^{13}C solid-state nuclear magnetic resonance spectra of some air-cured alkyd polyester paints

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High-resolution ^{13}C solid-state nuclear magnetic resonance spectra of air-cured linseed oil and a range of air-cured alkyd paint binders have been obtained using proton dipolar decoupling in conjunction with cross-polarization and fast magic angle spinning. ^1H spin–lattice relaxation times have been recorded in the solid state to optimize cross-polarization contact times. Most commonly encountered air-drying alkyd systems have been examined, including samples in the pigmented form. A range of modified alkyds has also been investigated by the technique. The results obtained in the solid state are compared to results previously obtained in the solution state and in the swollen state. Direct evidence of sample crosslinking has been obtained for the first time using nuclear magnetic resonance.

(Keywords: solids; nuclear magnetic resonance; alkyd paints; linseed oil; crosslinking; pigmentation)

INTRODUCTION

The analysis of alkyd paint binders by ^{13}C n.m.r. is a recently developed technique of great promise. Work in the solution state provides detailed information on the repeating units present in non-crosslinked materials[1].

When the crosslinked materials are swollen in deuterochloroform, good-quality ^{13}C spectra can be obtained from those parts of the macromolecule that are flexible[2]. This effectively accounts for all parts of the molecule except for crosslinks and those positions one or two bonds away from the crosslinks. In this paper the usefulness of ^{13}C cross-polarization (CP) magic angle spinning (MAS) n.m.r. spectroscopy[3] for the characterization of crosslinked alkyd paints has been studied, particularly the ability to differentiate between the rigid and flexible portions of the materials, and the effects of pigmentation.

EXPERIMENTAL

Materials

With the exception of the two-pack polyurethane paint, all samples have been examined previously, and details of their preparation are given elsewhere[1,2]. The former was a commercial system based on an aliphatic diisocyanate and a branched aromatic polyester. It was pigmented with rutile (titanium dioxide) and cured on a glass plate using the requisite catalyst. Samples of the dry film were cut into small discs for packing into the sample spinner.

Nuclear magnetic resonance spectroscopy

Prior to carrying out ^{13}C CP MAS studies it was necessary to optimize the CP contact times. ^1H spin–lattice relaxation times in the laboratory (T_1) and rotating ($T_{1\rho}$) frames were measured for the samples using a purpose-built spectrometer operating at 60 MHz[4]. The values obtained then allowed a suitable contact time to be chosen for the ^{13}C experiment.

High-resolution ^{13}C spectra were obtained using a previously described[5] purpose-built instrument operating at 22.63 MHz and a temperature of 300 K with spin-locked CP to enhance the signals. The samples were spun at the magic angle at a speed of about 2 kHz. A recycle time of 0.75 s was used throughout and between 20 000 and 90 000 transients were recorded, using a sweep width of 15.6 kHz. Chemical shifts were referenced externally from adamantane taking its shift to be 73.5 ppm from tetramethylsilane. Two ^{13}C pulse sequences were used with each sample, one to enhance the protonated species (CPST) and another to enhance quaternary signals (OFNQS). The latter sequence generally gave a poorer response than the former, and thus required a larger number of transients. Identical contact times were used in each case.

RESULTS AND DISCUSSION

^1H solid-state relaxation studies

Measurement of the ^1H spin-relaxation parameters is a necessary prerequisite of the CP experiment used to

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obtain ^{13}C solid spectra. However, these data themselves are also of interest in describing the morphology of a particular material. The T_1 and $T_{1\rho}$ values measured in this work are shown in *Table 1*. The $T_{1\rho}$ data are of particular interest because in all cases there appear to be two separate decay processes evident. These have been tabulated according to the actual relaxation time and its percentage. It can be inferred from previous studies that the longer $T_{1\rho}$ value is associated with a more rigid environment for the spins[4]. At present this remains only an empirical observation but the data in *Table 1* are indeed consistent with it. The cured linseed oil is a rubber-like material and has a high percentage (72%) of a quickly relaxing ^{1}H environment ($T_{1\rho}=0.48$ ms). The alkyds themselves have excess proportion of the more slowly relaxing ^{1}H environment, reflecting the relative brittleness of these materials. The differences between the two urethane paints in terms of the $T_{1\rho}$ populations is very encouraging since the recorded times are virtually identical and yet their populations are quite different.

