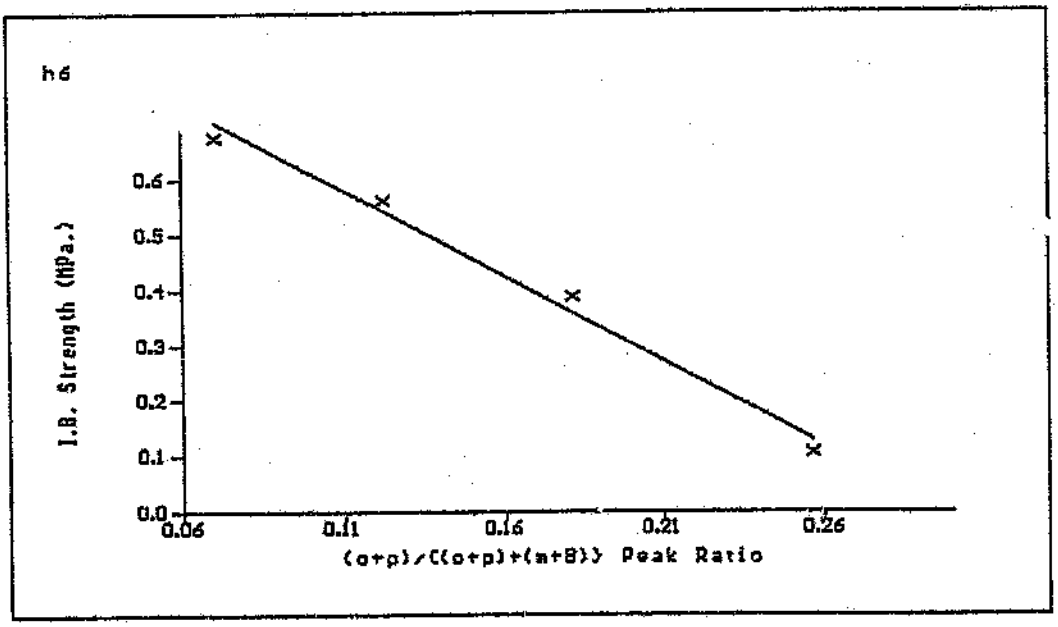


Fig. 9(f): ^{13}C NMR peak ratio for the (o+p)/{(o+p)+(m+B)} species to the I.B. strength Wet test for the B- series resins.

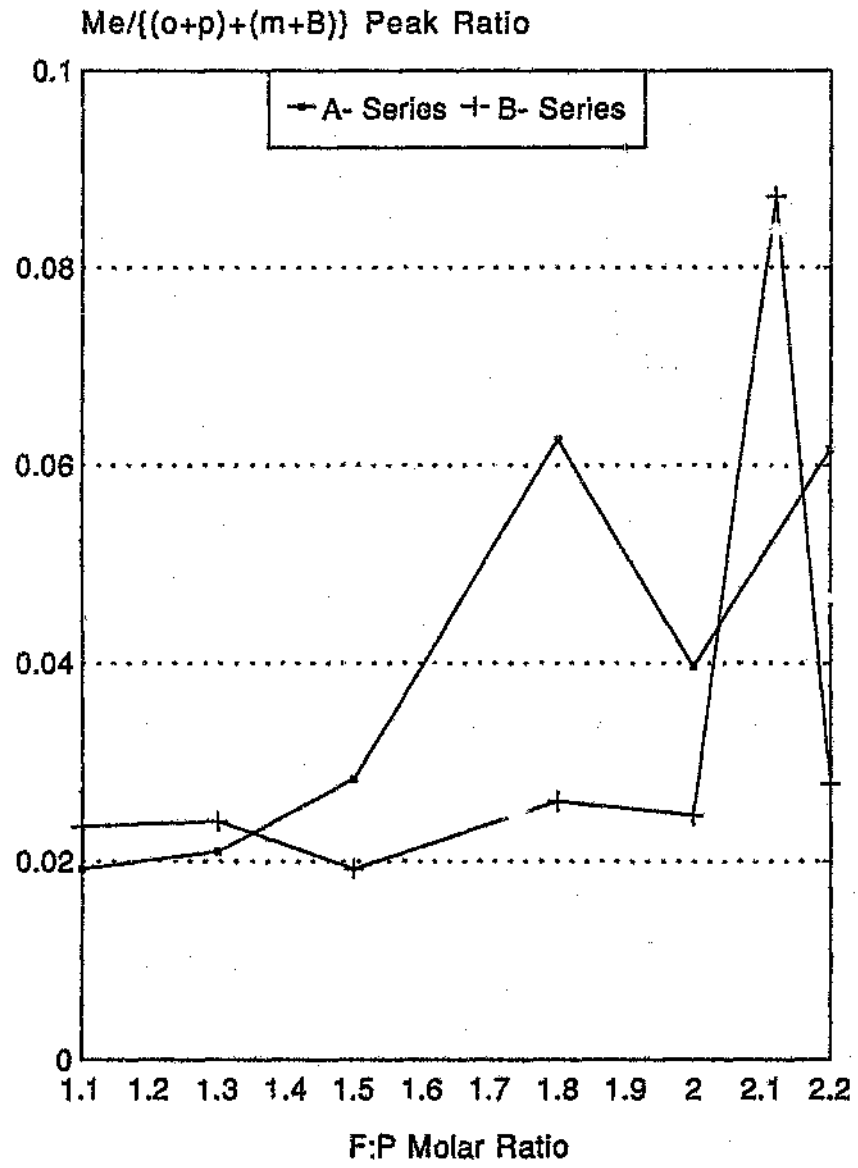


Fig 10: Calculated ^{13}C NMR peak ratios for the Me/{(o+p)+(m+B)} species for the A- and B- series resins

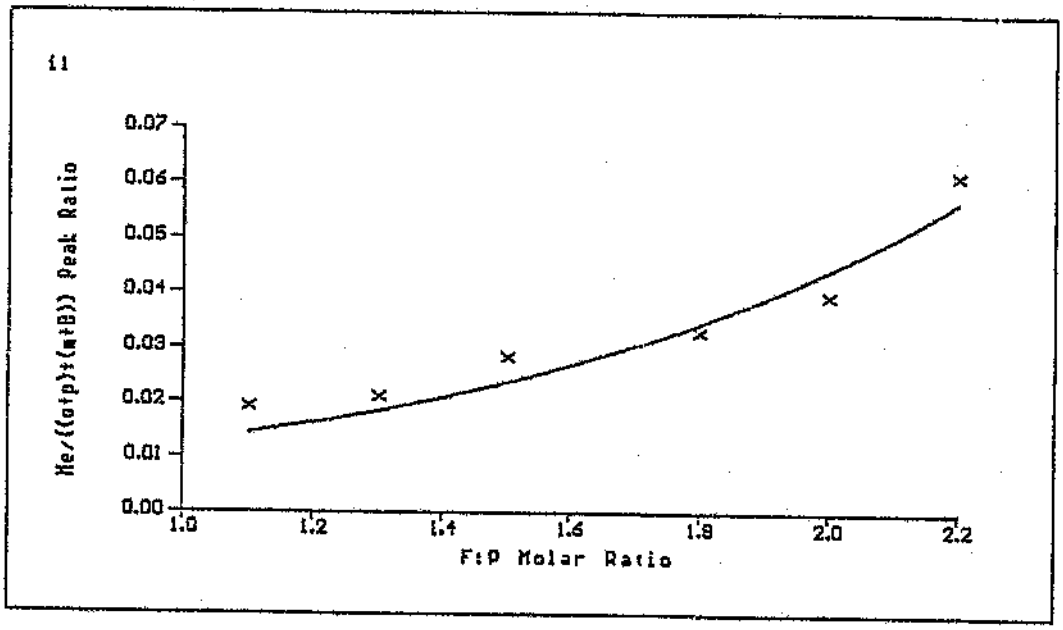


Fig. 10(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species for the A-series resins.

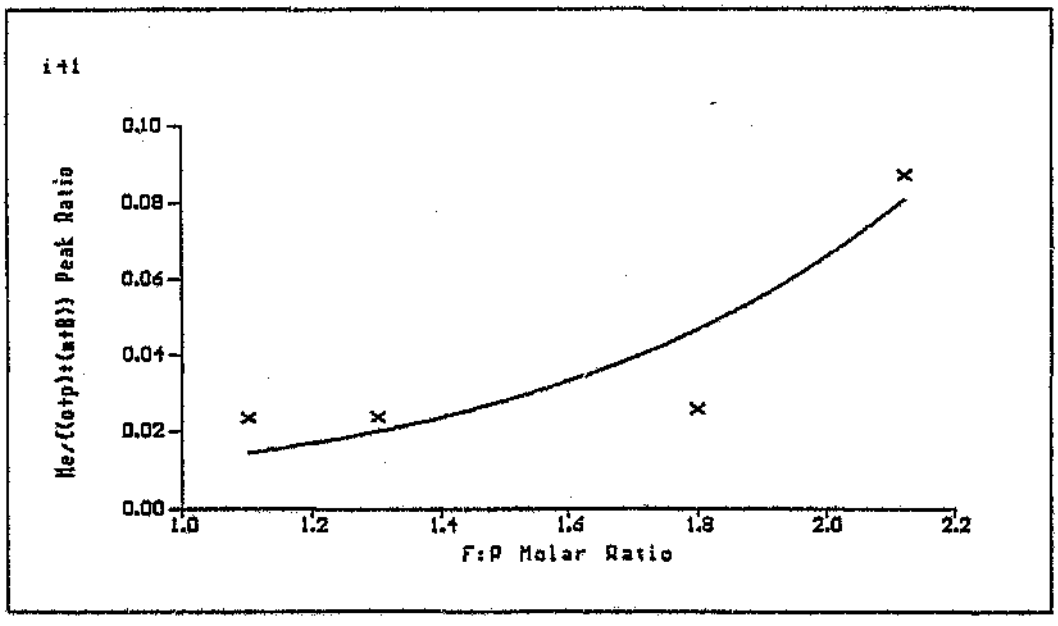


Fig. 10(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species for the B-series resins.

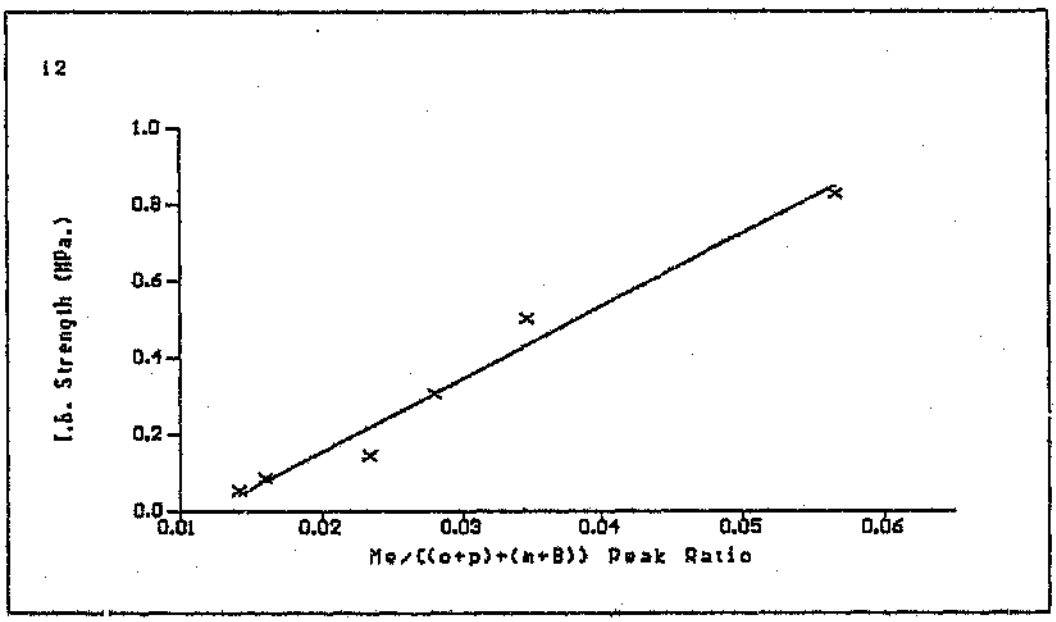


Fig. 10(c): ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species to the I.B. strength Dry test for the A- series resins.

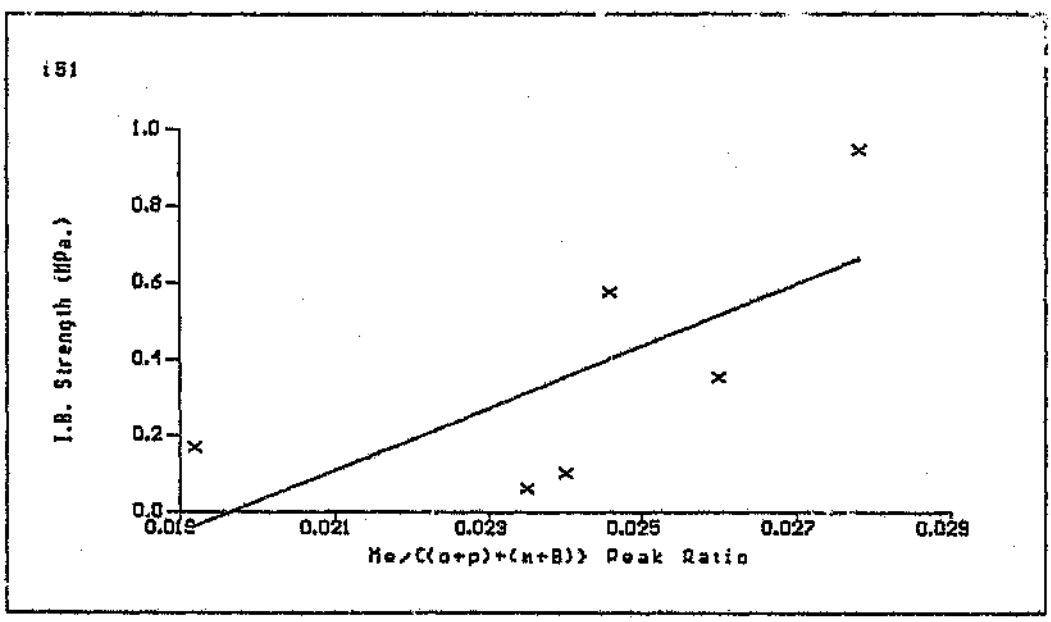


Fig. 10(d): ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species to the I.B. strength Dry test for the B- series resins.

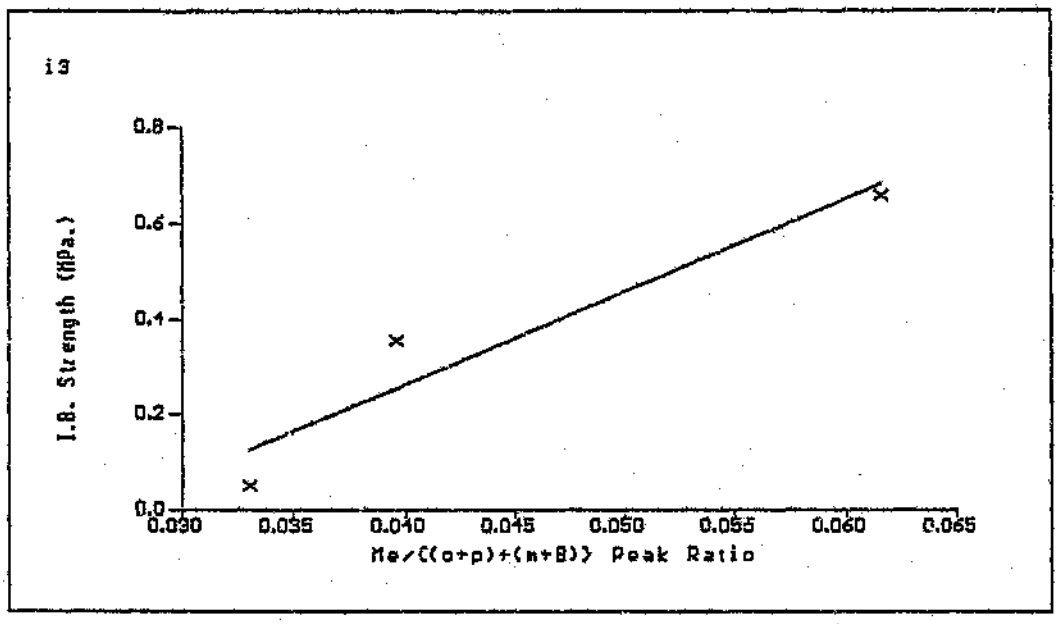


Fig. 10(e): ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species to the I.B. strength Wet test for the A- series resins.

