

¹³C CP–MAS solid-state n.m.r. spectra of stoving alkyd paints

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A range of commercial stoving alkyd paints based on urea formaldehyde and melamine formaldehyde have been investigated using solid state n.m.r. techniques. The ¹H relaxation times were measured to study the morphology of the materials, and to provide suitable values for the contact time used in the ¹³C cross-polarization experiments. ¹³C cross-polarization magic angle spinning spectra (CP-MAS) were recorded to examine the crosslinking mechanisms and to identify the repeating units present.

(Keywords: solids; nuclear magnetic resonance; stoving alkyds; crosslinking; pigmentation)

INTRODUCTION

Alkyd paint binders have been the subject of a number of recent studies using n.m.r. spectroscopy. The uncured materials can be examined in the solution-state using both ¹H and ¹³C techniques^{1,2}. Cured binders have been partially characterized by first swelling the material in deuteriochloroform and then recording the ¹³C n.m.r. spectrum in the normal manner³⁻⁵. High resolution signals are produced from the mobile portions of the macromolecule which are most affected by the swelling process. The technique has been applied to other polymer types including polyurethanes⁶ and styrene crosslinked polyesters⁷: no signals are observed from the more rigid regions of the material, such as the crosslinks and surrounding areas.

An initial study of a range of cured decorative alkyd paints has shown that the ¹³C cross-polarization magic angle spinning (CP-MAS) technique is complementary to the swollen-state technique and can provide information on the crosslinks present⁸. To provide a more rigorous test of the scope of the CP-MAS method a range of stoved alkyds has been examined, these materials having also been characterized in the swollen state⁵.

Stoved alkyds are surface coatings produced by the reaction between incompletely esterified glycerol and formaldehyde resins based on urea or melamine. The crosslinking reaction occurs at elevated temperatures, hence the term stoving alkyds. Urea formaldehyde (UF) and melamine formaldehyde (MF) resins have been studied by CP-MAS n.m.r. either as homopolymers⁹ or copolymers with acrylic resins^{10,11}. In this work, stoving alkyds based on n-butylated MF and UF resins are examined by ¹³C CP-MAS n.m.r. to study the crosslinking mechanisms at work, and to identify functional groups present.

EXPERIMENTAL

Materials

The materials used in this work have been examined previously by swollen-state ¹³C n.m.r. and details of their preparation are given elsewhere⁵. The cured paint films were cut into small discs and then packed into the glass sample rotor.

N.m.r. spectroscopy

¹H spin lattice relaxation times in the laboratory (T_1) and rotating ($T_1\rho$) frames of reference were measured on a purpose-built spectrometer operating at 60 MHz¹². The values obtained were used to select ¹³C CP contact times.

High resolution ¹³C solid-state spectra were obtained at 22.63 MHz with spin locked-CP. The samples were spun at the magic angle at *ca.* 3 kHz at 300 K, and a recycle time of 1 s was used throughout. A spectral width of 15.625 kHz was used and the signals were externally referenced to adamantane, taking its chemical shift to be 76.7 ppm to high frequency of tetramethylsilane. As in previous studies the cross-polarization with flip lock standard (CPST) and selection of non-protonated carbon (OFNQS) pulse sequences were used to enhance protonated and non-protonated species, respectively¹²: NQS window values of 40 μ s were used.

RESULTS AND DISCUSSION

¹H relaxation data

In order to optimize the CP experiment used in CP-MAS solid state n.m.r. of nuclei such as ¹³C, it is necessary to understand the ¹H relaxation parameters of the sample under investigation. Suitable contact times can be estimated if one has prior knowledge of a particular system but it is better to measure the ¹H data for each sample. The ¹H spin-lattice relaxation parameter

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Table 1 Stoving alkyd ¹H and ¹³C parameters