The effects of pigmentation can be seen by examination of the pentaerythritol alkyd sample in *Table 1*. The relative proportions of the two $T_{1\rho}$ components are about the same, but the actual times would appear to increase upon pigmentation. The vinyltoluene alkyd has one rather long $T_{1\rho}$ component, and this is in fact the most brittle of all the alkyds studied, due in part to the high concentration (40%) of vinyltoluene in the material.

Clearly further work is needed before definite conclusions can be reached but this approach opens up some interesting new avenues for research.

^{13}C cross-polarization magic angle spinning nuclear magnetic resonance

The key component in air-drying alkyd paints is the drying oil, i.e. the polyunsaturated alkyl groups introduced into the polyester material as potential crosslink sites[6]. Linseed oil is one such material that can be cured to form films in its own right when a catalyst is used. Although these are of no practical use, being too soft, they do provide an important view of the crosslinking behaviour of drying oils in alkyd polyesters.

Catalyst-dried linseed oil has been examined by swollen-state ^{13}C n.m.r. and found to show no signals from crosslink sites[7]. Initially this was thought to be due to the low crosslink density of the material, but for some reason most of the polyunsaturated carbon atoms gave no ^{13}C signals: clearly a lightly crosslinked material should show strong olefinic signals from the unused sites. The ^{13}C CP MAS spectrum of the cured linseed oil is shown in *Figure 1*, the left-hand trace being the CPST experiment and the right-hand trace the OFNQS experiment. The major chemical shifts are outlined in *Table 2*.

There is no sign of residual olefinic signals in the region of 120–140 ppm but there is a signal not seen in the gel spectrum of the material[7]. This is the signal at 42.8 ppm in the left-hand trace. The right-hand trace shows a signal at 42.8 ppm with an apparently greater intensity, suggesting it is quaternary. This signal is most likely to come from the quaternary carbon atoms formed during the crosslinking of the olefinic chains[6]. The OFNQS experiment gives signals at reduced intensity from protonated species, except for terminal methyl groups such as that at ~13 ppm in *Figure 1*. The carbonyl region shows evidence for an ester group at ~165 ppm which was not observed in the gel spectrum[7]. However, the signal intensity is not much greater than the background noise and so may be unreliable. The methine and methylene signals adjacent to the oxygen atoms of glycerol in the drying oil give only a diffuse signal at ~66 ppm in the CPST spectrum at *Figure 1*. The gel