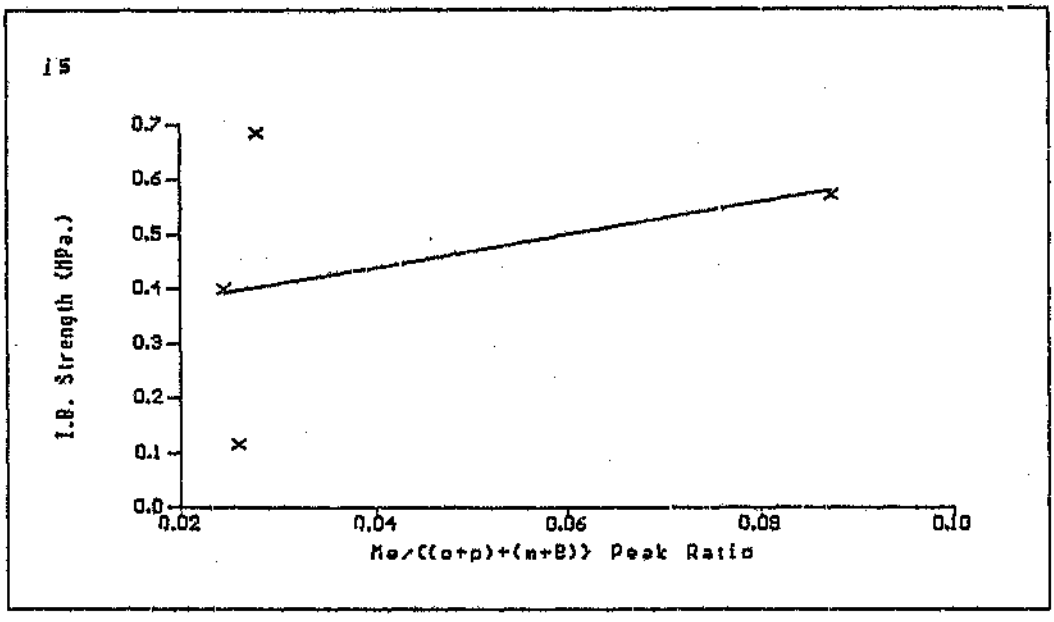


Fig. 10(f): ^{13}C NMR peak ratio for the Me/{(o+p)+(m+B)} species to the I.B. strength Wet test for the B- series resins.

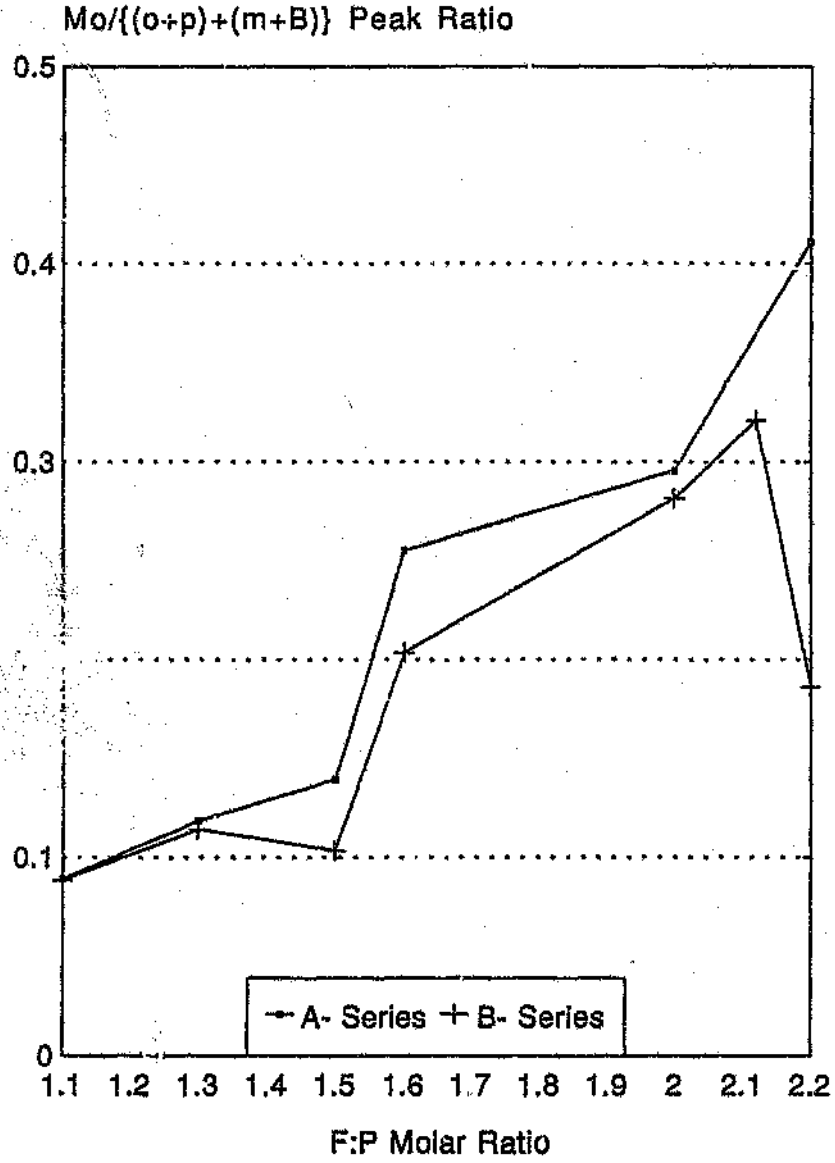


Fig 11: Calculated ^{13}C NMR peak ratios for the Mo/{(o+p)+(m+B)} species for the A- and B-series of resins.

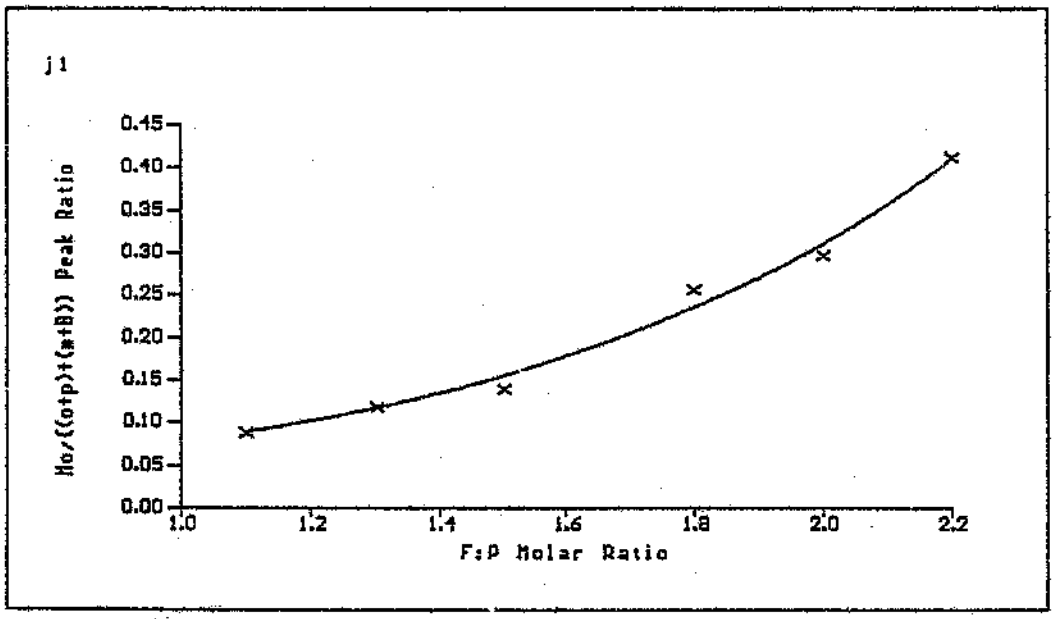


Fig. 11(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species for the A-series resins.

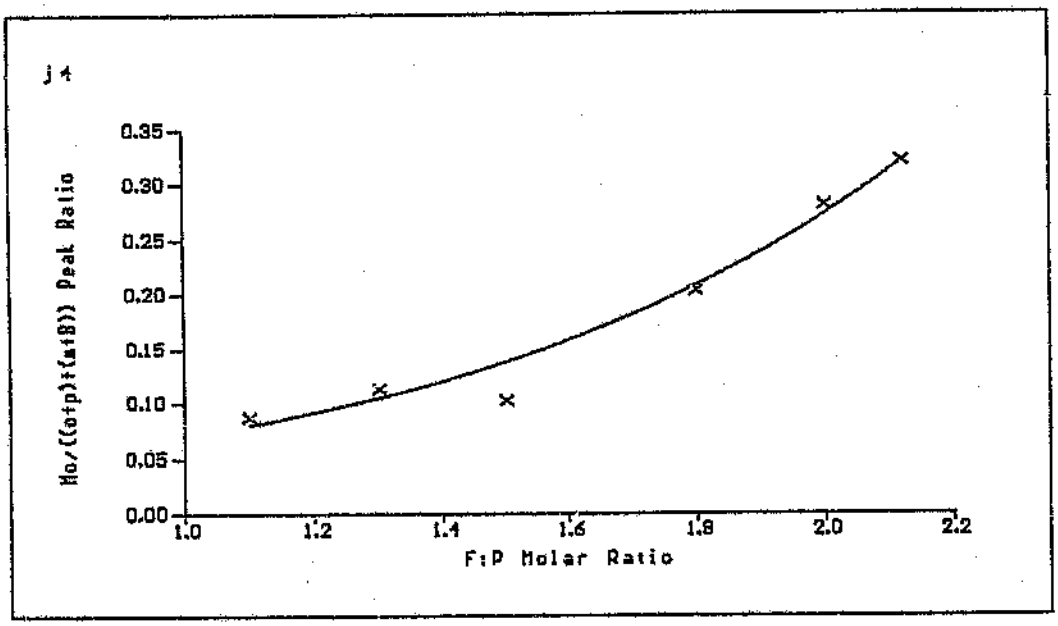


Fig. 11(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species for the B-series resins.

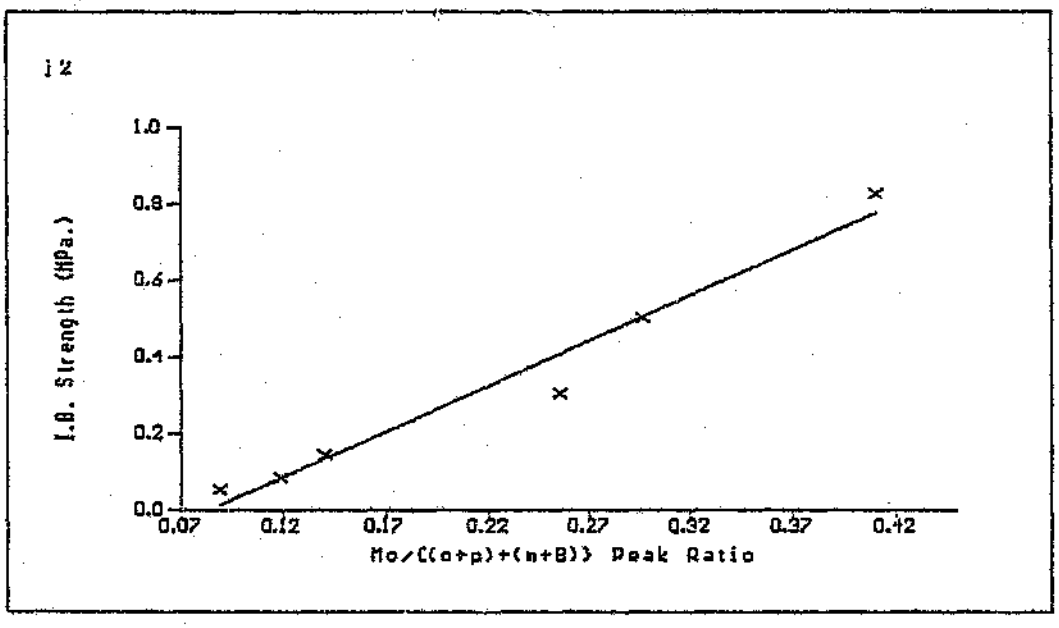


Fig. 11(c): ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species to the I.B. strength Dry test for the A- series resins.

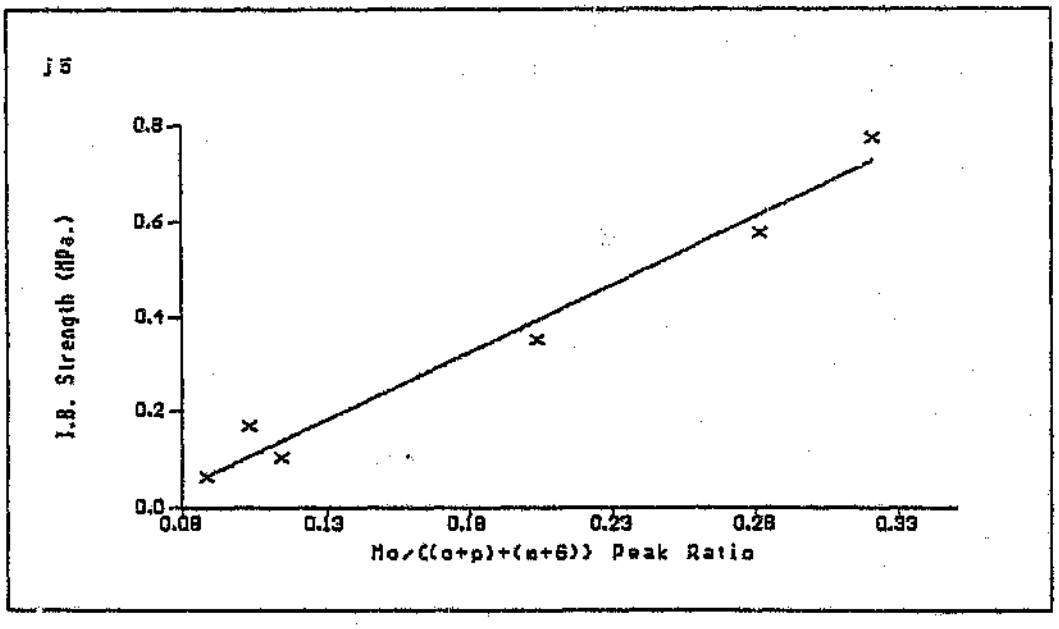


Fig. 11(d): ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species to the I.B. strength Dry test for the B- series resins.