	T_1	$T_{1\rho}$	(%)	Contact time (ms)	¹³ C transients (CPST/OFNQS)
Urea formaldehyde resin	0.4	5.0	50	1.5	43 000/45 000
		0.5	50		
Melamine formaldehyde resin	0.4	5.0	90	5.0	30 000/26 500
		1.0	10		
Coconut/UF	0.4	2.0	70	5.0	40 000/40 000
		0.5	30		
Castor/UF	0.3	6.0	80	5.0	24 000/27 000
		1.5	20		
Pelargonic/UF	0.5	3.0	70	3.0	44 000/44 000
		0.5	30		
Pelargonic/MF	0.4	3.0	70	3.0	44 000/40 000
		0.5	30	5.0	-/40 000
Coconut/MF	0.4	6.0	60	2.0	35 000/45 000
		2.0	40		
Styrene/MF	0.3	7.0	80	5.0	50 000/50 000
		1.5	20		
Pigmented styrene/MF	0.2	2.0	50	5.0	50 000/54 000
		0.5	50	3.0	54 000/-
Tall oil/UF/MF	0.4	2.0	30	3.0	35 000/50 000
		0.5	70		
Pigmented tall oil/UF/MF	0.1	3.0	70	3.0	34 000/54 000
		0.5	30		

in the rotating frame, $T_{1\rho}$ provides the key to CP experiments between ¹H and ¹³C because the rate of ¹H signal decay during the spin lock period affects the CP efficiency.

Typically, the ¹H relaxation behaviour is complex for polymeric systems, and the relaxation profile can be accounted for by at least two separate relaxation contributions. The actual $T_{1\rho}$ values and the relative amounts of each can be estimated, though the results may be affected by spin diffusion. A heterogeneous material, such as a polymer, might be expected to contain both rigid regions of crystallinity and mobile disordered or amorphous regions. The latter tend to have far shorter relaxation values than the former indicating the greater mobility of disordered regions, hence the $T_{1\rho}$ values can be monitored to infer the degree of order or rigidity within a sample. In the present study, the qualitative and quantitative differences in the measured $T_{1\rho}$ values are used to monitor the mobility of regions within the polymer and to examine the effects of crosslinking and pigmentation. The data are shown in *Table 1*.

The model compounds used in this work are crosslinked n-butylated UF and MF resins. These materials are of no practical use in themselves as coatings due to their brittleness but they do reveal the relaxation behaviour of an important portion of the stoved alkyd systems. The $T_{1\rho}$ values are very similar at 5.0 and 0.5 ms for UF and 5.0 and 1.0 ms for MF. This suggests that the ordered and disordered regions within the polymers have similar mobilities. However, there appears to be far more rigid material in the MF resin, probably reflecting a higher crosslink density due to the extra functionality in the melamine unit. From these data, CP contact times were selected for the ¹³C CP-MAS experiments, which are discussed below.

The $T_{1\rho}$ values from the stoving alkyds show some interesting variations. The coconut oil/UF material has lower $T_{1\rho}$ values than the coconut oil/MF material, probably reflecting a higher crosslink density in the latter. However the distribution of the two $T_{1\rho}$ components is

roughly equal showing that overall the morphologies of the materials are similar. The castor oil/UF alkyd would appear to be more crosslinked than the equivalent coconut oil system from the $T_{1\rho}$ values, but again the distribution of the components is similar. The castor oil alkyd has an additional site of crosslinking on the alkyd chain which produces a less mobile network on curing: the coconut oil alkyd merely crosslinks at the glycerol region.

Pelargonic acid alkyds are used to obtain a much shorter chain length material than naturally occurring triglycerides such as coconut oil and castor oil. In addition pentaerythritol and not glycerol is used as the polyol in the system. Interestingly there is little difference between the $T_{1\rho}$ data of the UF and MF stoved systems obtained from the pelargonic acid alkyd. A smaller, synthetic alkyd thus appears to crosslink more evenly with UF and MF resins: this is an empirical observation with these materials which are preferred for special applications¹³.

The styrene/MF system is based on a styrene-modified glycerol short oil alkyd which can crosslink with MF at elevated temperatures. It is quite different to the air-drying vinyl toluene modified glycerol long oil alkyds which were reported in earlier work⁸. The latter showed a T_1 value of 0.2 s and $T_{1\rho}$ values of 4.7 ms (70%) and 0.5 ms (30%). The stoved system has a much higher crosslink density although the alkyd regions of the two materials are similar.

