

New Insights into the Degradation Mechanism of Poly (Vinyl Chloride), Part (III): Implementation of New Costabilizers—Towards Heavy Metal Free Systems (HMFS)

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ABSTRACT: To replace zinc in PVC stabilized formulations and generate a Heavy Metal Free System (HMFS), different costabilizers (i.e., 6-amino-1,3 dimethyluracil (Uracil), sodium tetraborate (Borax), sodium phenyl phosphinate (SPP), and NPPD (*N*-phenyl-3-acetylpyrrolidin-2,4-dione), and their combinations) were tested. HCl evolution showed the outstanding performance of SPP, which was overshadowed by its poor color stability. To optimize the levels of costabilizers in the formulation, experimental design was applied to two different formulations. For a formulation containing Uracil + SPP + NPPD, the induction time (Ti) could reach up to 50 min. Moreover, an induction time of more than 80 min could be obtained with the combination of the costabilizers Borax + SPP + NPPD. The dynamic stability in terms of color measurements showed that excellent color control was achieved by the addition of 2phr of Borax into the formulation, with even better results than the mixture of the three costabilizers at their highest levels (Borax + SPP + NPPD). For a formulation containing Uracil + SPP + NPPD, the best results were again obtained by the combination of the highest levels of the three costabilizers. The

mechanistic action of SPP with a model compound (4C2H) was studied by ¹H and ³¹P-FNmr. The reaction was obscured by the fact that SPP underwent hydrolysis in aqueous conditions. However, the color measurements showed that because the initial color was poor, it is unlikely that SPP is acting as a peroxide decomposer in the conventional sense. In addition, the great extension in the Ti means that SPP must be inhibiting chain propagation and it may do this by stabilizing the carbocation generated during the dehydrochlorination process, along with its acid scavenging activity. Thus, when the costabilizer is totally consumed, the rate of free HCl evolution is very high, as the results confirm. The fact that phenyl phosphinic acid (PPA), the acid form, did not stabilize PVC seems to be in agreement with the above reasoning. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 122–143, 2005

Key words: poly (vinyl chloride); Heavy Metal Free Systems (HMFS); thermal degradation; stabilization; costabilizers; design of experiments; yellowness

INTRODUCTION

Current initiatives in the polymer industry center on improving the performance of materials, but within this context the greatest pressures are for the development of environmentally friendly systems. Poly (vinyl chloride) (PVC) is under heavy pressure generated by environmental groups to reduce the amount of heavy metals in PVC applications. Increasing awareness of exposure to metals in the workplace has resulted in a shift towards “nontoxic” systems. Since greater demands are being made on the use of environmentally friendly stabilizers, the performance contribution of

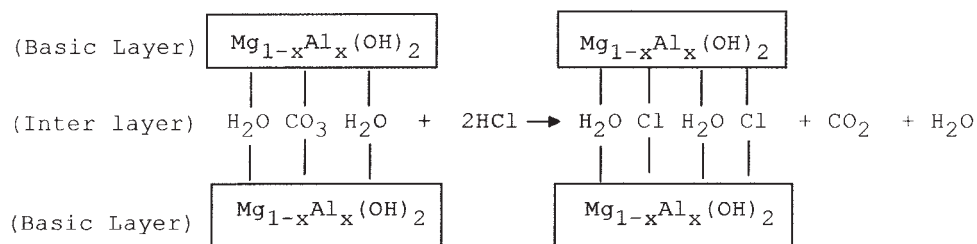
the organic costabilizers has become increasingly important.

The advances in stabilizer technology are based primarily on the use of organic costabilizers. Costabilizers form relatively stable complexes with the chloro derivatives of primary stabilizers (Lewis acids) and suppress their degradative effect. Nowadays, the term costabilizer has become more associated with materials that at relatively low levels enhance significantly the early color and mid-term control of the PVC formulation. There have been claims¹ that a blend of organic costabilizers based on urea derivatives shows no discoloration and loss of performance when used in rigid pipe grade formulations. This was attributed to the presence of very strong nucleophilic sites, combined with electron donating groups.