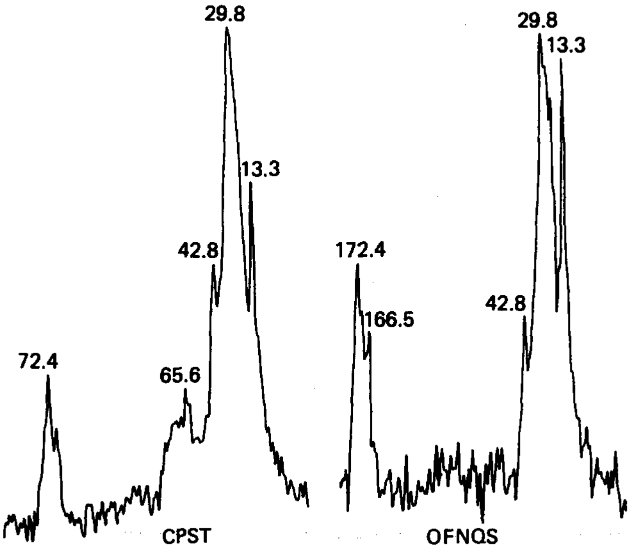

Figure 1 ^{13}C CP MAS spectra of cured linseed oil

Table 1 Alkyd ^{1}H and ^{13}C solid-state experimental parameters

	T_1 (s)	$T_{1\rho}$ (ms)	Contact time (ms)	^{13}C scans (CPST/OFNQS)
Linseed oil	0.11	1.13 28 0.48 72	0.75	22 000/45 000
Glycerol alkyd	0.17	2.20 55 0.61 45	2.0	80 000/90 000
Pentaerythritol alkyd	0.19	2.59 58 0.87 41	1.5	22 000/25 000
Silicone alkyd	0.22	2.48 61 0.62 39	2.0	35 000/65 000
Urethane alkyd	0.18	2.84 55 0.77 45	0.75	30 000/50 000
Two-pack polyurethane	0.24	2.85 71 0.70 29	1.0	45 000/45 000
Vinyltoluene alkyd	0.23	4.70 75 0.53 25	2.0	35 000/60 000

Table 2 Alkyd ^{13}C solid-state chemical shifts

Linseed oil	13.3, 29.8, 42.8, 65.6, 166.5, 172.4
Glycerol alkyd	13.3, 30.1, 42.9, 64.1, 129.3, 133.8, 165.8
Pentaerythritol alkyd	13.4, 28.9, 42.2, 63.6, 130.2, 134.0, 166.3, 172.3
Silicone alkyd	13.2, 16.2, 29.2, 42.2, 62.0, 128.7, 133.2, 166.2, 172.1
Urethane alkyd	13.9, 29.2, 42.2, 64.6, 130.2, 135.2, 173.0
Two-pack polyurethane	7.1, 27.5, 41.1, 65.4, 129.8, 134.5, 149.2, 156.9, 166.2
Vinyltoluene alkyd	12.8, 20.2, 28.9, 39.1, 42.4, 63.5, 129.1, 134.6, 142.7, 165.3, 171.5

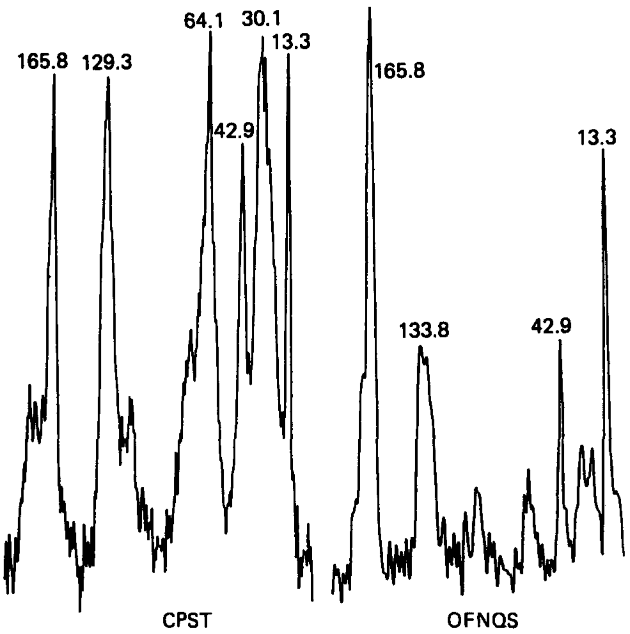

Figure 2 ^{13}C CP MAS spectra of cured glycerol phthalate alkyd

spectrum gave the expected 2:1 doublet at 69 and 62 ppm that is also seen in the uncured oil in solution[7].

An alkyd paint can be produced from linseed oil by incorporating an aromatic diacid into the system[6]. A polyester produced from phthalic anhydride and linseed oil can be crosslinked to give a paint film. The ^{13}C CP MAS spectra obtained from this material are shown in *Figure 2* and the chemical shifts of the major signals are shown in *Table 2*. Signals are apparent from the phthalate groups at 129.3 and 165.8 ppm for the aromatic and carboxyl carbons, respectively. The carboxyl signal from the linseed groups is just visible at 172.0 ppm in the OFNQS trace.