The tall oil/UF/MF alkyd is based on an alkyd which contains a significant amount of linoleate groups. Swollen state ¹³C n.m.r. has shown that the tall oil/UF/MF system is more crosslinked than the coconut/MF system, presumably due to additional crosslinking of the linoleate groups⁵. The T_1 and $T_{1\rho}$ values of the two materials are virtually identical but surprisingly there is more of the shorter $T_{1\rho}$ component in the tall oil/UF/MF system: in fact this is the only stoving alkyd behaving in this manner, and as such warrants further investigation.

The effect of pigmentation upon T_1 and $T_{1\rho}$ was

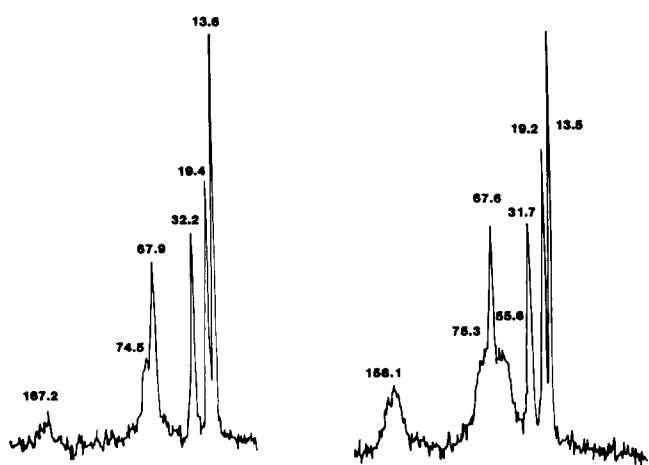


Figure 1 CM-MAS ¹³C spectra of cured melamine formaldehyde (left) and urea formaldehyde (right) resins

studied for the tall oil and the styrene stoving alkyds. Both alkyds were pigmented with *ca.* 20% rutile titanium dioxide: talc was used as a filler for the styrene alkyd and diatomaceous earth for the tall oil alkyd. The pigmented styrene/MF alkyd gives lower T_1 and $T_{1\rho}$ values than the unpigmented material. A previous example of pigmentation has been shown to reduce $T_{1\rho}$ values: with an air-dried epoxy ester system pigmentation with 20% rutile titanium dioxide reduced the $T_{1\rho}$ values from 3.0 ms (80%) and 1.0 ms (20%) to 2.0 ms (70%) and 0.5 ms (30%), respectively¹⁴. It is possible that pigmentation provides a further relaxation mechanism for the alkyd binders such as the presence of paramagnetic titanium species in the rutile pigment.

However the same effect is not observed with the tall oil/UF/MF system, where the $T_{1\rho}$ values appear to increase on pigmentation. The ratios of the two $T_{1\rho}$ components have also changed significantly. To clarify the effect of the pigment it may be necessary to repeat the experiments with a synthetically produced pigmented system in which the effects of paramagnetic impurities can be monitored, rather than continue to use commercial paint systems. In all cases values of T_1 are in the range 0.1–0.5 s, and are observed to be single-exponential within experimental error. Recycle delays of 1 s in the ¹³C CP experiment are therefore reasonable.

¹³C MAS-n.m.r. spectroscopy

Using the ¹H relaxation data obtained from each sample an optimum CP contact time was selected and CPST and OFNQS ¹³C spectra were recorded¹². The contact times used are shown in Table 1 and are sufficiently short to discriminate against quaternary carbons.

The ¹³C CP-MAS n.m.r. spectra of the crosslinked UF and MF resins are shown in Figure 1. Residual n-butyl groups within the materials give rise to the signals at ~14, ~19, ~32 and ~68 ppm. The urea carbonyl gives a very distinct signal at 158.1 ppm using the CPST sequence: with the OFNQS sequence the intensities of the other signals decrease significantly. The remaining signals at 55.6 ppm are from methylene groups bonded to two nitrogen units such as >NCH₂N<, and those at 75.3 ppm are from >NCH₂OC₄H₉ and related species.