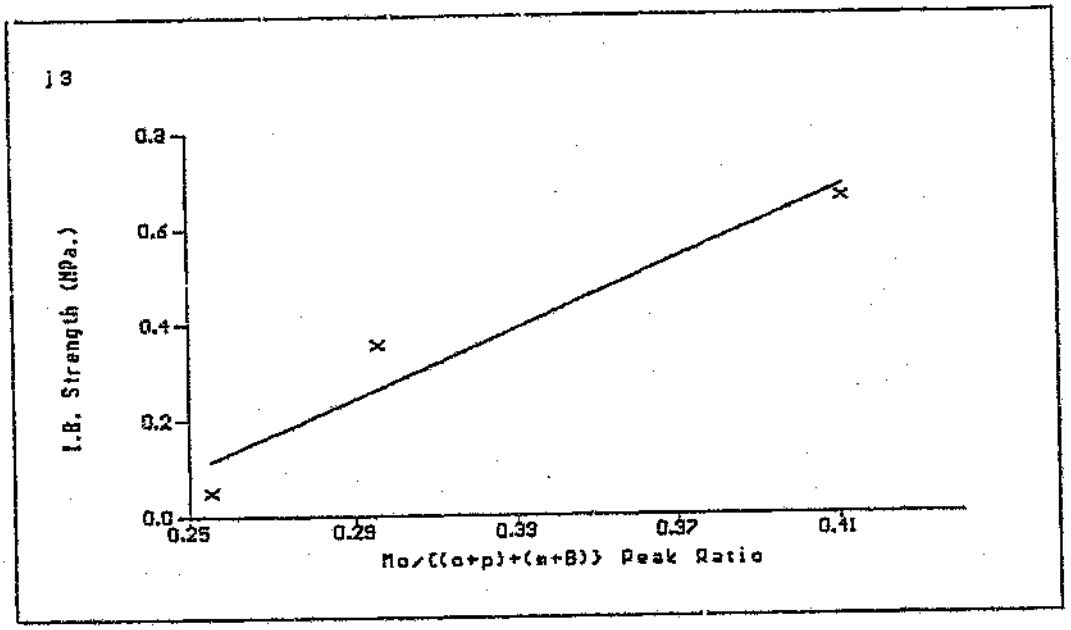


Fig. 11(e): ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species to the I.B. strength Wet test for the A- series resins.

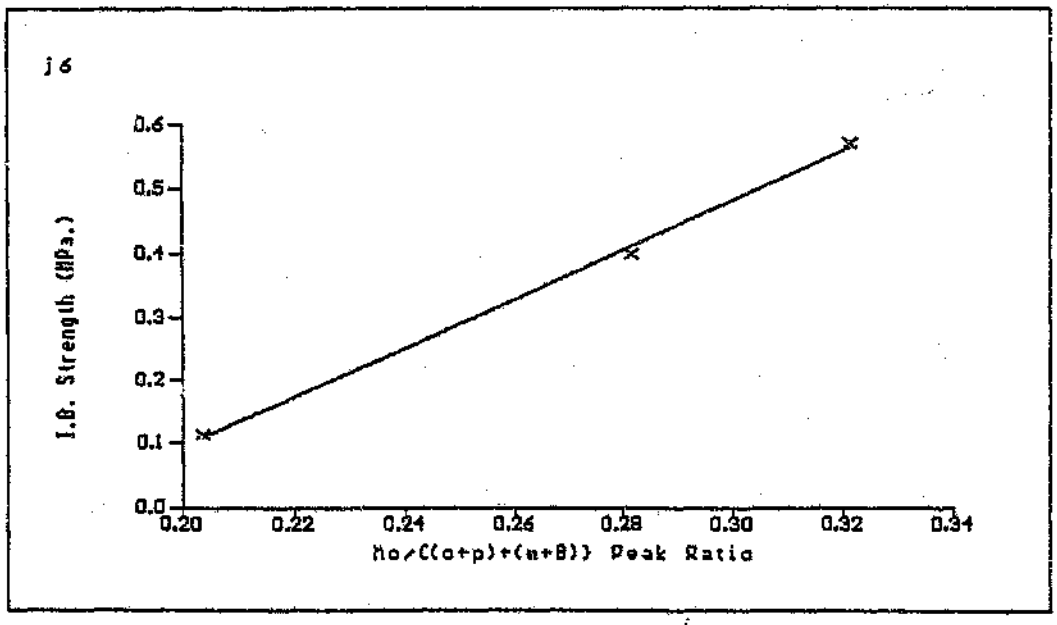


Fig. 11(f): ^{13}C NMR peak ratio for the Mo/{(o+p)+(m+B)} species to the I.B. strength Wet test for the B- series resins.

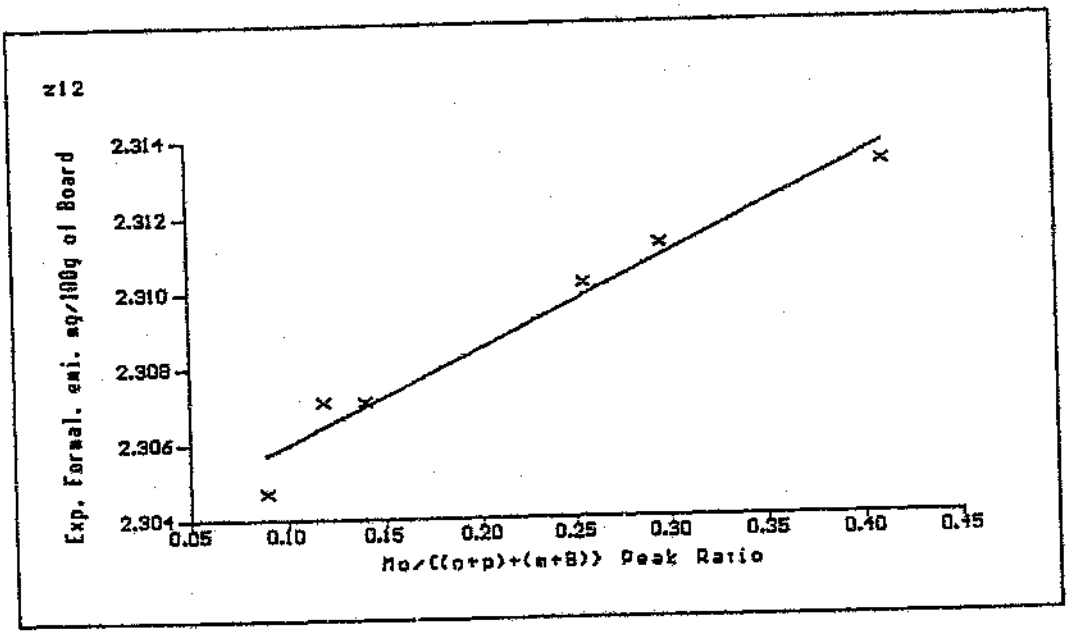


Fig 11(g) : ^{13}C NMR Peak ratio of Mo/{(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the A-series resins.

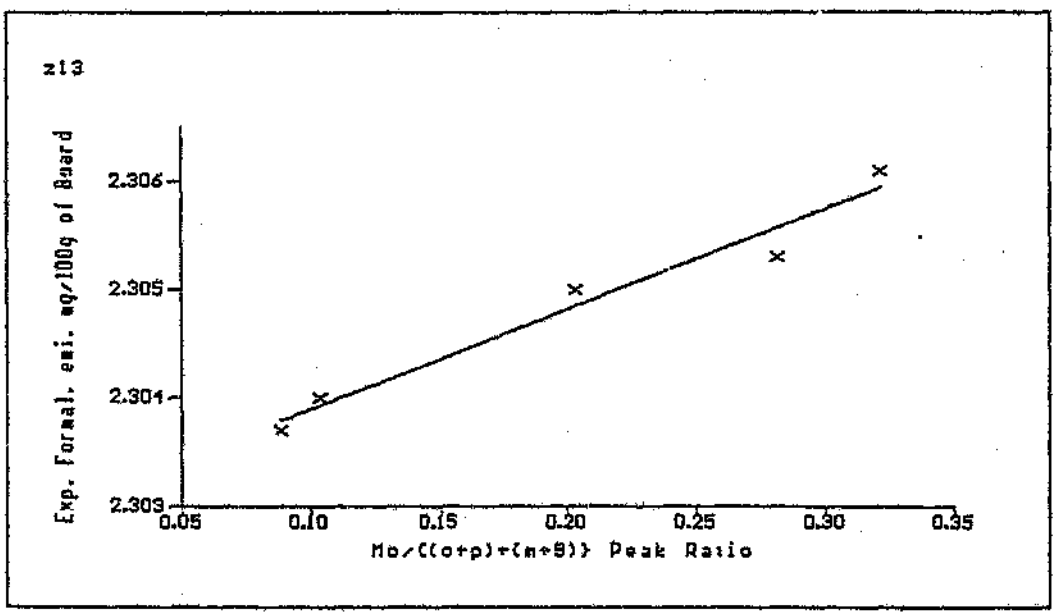


Fig 11(h) : ^{13}C NMR Peak ratio of Mo/{(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the B-series resins.

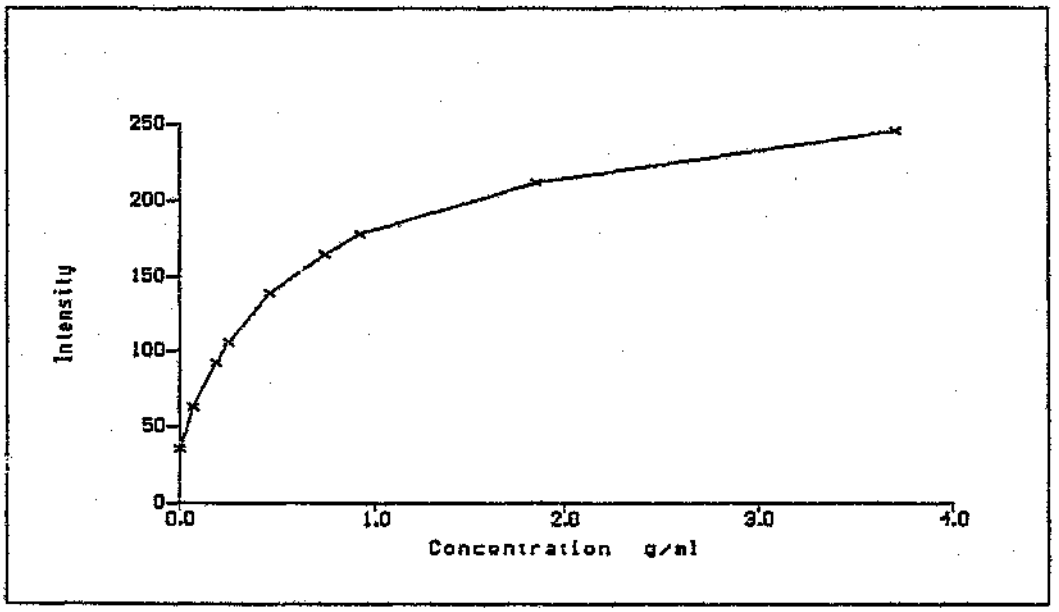


Fig. 12: Graph relating the fluorescence and the formaldehyde concentration for the standard solutions.

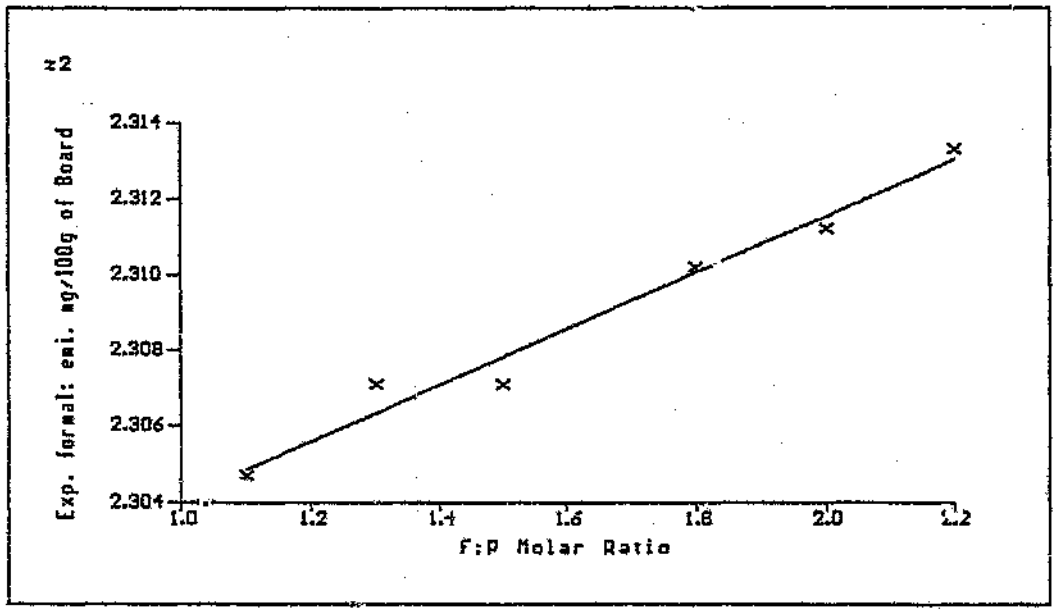


Fig. 13(a): Relating F:P molar ratio to the experimental formaldehyde emission data (by WKI method) for the particleboards made with the A-series resins.

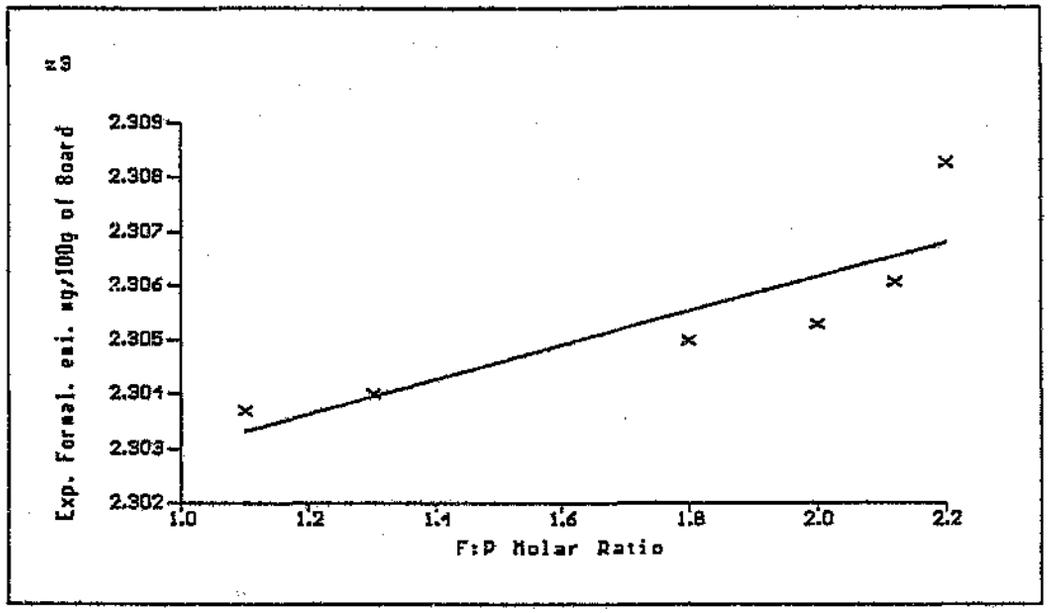


Fig. 13(b): Relating F:P molar ratio to the experimental formaldehyde emission data (by WKI method) for the particleboards made with the B-series resins.