The linseed portion of the material gives rise to a similar series of signals to those seen in *Figure 1* from linseed oil itself, including a signal of 42.9 ppm from the crosslink site. This peak appears far more pronounced in *Figure 2*, which would seem to relate to the known higher crosslink density of an alkyd compared to linseed oil itself. Certain alkyds can be cured by the action of heat rather than oxidation[8]: these materials show no signals at ~42 ppm in their solid-state ^{13}C spectra[9].

Modern commercial air-drying alkyd materials, especially those used for decorative paints, are based on pentaerythritol rather than glycerol[6]. This produces a more consistent product since only primary alcohol groups are present. The ^{13}C CP MAS spectrum obtained with an alkyd based on linseed oil, pentaerythritol and phthalic anhydride has an overall appearance that is similar to the glycerol alkyd shown in *Figure 2* except that the linseed carbonyl signal is now clearly resolved from the phthalate carbonyl. Some of the signal intensity at 42.2 ppm in the former must actually be from the quaternary carbon atoms at the pentaerythritol units in the material[1]. The same material was examined after pigmentation with titanium dioxide and the spectra are shown in *Figure 3*. The spectra are if anything of better quality than those from the unpigmented material and a smaller number of scans were recorded. This is most encouraging since from an analytical standpoint most paint samples of interest will be encountered with pigment present.

The OFNQS spectrum in *Figure 3* shows a strong signal at 134.0 ppm. This signal cannot be seen in the CPST spectrum of this alkyd or the glycerol alkyd in *Figure 2*. A similar signal is present in the OFNQS spectrum in *Figure 2* and so it may be associated with a quaternary olefinic signal produced by crosslinking. Another possibility is that it is from the quaternary phthalate carbon atoms adjacent to the carbonyl group, although in the solution state a chemical shift of ~131 ppm is observed. This may explain the absence of such a signal in the spectra of cured linseed oil. It should be stressed, however, that the measured chemical shifts in the solid state do vary somewhat due to different sample magnetic susceptibilities[5]. At this stage it is not clear what exact differences may be encountered with alkyd polymers.

Where alkyds with particular properties are required, modifying monomer units can be introduced at the manufacture stage[6]. The spectra obtained from a phenylmethyl silicone-modified alkyd are shown in *Figure 4*. This particular modifier has a complex siloxane backbone but the solution-state ^{13}C spectrum shows only four signals: at 134.1 and 128.0 ppm from the phenyl groups, and at 17.5 and 16.3 ppm from the methyl groups[1]. These four signals are still visible in the swollen-state spectrum of the cured alkyd[2].

In the solid-state spectrum the methyl groups produce a composite signal at 16.2 ppm but the phenyl groups are

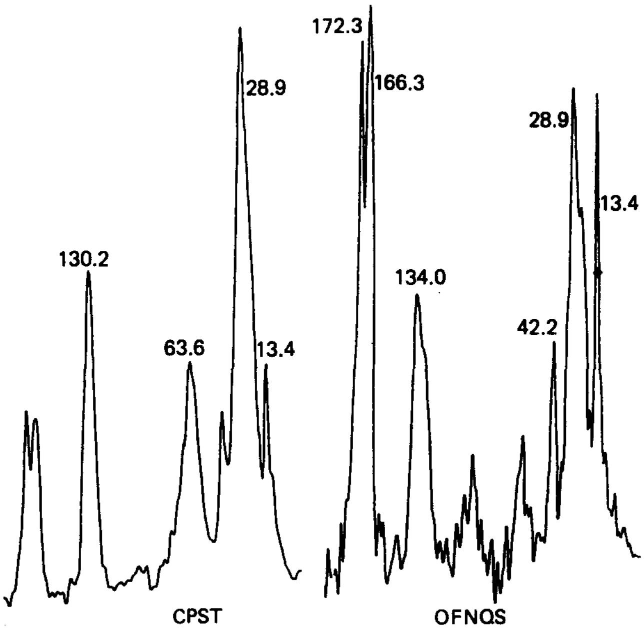

Figure 3 ^{13}C CP MAS spectra of cured pigmented pentaerythritol phthalate alkyd