The crosslinked MF resin CPST spectrum is rather similar in appearance except that only signals of the type

>NCH₂OC₄H₉ are seen in the 55–75 ppm region at 74.5 ppm. The signals from the n-butoxy groups are still present and the imine signal from the melamine gives a fairly weak signal at 167.2 ppm. Overall the n-butylated MF and UF resins do not appear to show the marked ¹⁴N quadrupolar effects reported for other amino resin systems when using the ¹³C CP-MAS technique⁹.

The stoved alkyd based on a coconut oil alkyd and UF gives the CPST ¹³C spectrum shown in Figure 2. The largest peak in the spectrum arises from the polyol units of the material at 67.0 ppm. In the swollen state ¹³C spectrum of the material the signals from this region are noticeably weak because this is the crosslinking site of the short oil alkyd with the UF resin⁵. The CP-MAS technique appears to be far better at detecting these crosslink sites. However, the technique does not show the same degree of resolution as swollen state ¹³C n.m.r. and the two different alkyd carbonyl regions can only just be differentiated at 165.8 and 171.7 ppm. However there is a broad signal in the urea carbonyl region of *ca.* 158 ppm which, if not of quadrupolar origin, might be enhanced using deconvolution techniques. Residual n-butyl groups can be seen via the small signals at *ca.* 19 and 22 ppm; the remaining signals of which are masked by the methyl and methylene signals from the alkyd at 13.8 and 30.4 ppm. The remaining signals centred at 130 ppm are from the phthalate groups within the alkyd.

The castor oil/UF stoved alkyd gives a similar CPST ¹³C spectrum to the coconut oil alkyd described above. The major peaks are shown in Table 2 and the most noticeable difference is that the castor oil system does not show a broad region at *ca.* 158 ppm. The signal from the crosslink sites at 67.5 ppm is again very strong: the swollen state ¹³C spectrum from the castor oil/UF alkyd suggests that it is more crosslinked than the coconut oil/UF alkyd, as very little was observed in the 65–70 ppm region⁵. Thus, the probable major difference between the CP-MAS ¹³C spectra of these two stoving alkyds is the larger signal at 67.5 ppm in the castor oil/UF alkyd reflecting its greater crosslink density.

The ¹³C spectra obtained from a pelargonic acid/UF alkyd gave the chemical shift data shown in Table 2. The CPST spectrum, shown in Figure 3, has a much more intense signal at 13.0 ppm from the terminal methyl

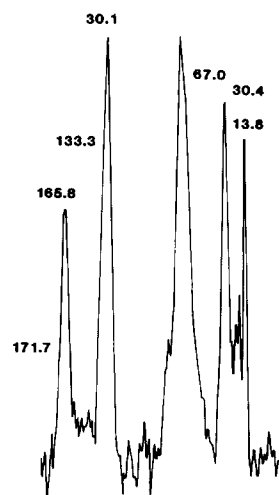


Figure 2 CP-MAS ¹³C spectra of coconut oil/UF alkyd

Table 2 Stoving alkyd ¹³C chemical shifts (in ppm)

Urea formaldehyde resin	13.5, 19.2, 31.7, 55.6, 67.6, 75.3, 158.1
Melamine formaldehyde resin	13.6, 19.4, 32.2, 67.9, 74.5, 167.2
Coconut/UF	13.8, 19.5, 22.4, 30.4, 67.0, 130.1, 133.3(?), 158, 165.8, 171.7(?)
Castor/UF	13.6, 19.3(?), 22.6, 29.9, 67.5, 126.8, 129.2, 130.6, 134.9, 167.1, 171.6
Pelargonic/UF	13.0, 18.0, 29.1, 40.9, 67.0, 130.4, 164.6, 167.3, 172.0
Pelargonic/MF	13.6, 19.3, 22.7, 30.8, 42.4, 67.4, 131.1, 133.1, 166.3, 172.7
Coconut/MF	13.4, 19.2, 22.7, 29.4, 66.0, 127.0, 129.4, 131.2, 134.9, 165.5, 167.1, 171.0
Styrene/MF	13.5, 19.2, 28.5, 39.7, 66.0, 129.1, 133.8, 146.1, 165.8, 167.5, 171.0
Pigmented styrene/MF	14.1, 18.9, 29.3, 64.5, 68.7, 128.1, 130.3, 134.3, 165.1, 169.0
Tall oil/UF/MF	13.4, 22.5, 29.1, 61.3, 64.3, 67.3, 128.4, 130.0, 135.3, 164.8, 167.6, 172.0
Pigmented tall oil/UF/MF	13.3, 29.3, 61.5, 124.9, 129.2, 134.8, 165.5, 167.0, 172.4