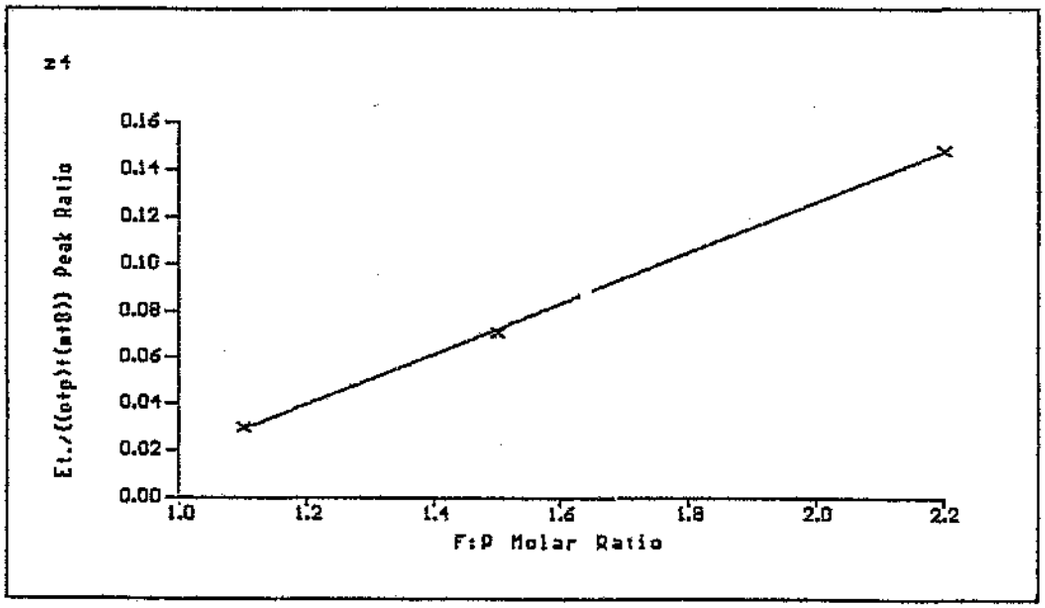


Fig. 14(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Ether/{(o+p)+(m+B)} species for the A-series resins.

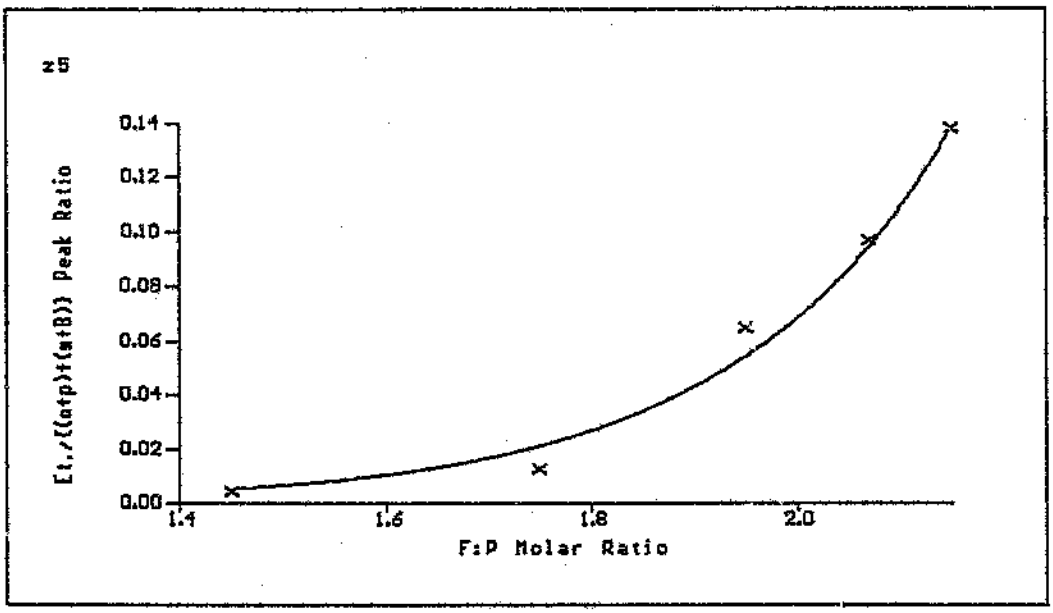


Fig. 14(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Ether/{(o+p)+(m+B)} species for the B-series resins.

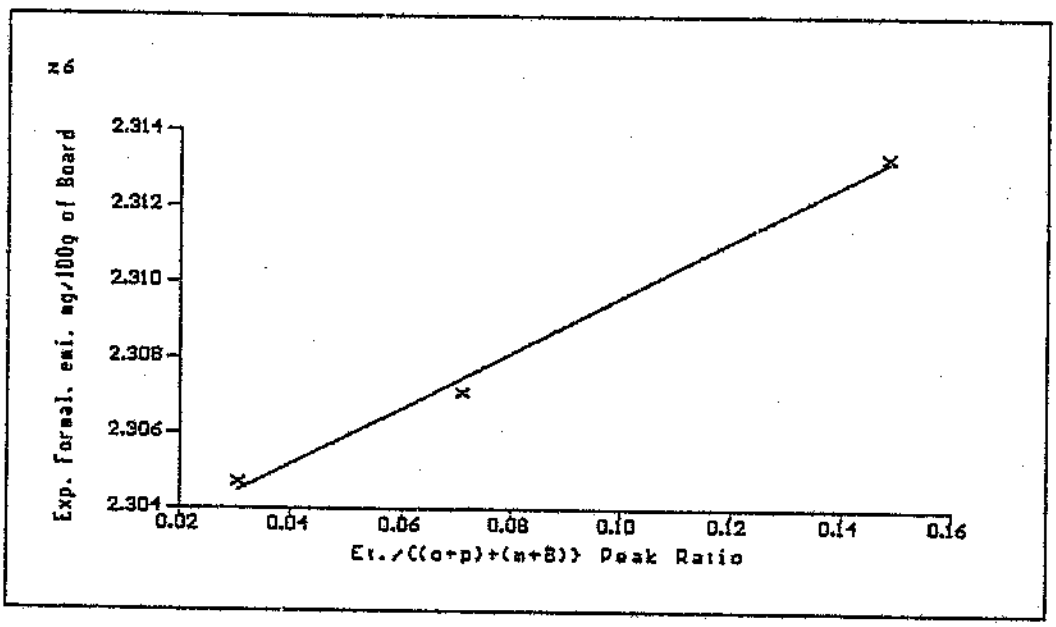


Fig 14(g) : ^{13}C NMR Peak ratio of total Ether/{(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the A- series resins.

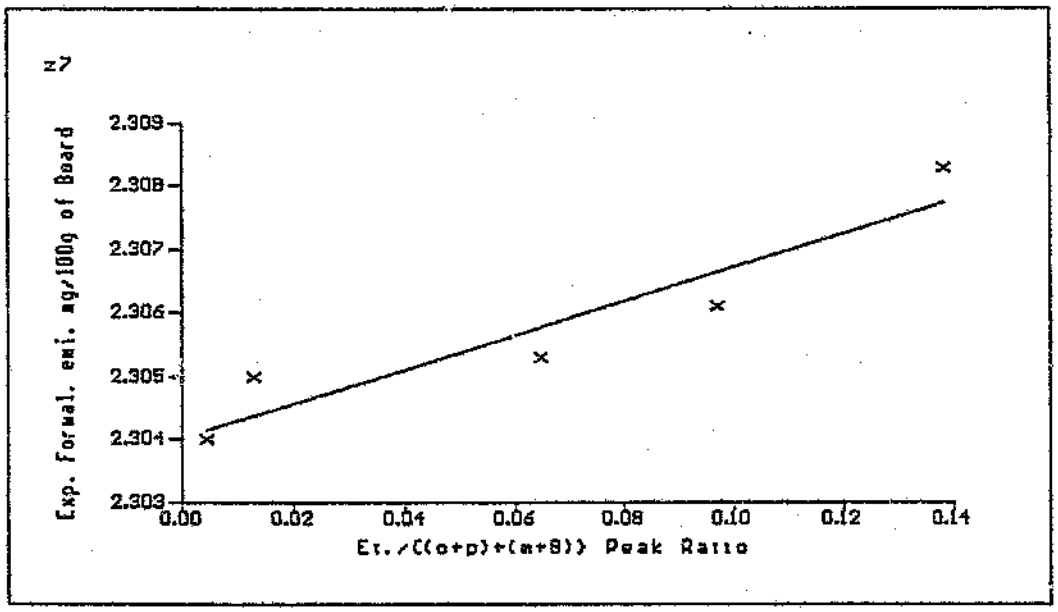


Fig. 14(h) : ^{13}C NMR Peak ratio of total Ether/{(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the B- series resins.

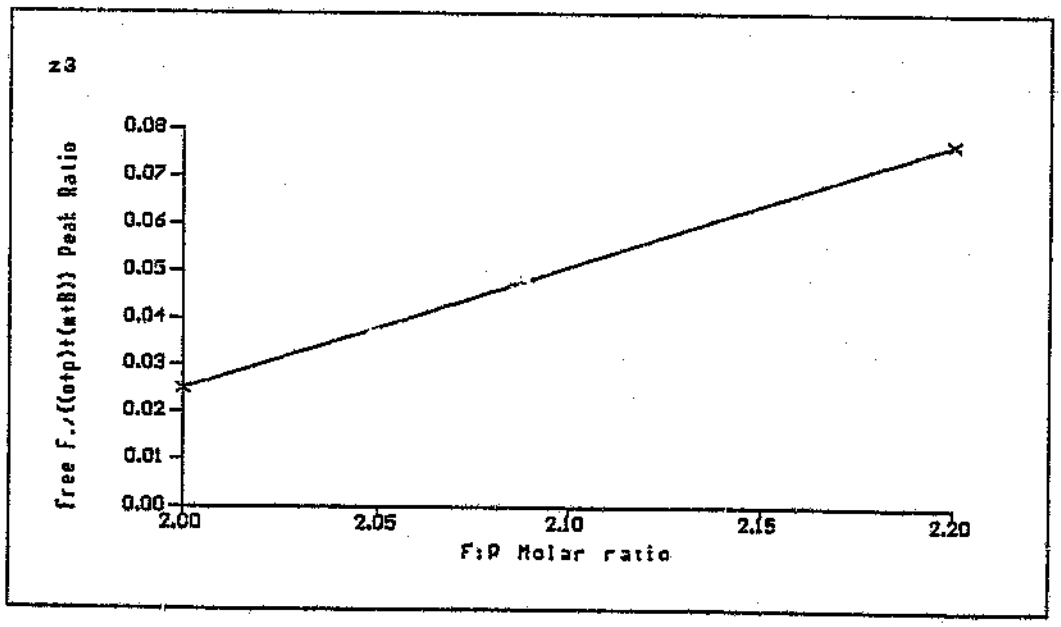


Fig. 15(a): F:P molar ratio versus the ^{13}C NMR peak ratio for the Free formaldehyde/{(o+p)+(m+B)} species for the A- series resins.

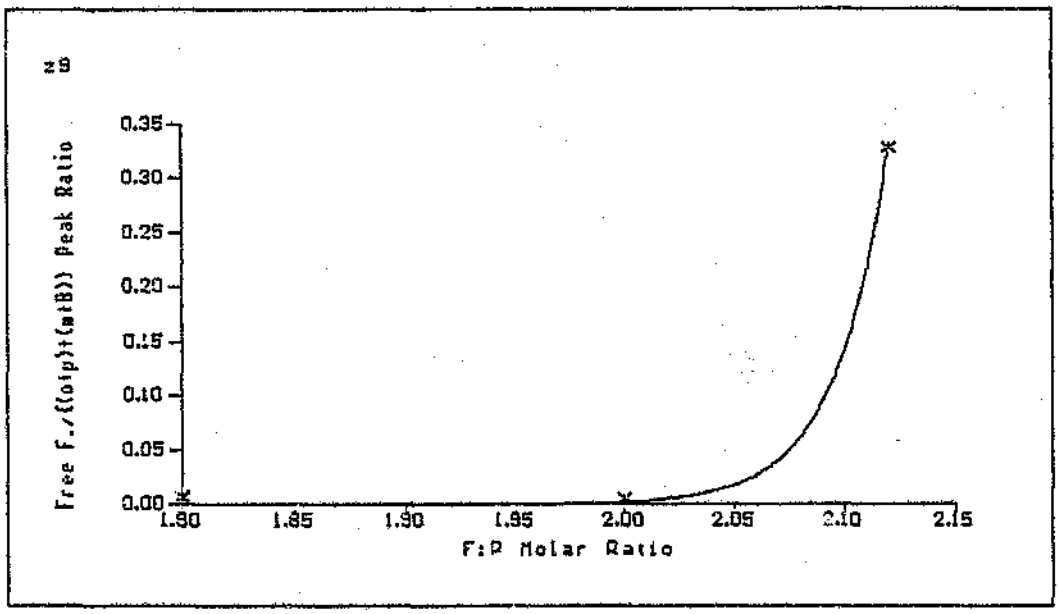


Fig. 15(b): F:P molar ratio versus the ^{13}C NMR peak ratio for the Free formaldehyde /{(o+p)+(m+B)} species for the B- series resins.

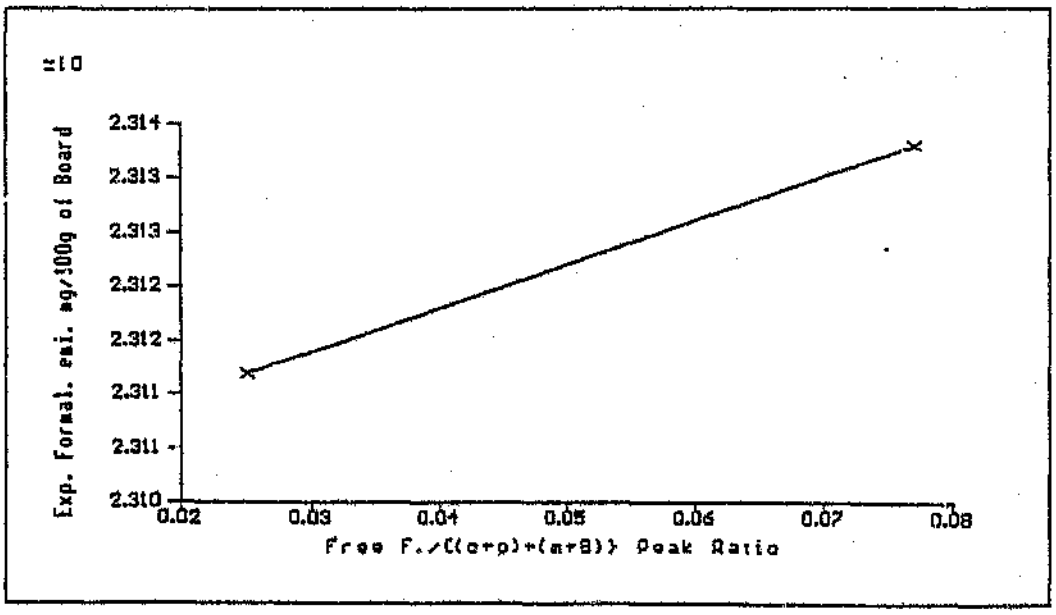


Fig. 15(c) : ^{13}C NMR Peak ratio of total free formaldehyde/ {(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the A- series resins.