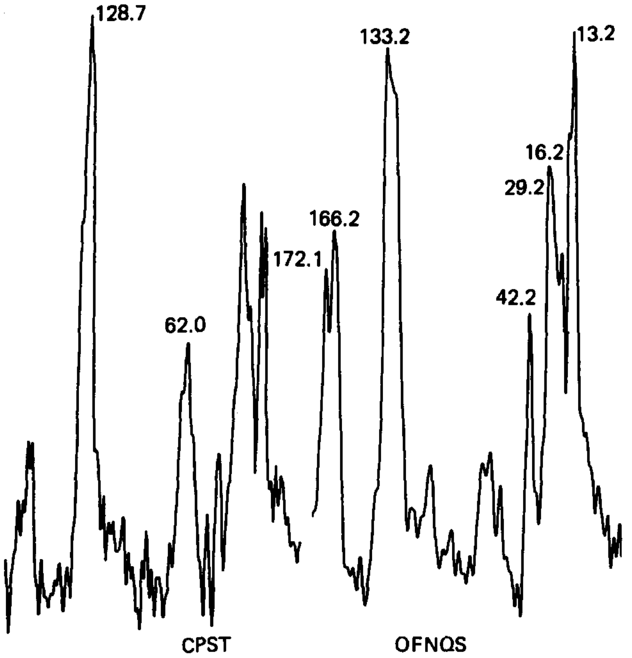

Figure 4 ^{13}C CP MAS spectra of cured silicone-modified alkyd

not so easily distinguished. The OFNQS spectrum in *Figure 4* shows a signal at 133.2 ppm, but this may be the signal from the quaternary groups seen in the alkyd spectra above. The phenyl groups should appear in the non-quaternary CPST spectrum, although greater resolution may be required to differentiate them from the phthalate groups. Clearly the more complex the alkyd becomes, the more resolution problems may ben encountered.

The remaining features of the spectra in *Figure 4* seem typical of the pentaerythritol alkyd above, i.e. well resolved carbonyl signals, and a strong quaternary signal at 41.2 ppm, in addition to a good resolution of the methyl signals from the silicone itself and the drying oil at 16.2 and 13.2 ppm. A range of silicone alkyds are available that have different silicone modifiers present, which would merit examination by solid-state ^{13}C n.m.r.

Another important class of modified alkyds are those that contain polyurethanes[6]. Most polyurethane varnishes are in fact alkyds modified with toluene diisocyanate. The urethane units that are formed can form hydrogen bonds between adjacent polymer chains to provide toughness. However, the hydrogen bonds are still intact in the swollen state so that the urethane carbonyl signal is only just visible in the ^{13}C gel spectrum despite being very distinct in the solution state[2]. The solid-state ^{13}C spectra from a urethane alkyd are shown in *Figure 5*. There is no evidence of the urethane carbonyl at the expected position at ~ 154 ppm. This may be due to quadrupolar interaction with the ^{14}N present in the urethane, although urethane carbonyls have been observed in the solid spectra of a range of foams based on toluene diisocyanate[10]. There is no evidence of abnormal ^{1}H relaxation in the system since the data in *Table 1* are similar to the other alkyds studied.

The phthalate carbonyl signal at 166.8 ppm is low in intensity, which suggests that in this system all aromatic carbonyl groups give weak signals. The OFNQS spectrum shows strong signals from the quaternary sites at 135.2 and 42.2 ppm.

Aliphatic polyurethane systems are also used as paints although these are not air-curing and are two-pack materials[11]. The ^{13}C solid spectra from a typical material is shown in *Figure 6*. The two components are a branched phthalate polyester and a hexamethylene diisocyanate-based material, made up with a suitable catalyst and pigmented with rutile titanium dioxide. The aliphatic urethane gives a strong signal at 156.9 ppm, the expected region for this functionality. The carbonyl is even clearly visible in the CPST spectrum in *Figure 6*. The OFNQS spectrum shows the presence of additional signals at 149.2 ppm and perhaps at 160.8 ppm, which may be due to other species formed in the reaction. The material itself is much more crosslinked than the air-dried polyurethane alkyd and gave very little information in the ^{13}C gel spectrum[2]. The OFNQS spectrum shows a strong signal at 134.5 ppm. Since no drying oil is present in the two-