OFNQS ¹³C spectrum with a 5 ms contact time gives the spectrum shown in *Figure 4*, where the signal at 166.3 ppm is much larger relative to the pentaerythritol quaternary signal at 42.4 ppm. This is good evidence that the longer contact time can resolve the imine signal from the carbonyl signal.

The $T_{1\rho}$ data obtained from the two coconut oil alkyds show that the MF material is the more crosslinked. A low CP contact time of 2 ms would be expected to enhance the alkyd regions of the material according to the results described above for the pelargonic acid/MF alkyd. The CPST and OFNQS ¹³C spectra obtained from the coconut oil/MF alkyd are shown in *Figure 5*, and the former spectrum appears to have weak residual n-butyl signals from the MF regions. The crosslink sites at glycerol give a very large signal at 66.0 ppm without interference from the carbon atoms on heteroatom sites in the melamine unit which also occur in this region. The carbonyl signals are relatively weak in the CPST spectrum, but the OFNQS spectrum allows the carbonyl fine structure to be seen at 165.5, 167.1 and 171.0 ppm. Again the choice of contact time has also perturbed the imine signal from the MF units that would appear at ca. 167 ppm.

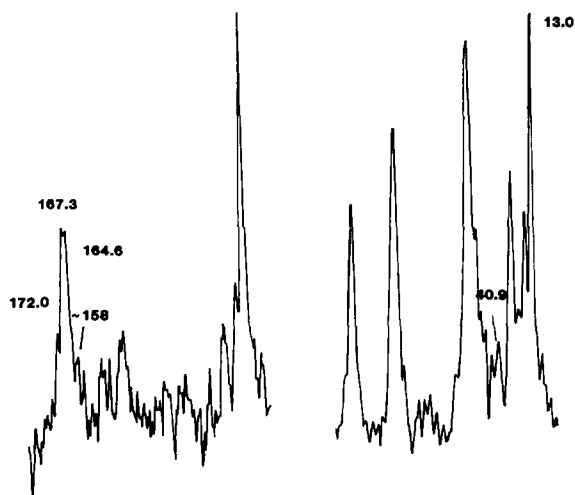


Figure 3 CP-MAS ¹³C spectra of pelargonic acid/UF alkyd. OFNQS (left); CPST (right)

group, reflecting the shorter chain length of the pelargonic acid with respect to coconut oil and castor oil. The pelargonic alkyd is based on pentaerythritol which gives a distinct signal at 40.9 ppm from the quaternary carbon atom. The OFNQS ¹³C spectrum of the stoved alkyd (*Figure 3*) is poor in quality but shows detailed structure in the carbonyl region with ester signals at 164.6, 167.3 and 172.0 ppm, and the suggestion of a urea carbonyl signal at ca. 158 ppm. The CPST spectrum does not reveal the same degree of complexity in the carbonyl region.

It is more difficult to observe the amino portion of the stoved MF alkyds since the melamine imine unit appears to be coincident with the aromatic ester carbonyls of the alkyd seen at ca. 167 ppm. However the $T_{1\rho}$ data from the MF resin itself shown in *Table 1* suggest that a long CP contact time might favour the less mobile MF signals. The CPST ¹³C spectrum of the pelargonic acid/MF alkyd using a 3 ms CP contact time gives a similar spectrum to the pelargonic acid/UF alkyd shown in *Figure 3*. The

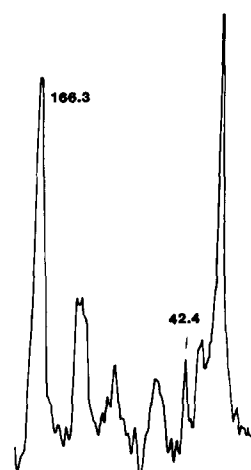


Figure 4 CP-MAS ¹³C spectrum of pelargonic acid/MF alkyd with increased contact time