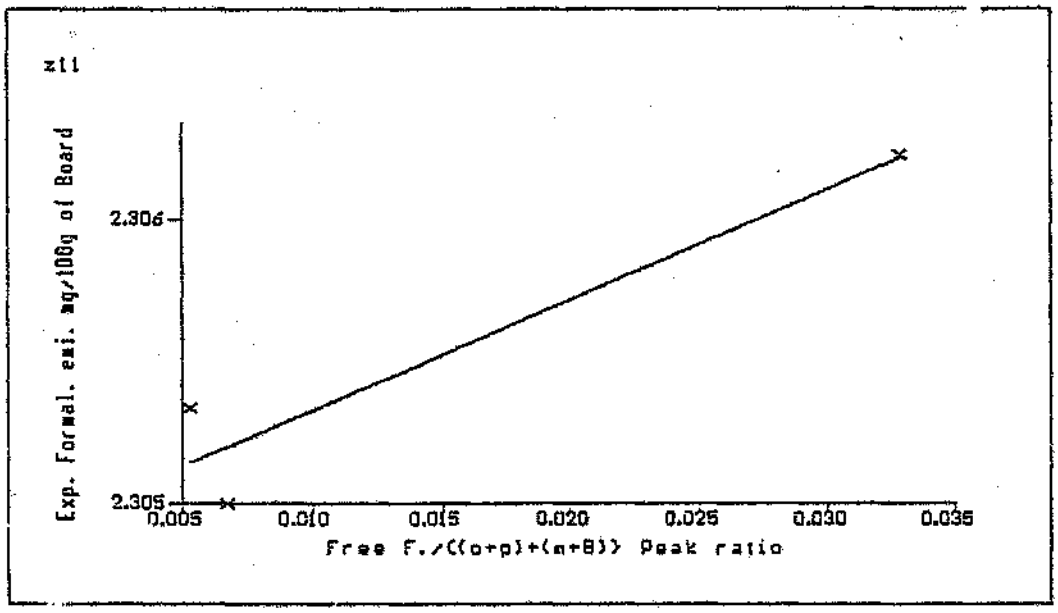
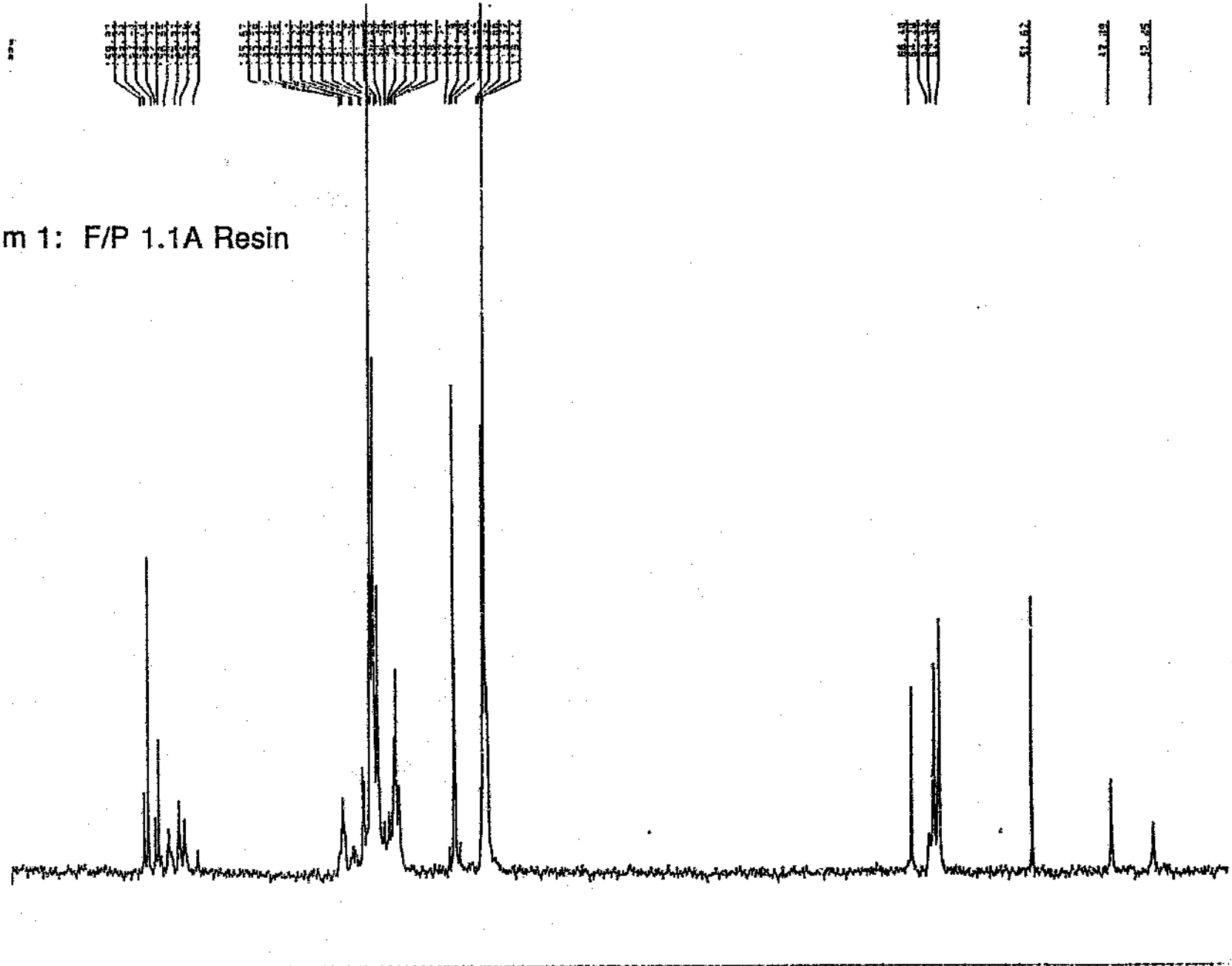


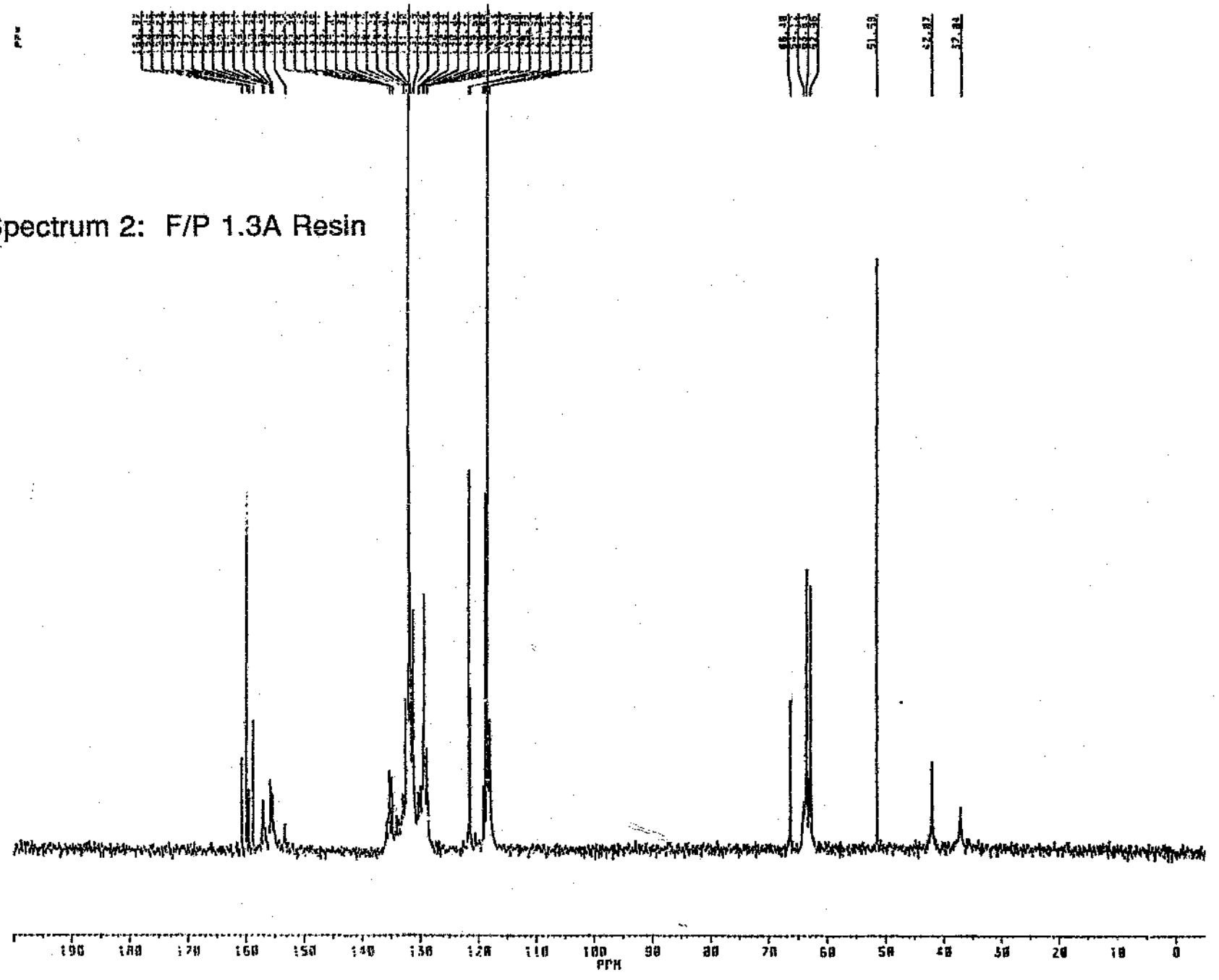
Fig 15(d) : ^{13}C NMR Peak ratio of total Free formaldehyde/ {(o+p)+(m+B)} species versus experimental formaldehyde emission data (by WKI method) for the boards made with the B- series resins.