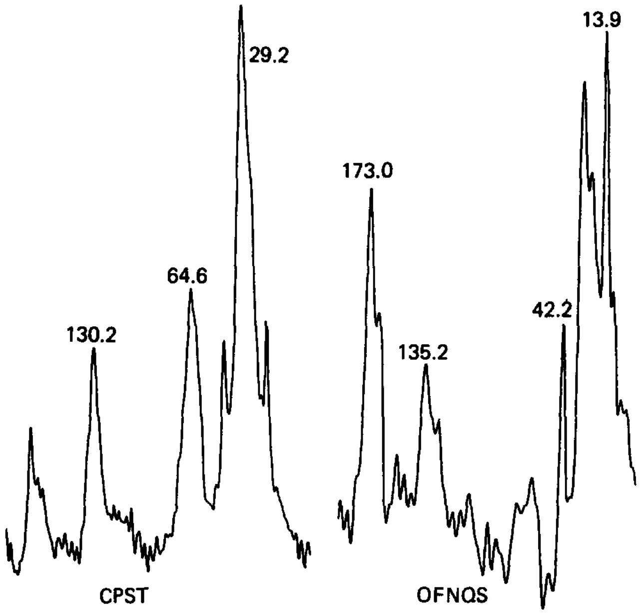

Figure 5 ^{13}C CP MAS spectra of cured aromatic urethane-modified alkyd

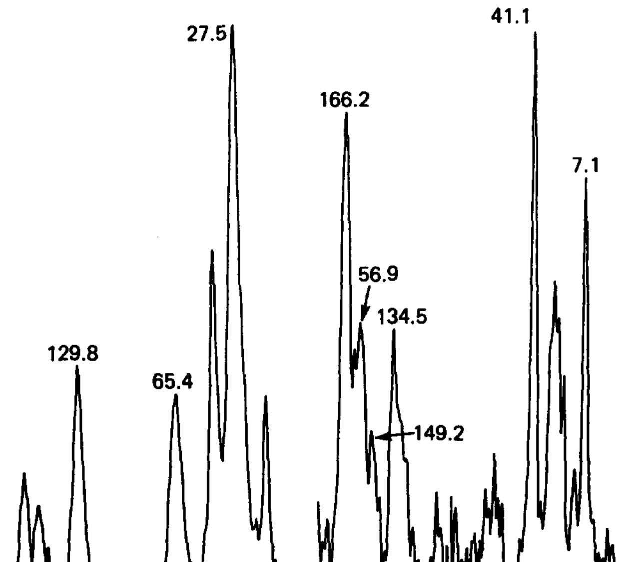

Figure 6 ^{13}C CP MAS spectra of cured pigmented two-pack aliphatic urethane paint

pack material, the signal here must be due to the quaternary signal of the phthalate units alone.

The signal at 41.1 ppm is a quaternary signal from the branched polyester portion of the polymer which is based on trimethylolpropane. The signal at 7.2 ppm is characteristic of the methyl groups in these systems and the signal at 65.4 ppm is a primary carbon adjacent to an oxygen atom. Finally the broad signal at ~27 ppm is from the hexamethylene units of the urethane.

The final material to be examined was a vinyltoluene-modified alkyd, based on glycerol and phthalate. As mentioned above, the ^{1}H $T_{1\rho}$ values of this material shown in *Table 1* are significantly different from the other alkyds and this probably reflects the high level (40%) of vinyltoluene present. The ^{13}C solid-state spectra obtained from the material are shown in *Figure 7*. The dominant signals are from polyvinyltoluene at 142.7, 129.1, 39.1 and 20.5 ppm, although some of the fine structure visible in the solution-state spectrum of polyvinyltoluene itself cannot be seen[1]. In particular, there is no clear evidence for the *ortho* isomer of the polymer, which in the solution state gives signals from the quaternary aromatic carbons at 145.6 and 137.1 ppm. The OFNQS spectrum in *Figure 7* has signals at 142.7 and 134.6 ppm, which are probably from the quaternary positions of *para*-polyvinyltoluene. However, the *ortho* isomer is known to be predominant both in the homopolymer[12] and in the ^{13}C swollen-state spectrum of the vinyltoluene alkyd[2]. Clearly this range of alkyds merits further study.