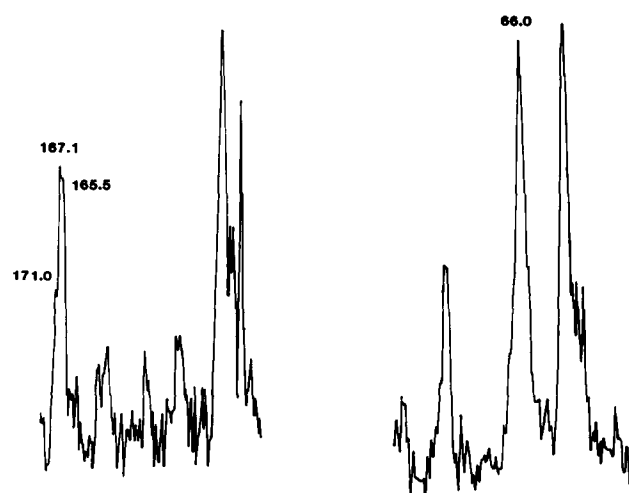


Figure 5 CP-MAS ¹³C spectra of coconut oil/MF alkyd. OFNQS (left); CPST (right)

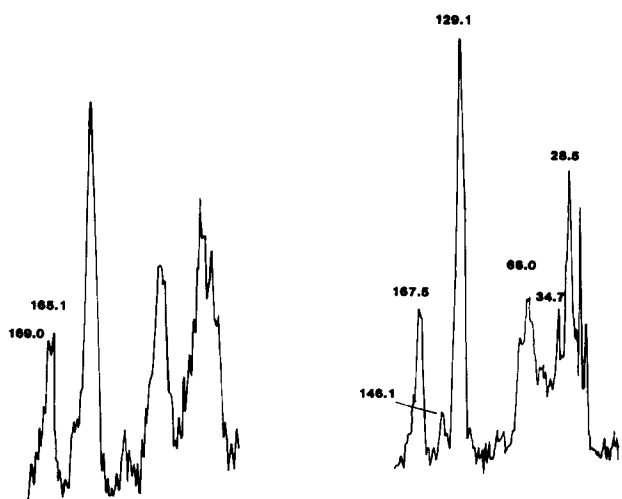


Figure 6 CP-MAS ¹³C spectra of styrene/MF alkyd. CPST pigmented (left) and unpigmented (right)

In order to examine the effects of pigmentation on the CP-MAS ¹³C spectra of stoving alkyds, two systems were studied with and without pigment present. Both contained commercial pigment systems based on rutile titanium dioxide, an inorganic filler and an organic pigment. A styrenated short oil glycerol alkyd and a short oil tall oil glycerol alkyd were used with MF and a MF/UF mixture, respectively.

The unpigmented styrene/MF alkyd gives the CPST ¹³C spectrum shown in Figure 6 where signals from the alkyd and polystyrene can be seen. The latter gives signals at 39.7 ppm from the aliphatic region and signals at 129.1 and 146.1 ppm from the aromatic carbon atoms which correlates well with data obtained on styrene crosslinked maleic anhydride polyesters¹⁵. The signal from the crosslink sites of the alkyd at 66.0 ppm is quite small relative to the materials studied above. This is because the alkyd used is based on soya oil which itself can crosslink and the crosslinking reaction can be studied by swollen-state ¹³C n.m.r.⁵. Similarly the signal at 28.5 ppm is of lower intensity relative to the non-drying alkyds described above due to the presence of linoleate in the alkyd resulting in fewer saturated aliphatic carbons being present. The CPST spectrum gives a broad, unresolved carbonyl signal at 167.5 ppm whereas the OFNQS spectrum shows three peaks at 165.8, 167.2 and 171.0 ppm.