Spectrum 1: F/P 1.1A Resin

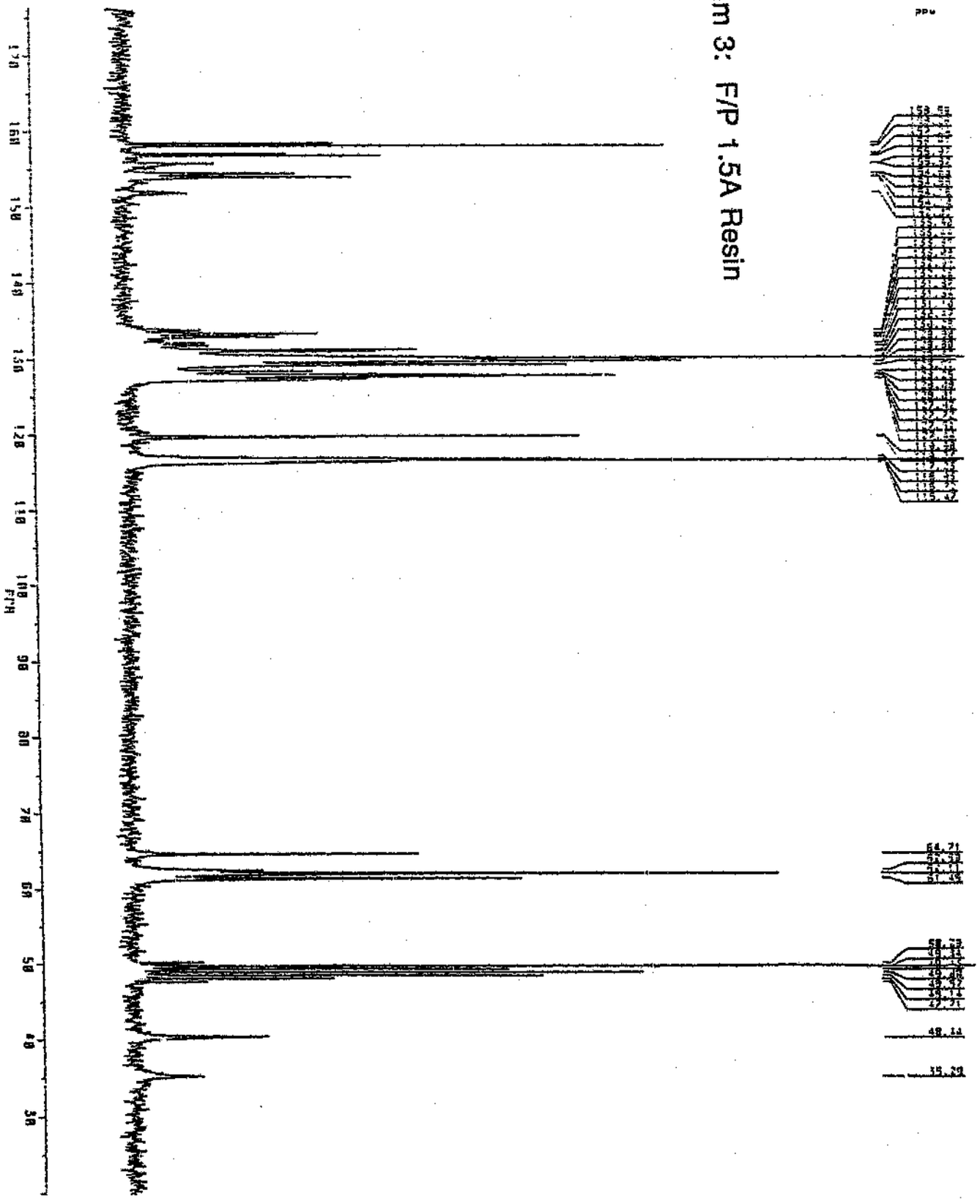


211

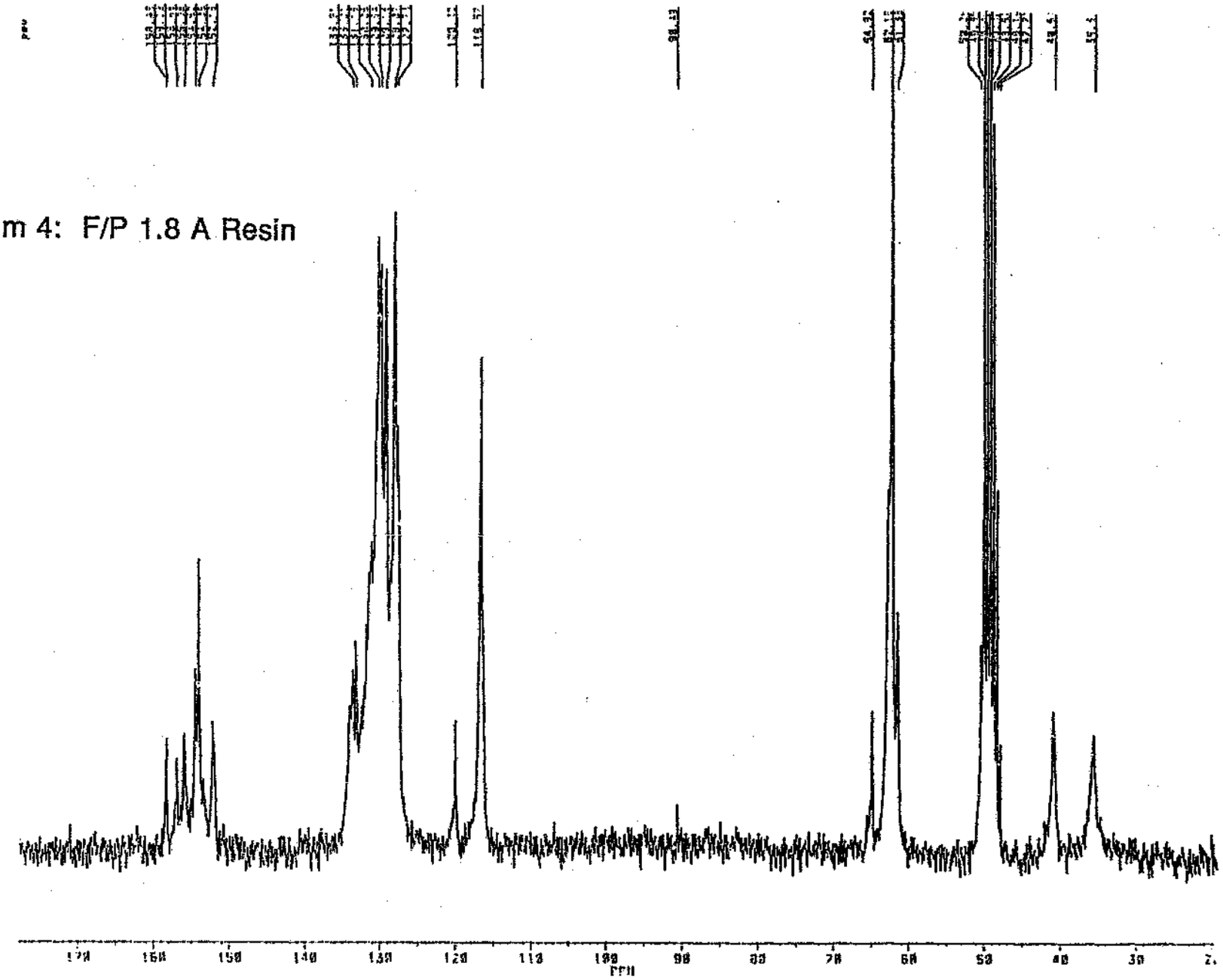
Spectrum 2: F/P 1.3A Resin



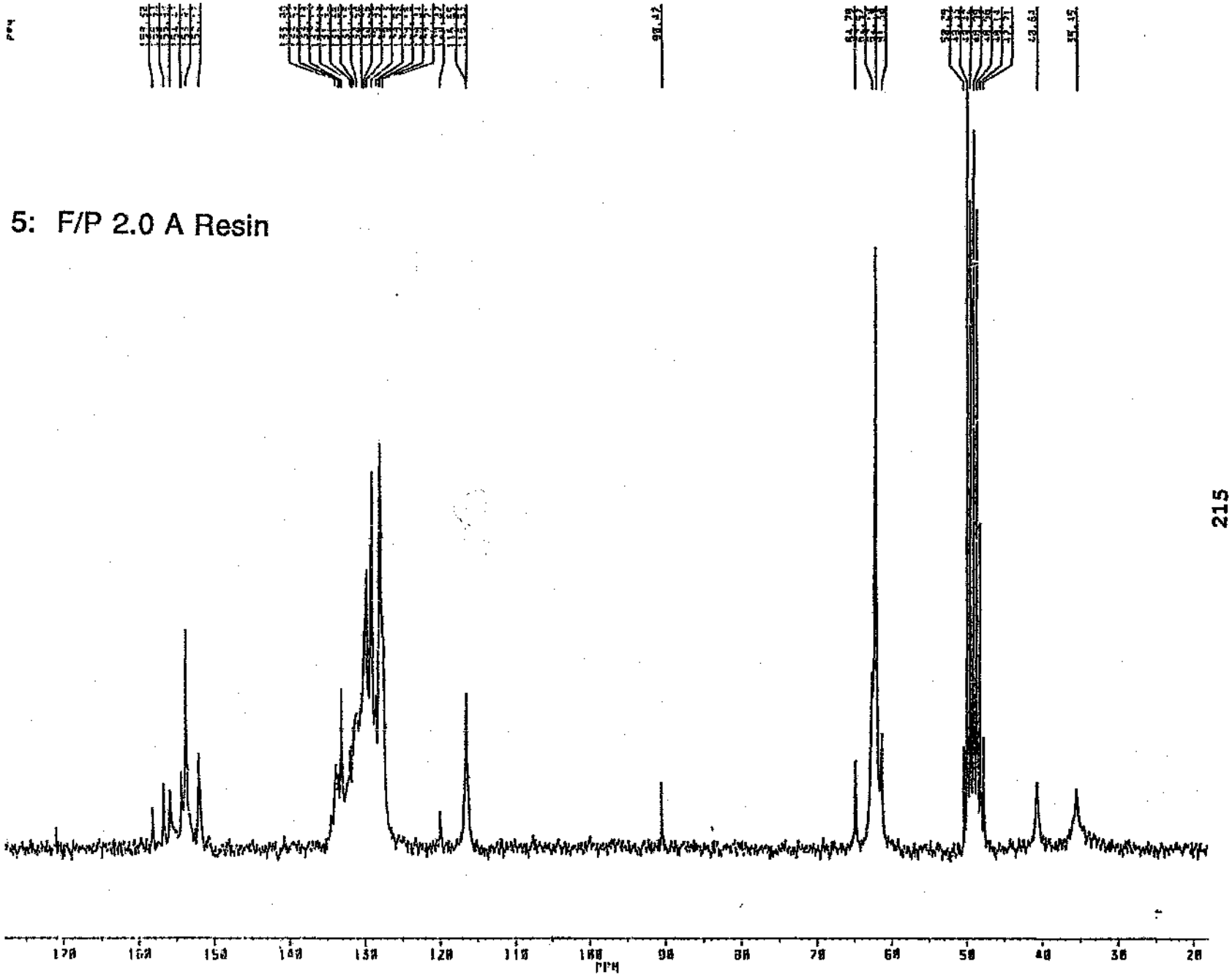
Spectrum 3: F/P 1.5A Resin



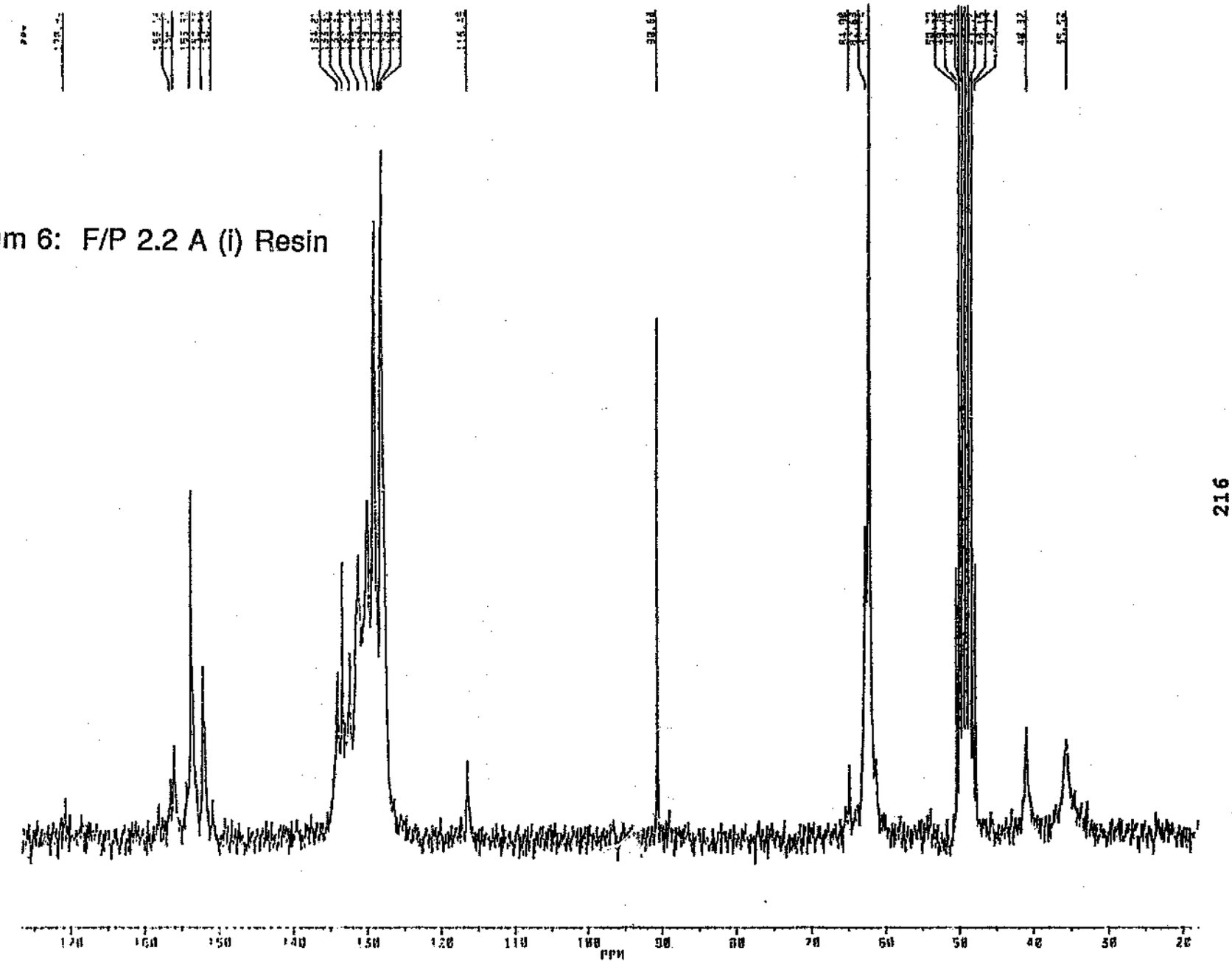
Spectrum 4: F/P 1.8 A Resin



Spectrum 5: F/P 2.0 A Resin

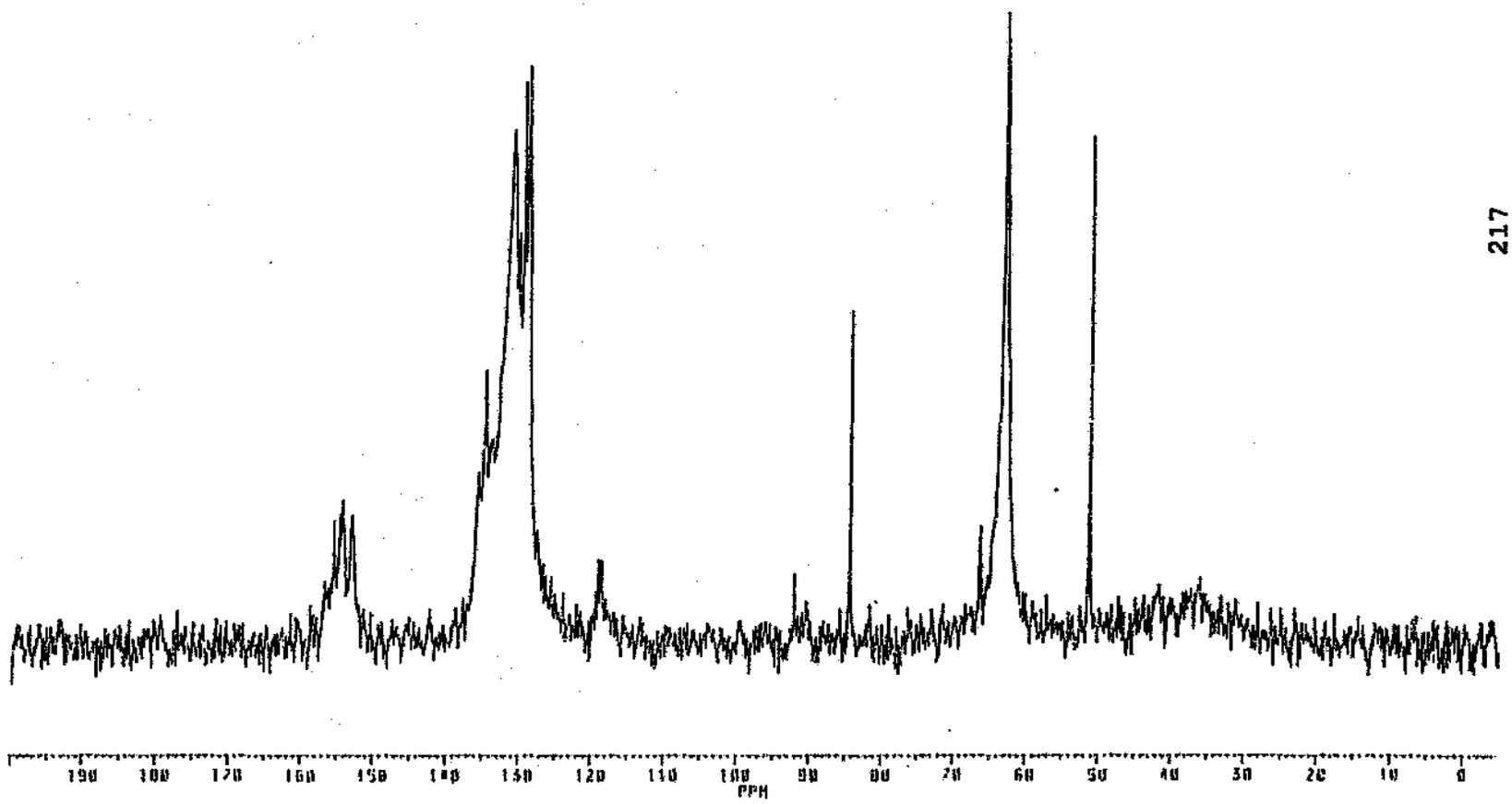


Spectrum 6: F/P 2.2 A (i) Resin

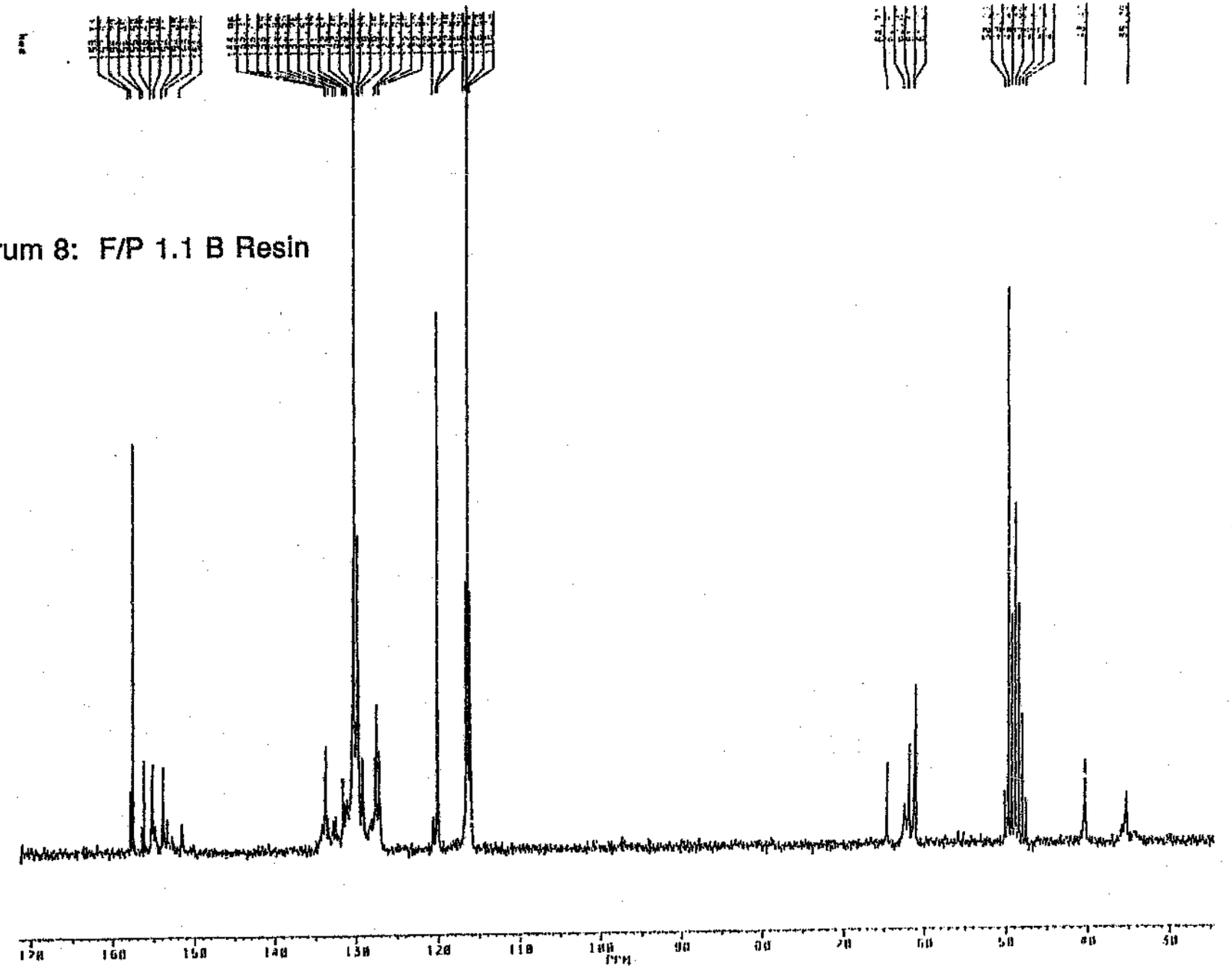


21.6

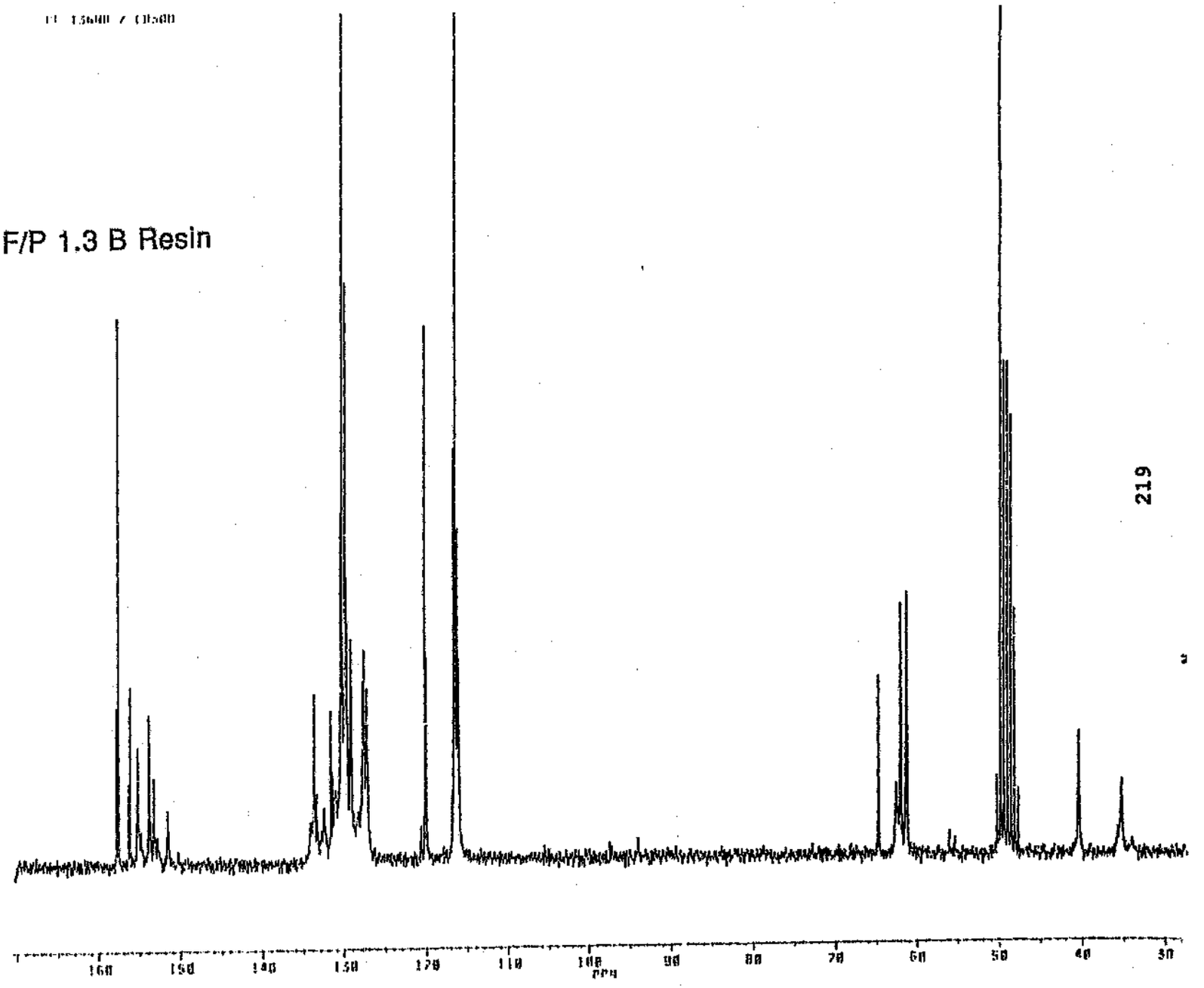