Another interesting point is that the signal at 134.6 ppm in the OFNQS spectrum in *Figure 7* matches well with the signal at 134.7 ppm in the solution-state spectrum of polyvinyltoluene, corresponding to the site of substitution of the *para* methyl group. The alkyd itself had a high vinyltoluene content and so such a signal would be anticipated. The site of substitution of the phthalate groups in the alkyds described above was also assumed to give a signal at ~134 ppm even though the corresponding solution-state signal appeared at ~131 ppm[1]. Clearly there is something unusual about carbonyl-bearing aromatic carbon atoms that can produce large changes between the measured chemical shifts in the solution state and in the solid state. This has also been observed with a range of polyesters based on maleic anhydride using a variety of aromatic diacids[13].

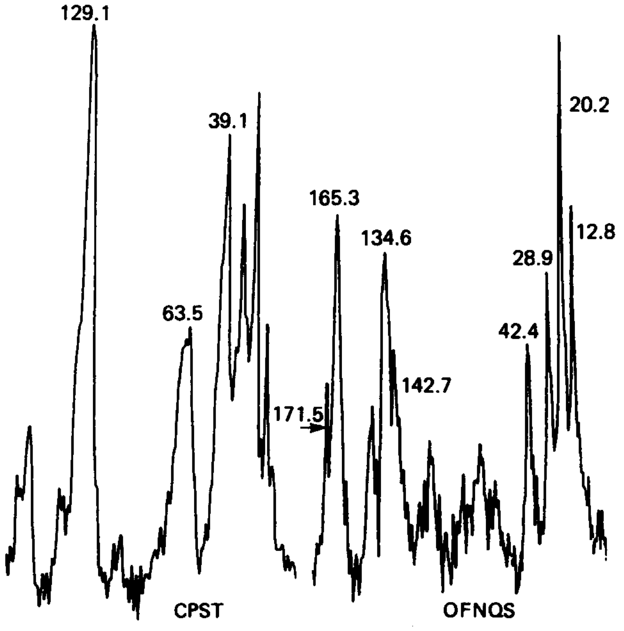

Figure 7 ^{13}C CP MAS spectra of cured vinyltoluene-modified alkyd

The elimination of the signal at 39.1 ppm from the methylene and methine groups of polyvinyltoluene shows the usefulness of the OFNQS pulse sequence. The CPST spectrum in *Figure 7* shows little evidence of the drying oil quaternary crosslink signal at 42.4 ppm, yet in the OFNQS spectrum it is clearly visible due to the suppression of the protonated signals. The OFNQS spectrum also shows the relative amounts of the ester carbonyl groups at 171.5 and 165.3 ppm. This shows good agreement with the solution-state spectrum and clearly illustrates the low level of drying oil used in vinyltoluene-modified alkyds.

CONCLUSIONS

^{13}C CP MAS n.m.r. has been used to characterize a range of air-cured alkyd paints. Values for CP contact times have been estimated having measured the ^{1}H spin–lattice relaxation parameters of the materials, and these data themselves reveal interesting features about the sample morphology. The ^{13}C solid-state spectra obtained correlate well with previous studies in the solution state and in the swollen state. In general, resolution is not as good as in the swollen state, but clear evidence of drying oil crosslinks has been obtained. Pigmented systems give especially good spectra despite the low levels of binder present. Modifying units with the paints such as silicones and vinyl polymers can be clearly detected although the method is not as good for an aromatic polyurethane alkyd. However, an aliphatic polyurethane paint does give good spectra. The ^{13}C CP MAS technique shows great promise for heat-cured alkyds and other polyurethane and polyester thermoset systems.

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