Pigmentation of the styrene/MF alkyd reduces the signal to noise ratio of the spectra as expected. The $T_1\rho$ values shown in Table 1 decrease significantly with pigmentation, but there is no great change in the CPST ¹³C spectrum obtained using the same 5 ms contact time as the unpigmented styrene/MF alkyd: the signal from the crosslink region of the former is perhaps slightly larger. The CPST experiment was repeated with a 3 ms contact time to examine the more quickly relaxing signals, and the resulting spectrum is shown in Figure 6. The spectrum is similar to that obtained with a 5 ms contact time except that the carbonyl intensity is smaller and two peaks at 165.1 and 169.0 ppm can be resolved. The MF region of the alkyd should be less responsive to a shorter contact time than the alkyd, hence it may be possible to resolve the alkyd carbonyls from the MF imine signal. There is also a slight decrease in intensity in the 67 ppm region suggesting that the MF resin signals in

this region are also being lost. The same effects of lowering the contact time are also observed with the OFNQS ¹³C spectra of the pigmented styrene/MF alkyd.

The tall oil/UF/MF alkyd is a similar system to the styrene/MF alkyd in that the tall oil alkyd contains linoleate chains that can crosslink when heated. Consequently the signals at 29.1 and 64.3 ppm seen in the CPST ¹³C spectrum shown in Figure 7 are of lower intensity than those found in equivalent non-drying alkyd systems. The carbonyl region of the tall oil system is well defined with clear signals at 164.8, 167.6 and 172.0 ppm, with a probable urea carbonyl from the UF region at ca. 158 ppm. The MF content of the material is only 5% and it is unlikely to be seen, especially since a 3 ms contact time has been used. The OFNQS spectrum of the material does not provide any additional information.

Pigmentation of the tall oil/UF/MF alkyd has the reverse effect to that described above with the styrene/MF alkyd. The $T_1\rho$ values increase and their relative proportions are reversed; and the signal to noise ratio of the CP-MAS ¹³C spectra is not affected by pigmentation. This raises the possibility that impurities in the pigment systems may account for the changes observed: both systems were of commercial origin and of nominal pigment composition only. Well characterized pigment systems should be studied to clarify this point. Although the nature of the pigment affects the ¹³C spectra, the results obtained so far suggest that commercial paint systems can be studied directly as the pigmented materials by the CP-MAS ¹³C n.m.r. technique.

The pigmented tall oil/UF/MF alkyd shows the same information as the unpigmented material, particularly in the important carbonyl region. The CPST ¹³C spectrum shows a shoulder at ca. 158 ppm for the UF component and the OFNQS ¹³C spectrum, shown in Figure 7 shows this even more clearly.

CONCLUSIONS

Most common stoving alkyd systems based on UF and MF resins can be characterized using CP-MAS ¹³C n.m.r. spectroscopy. It is possible to differentiate between alkyds based on coconut oil, castor oil, pelargonic acid

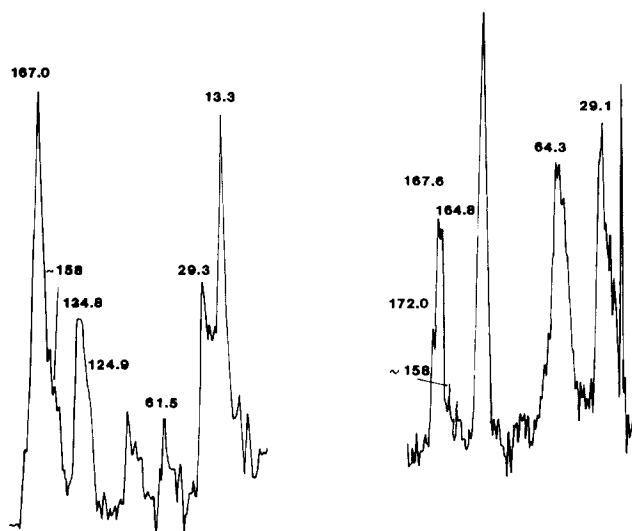


Figure 7 CP-MAS ¹³C spectrum of tall oil/UF/MF alkyd. OFNQS pigmented (left) and CPST unpigmented (right)

and styrenated alkyd. Important information on the polyol crosslink sites and different degrees of crosslinking can be obtained using ¹H relaxation studies. The effects of titanium dioxide pigmentation have been examined and useful ¹³C and ¹H spectra can be obtained.

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