Spectrum 7: F/P 2.2 A (ii) Resin



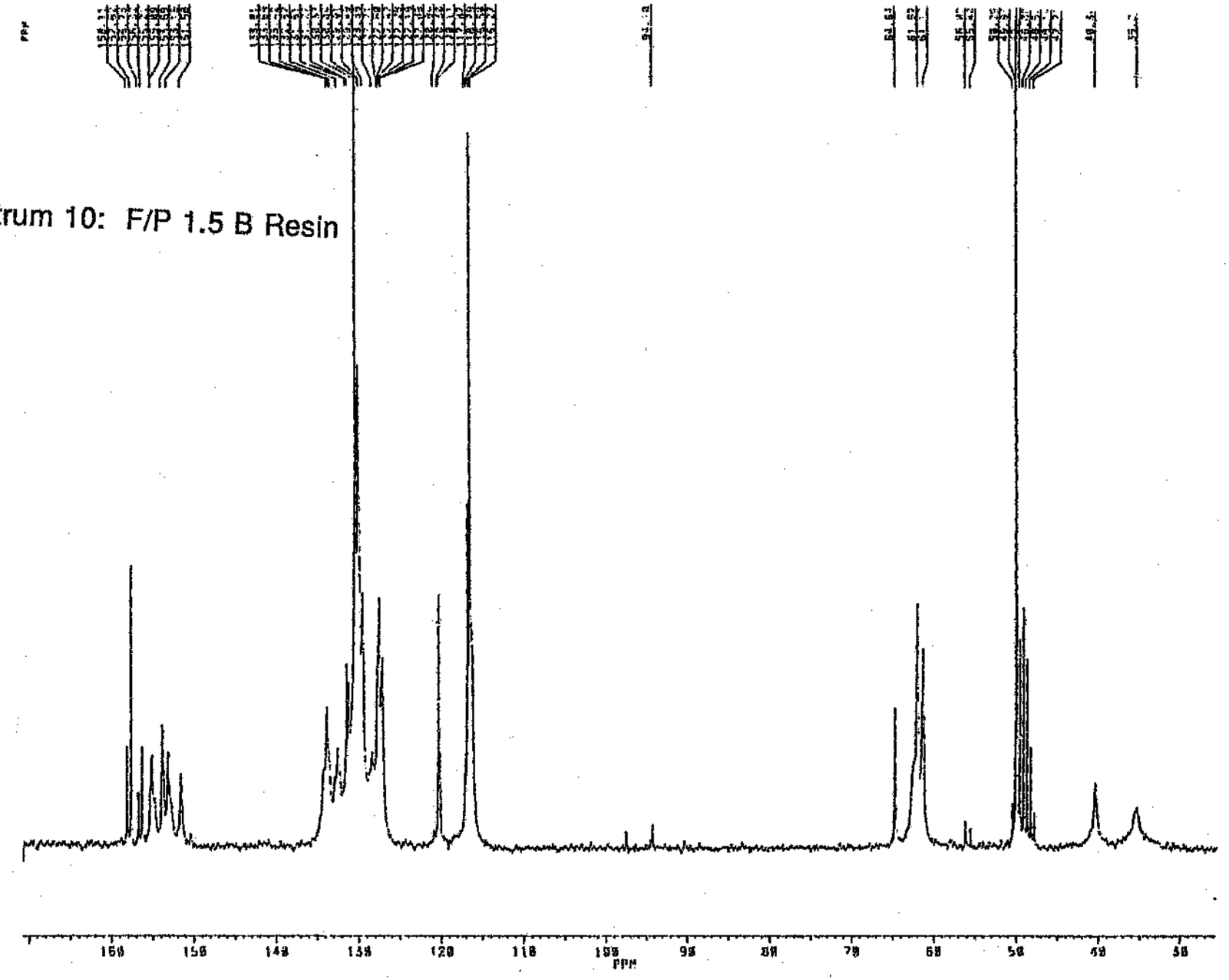
Spectrum 8: F/P 1.1 B Resin



Spectrum 9: F/P 1.3 B Resin

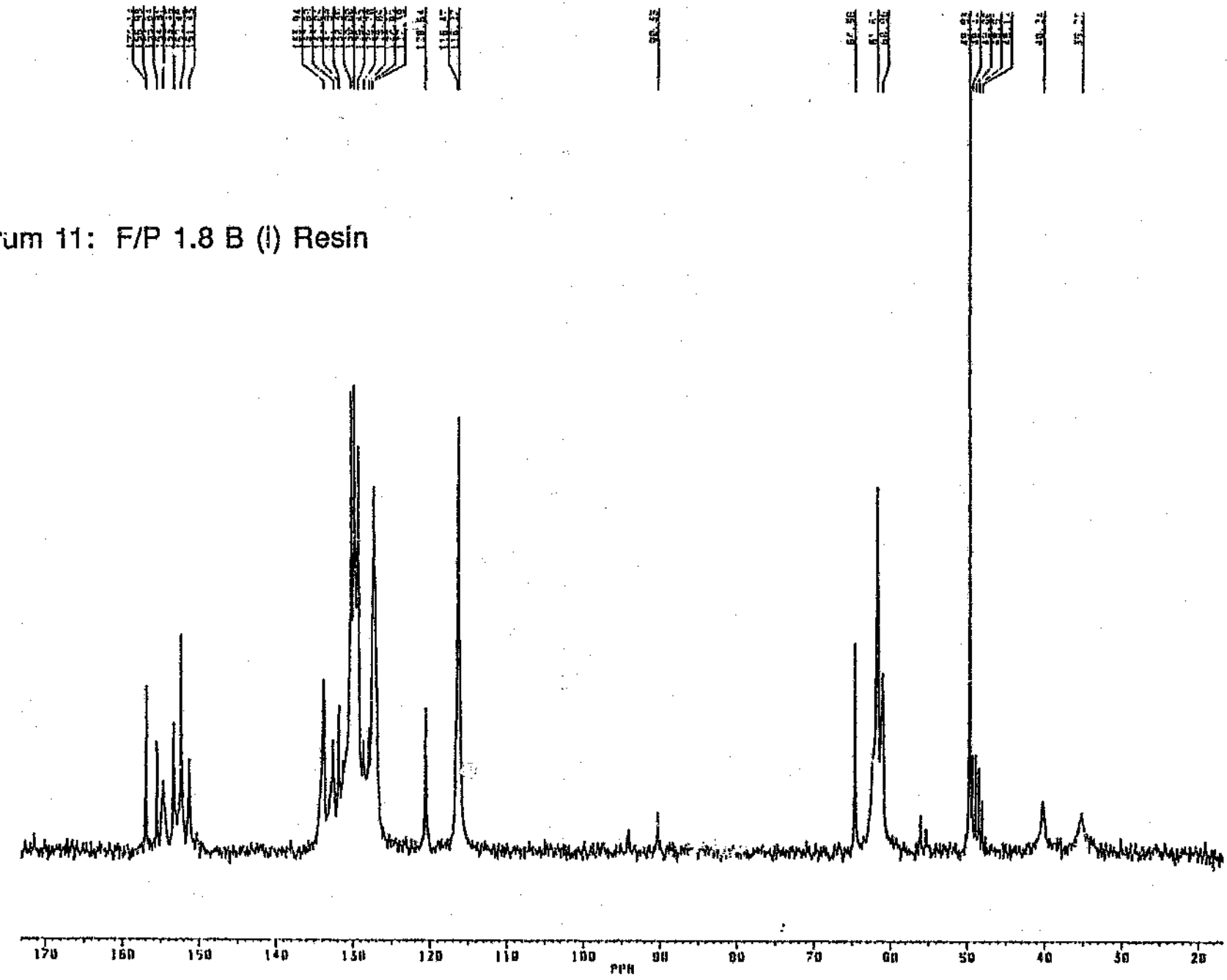


Spectrum 10: F/P 1.5 B Resin

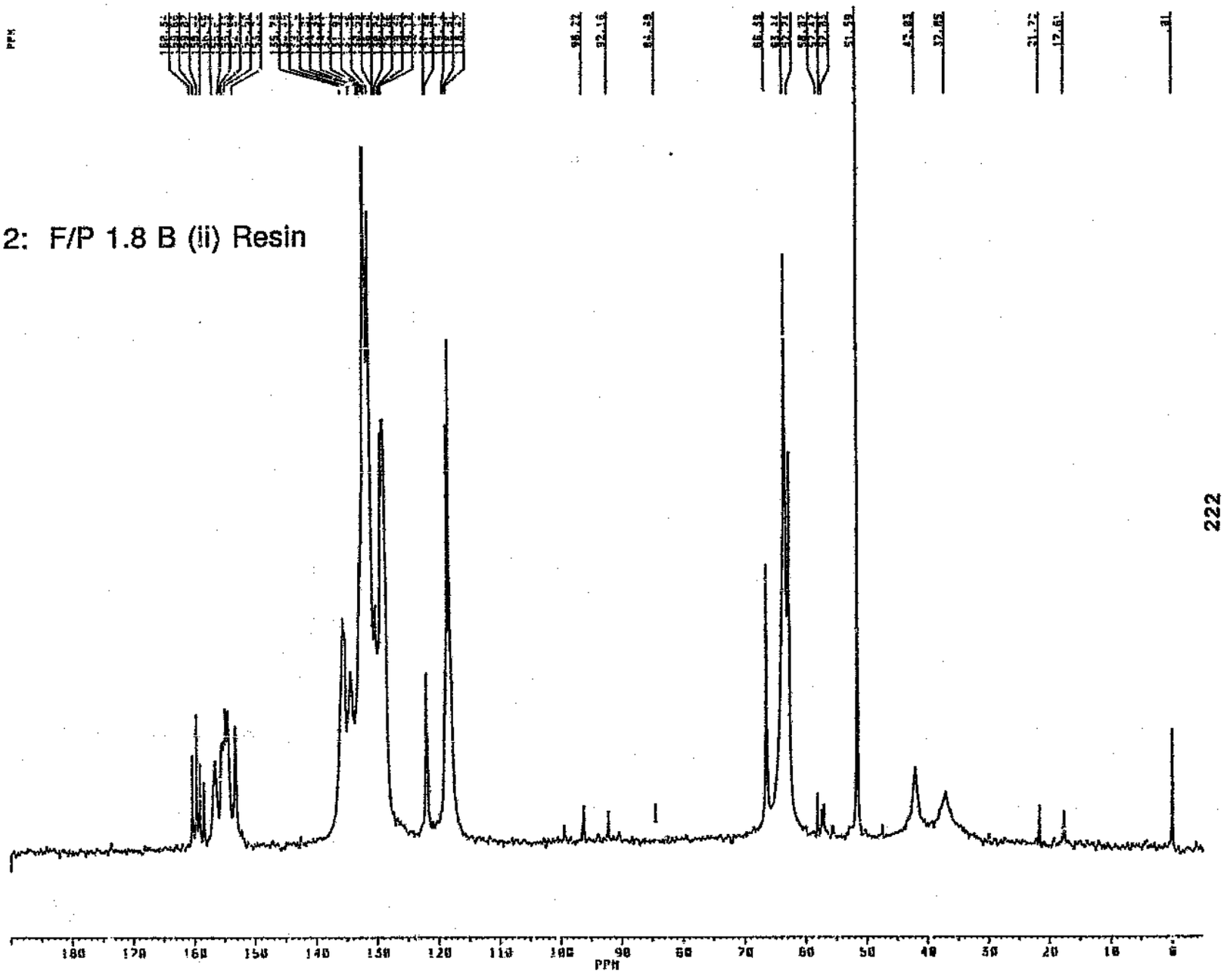


220

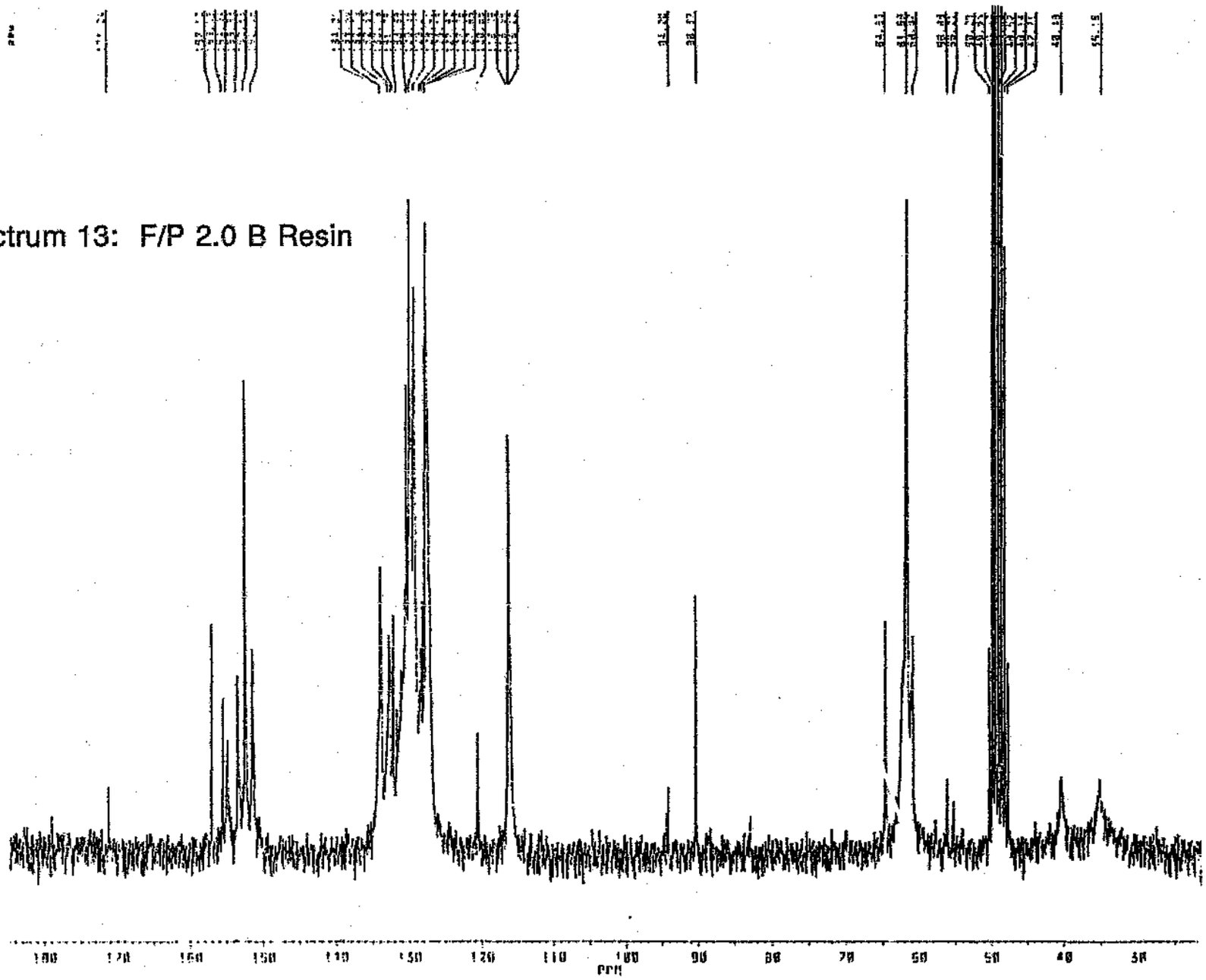
Spectrum 11: F/P 1.8 B (I) Resin



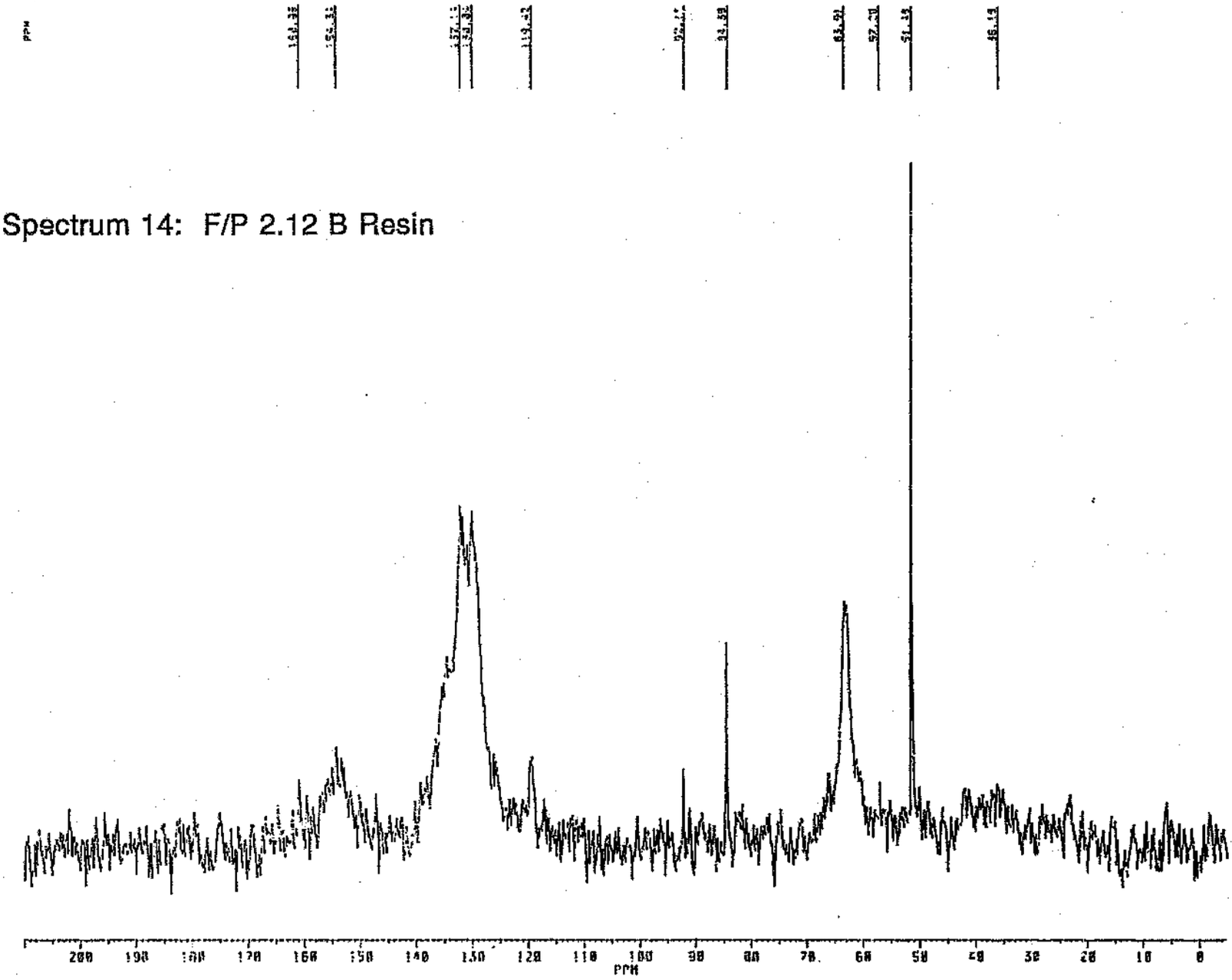
Spectrum 12: F/P 1.8 B (ii) Resin



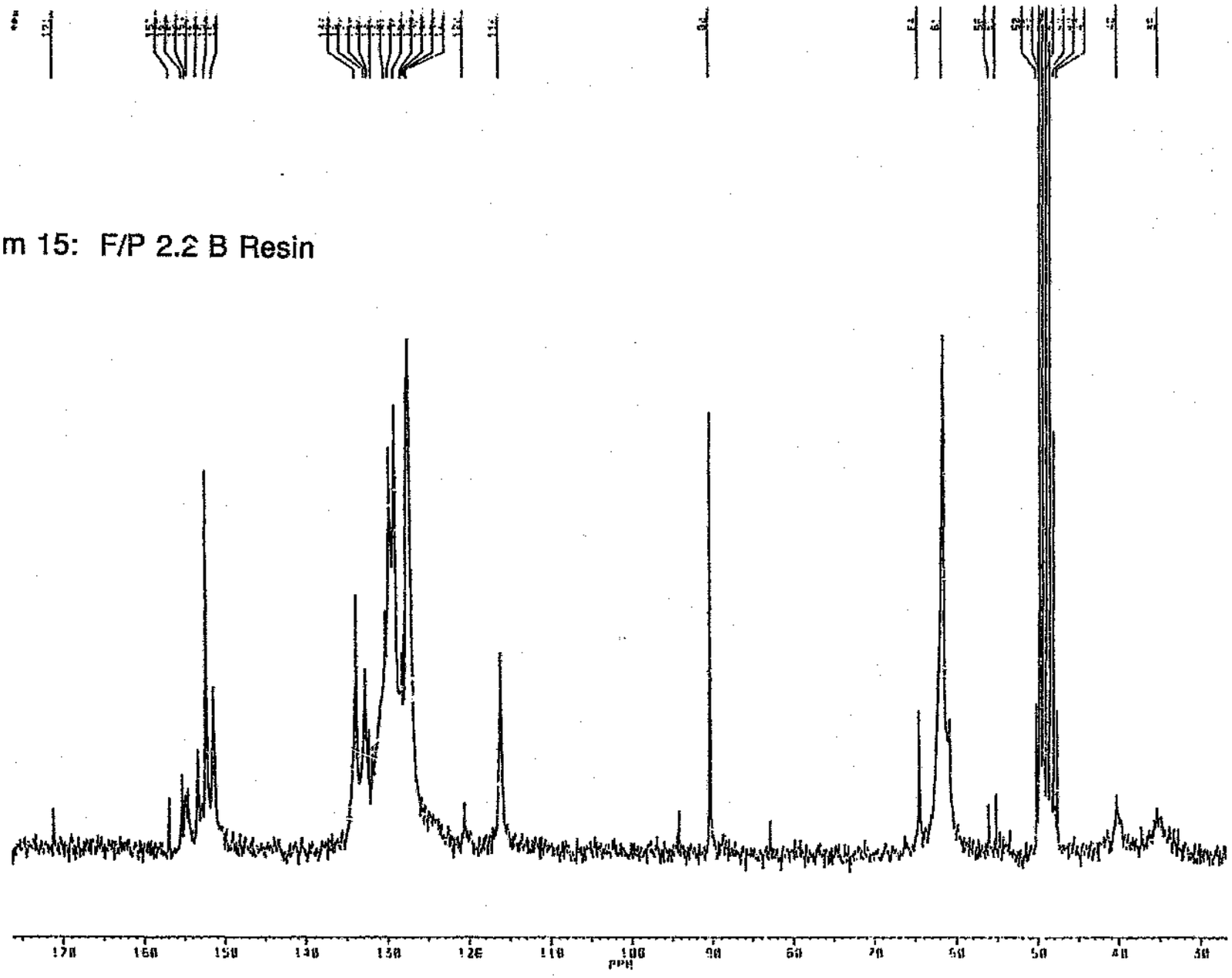
Spectrum 13: F/P 2.0 B Resin



Spectrum 14: F/P 2.12 B Resin



Spectrum 15: F/P 2.2 B Resin



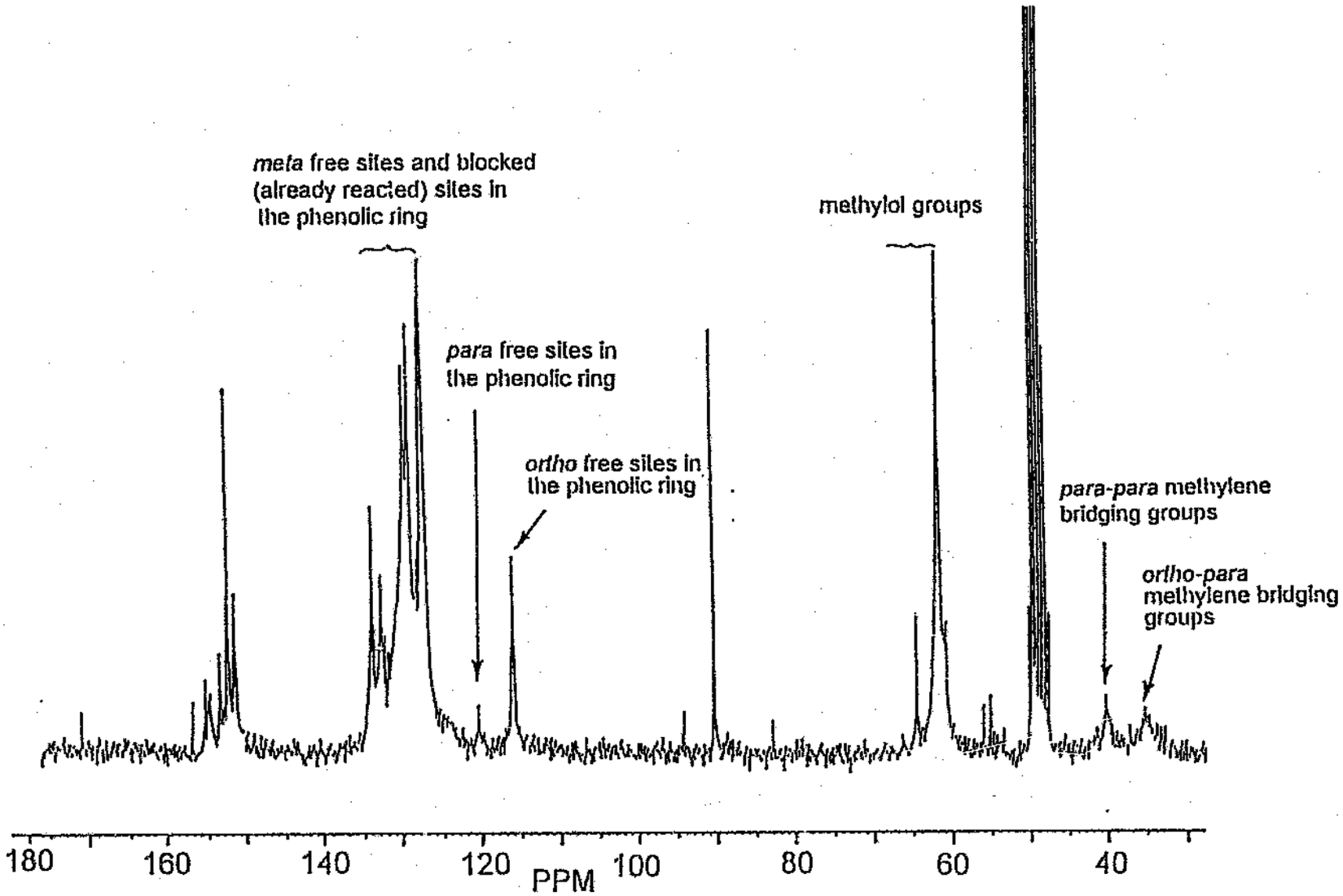
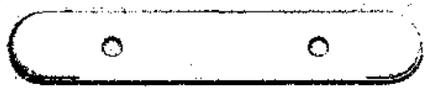


Fig 1 - ^{13}C NMR of PF resin of molar ratio P : F = 1 : 2.2 (B-series) indicating the signals of groups taken in consideration for peak intensity ratios.





Author: Panamgama Lalantha A.

Name of thesis: An analytical view of partideboard with special reference to phenol-formaldehyde resins.

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