The use of 6-amino-1,3 dimethyluracil (Uracil) derivatives stems from the fact that since they do not require the use of zinc salts to catalyze their stabilization mechanism, the possibility of zinc free additives

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Scheme 1 Structure of hydrotalcites.

has been raised. Their mechanistic action² seems to take place via substitution of labile chlorines by *N*-alkylation reaction, stopping the growth of the polyene sequences. Their outstanding performance in terms of color control has been linked to the conjugation and electron transfer that is available within the molecule.³

The advantage of adding Borax into the formulation is similar to that of hydrotalcites: it can scavenge HCl by reacting with the hydroxide groups. This reaction allows hydrotalcite-like clays to be used as HCl scavengers in PVC stabilization in an ion-exchange reaction⁴ (Scheme 1). They are claimed to provide good heat stability and transparency.⁵

Many borates occur naturally, usually in hydrated form. The structure of the anions is generally cyclic or of linear polymers by linking together BO_3 units by shared oxygen atoms.⁶ In addition to this, Borax is cheap, so large amounts can be added at no extra cost. Minsker et al.⁷ have indicated that borates can inhibit PVC degradation and eliminate the catalytic effect of HCl by chemically reacting with it. However, they also pointed out that in some cases, anions such as $\text{B}_4\text{O}_7^{3-}$ may also promote dehydrochlorination of PVC.

There is not much information available about the specific chemistry of phosphinates. Typically, SPP is considered to be a peroxide decomposer and, although throughout this work the thermal degradation

of PVC is being considered, there is no doubt that there may be oxygen-containing groups as a result of the interaction of molecular oxygen with weak structures of PVC. In addition, SPP being a salt, it could also scavenge HCl to produce the correspondent acid and harmless NaCl. Therefore, the mechanistic action of SPP could be *a priori*, at least, a twofold one.

EXPERIMENTAL PROCEDURES

Materials

PVC Solvic 271 GC, PVC Pevikon P14, DOP (dioctylphthalate), NPPD (*N*-phenyl-3-acetylpyrrolidin-2,4-dione), PPA (phenyl phosphinic acid), Borax (sodium tetraborate), and Uracil (6-amino-1,3-dimethyluracil) were supplied by Akros Chemicals (Akzo Nobel). SPP (phenyl phosphinic acid, sodium salt hydrate) was obtained from Aldrich. d_8 -THF was obtained from Gross Scientific Instruments Ltd.

Synthesis and techniques

Synthesis of 4-chloro-2-hexane (4C2H), Induction Time (Ti) to Dehydrochlorination Measurements, and Design of Experiments (DOE) have been described elsewhere.^{8,9}

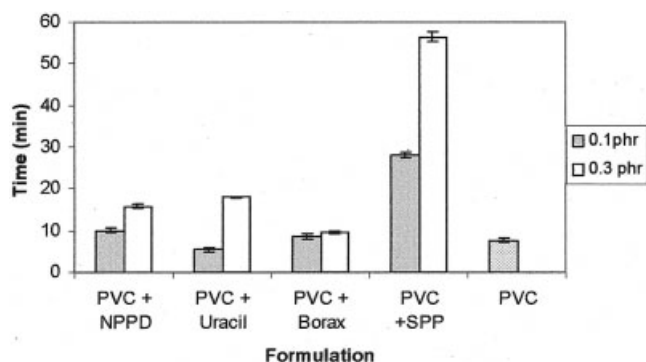


Figure 1 Ti to DHC values for samples containing NPPD, Uracil, Borax, and SPP.

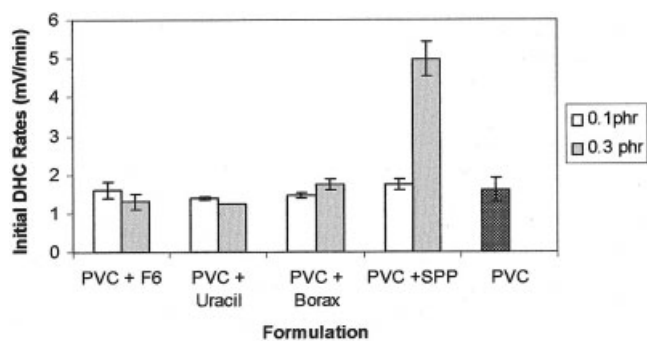


Figure 2 Initial DHC rates for samples containing NPPD, Uracil, Borax, and SPP.

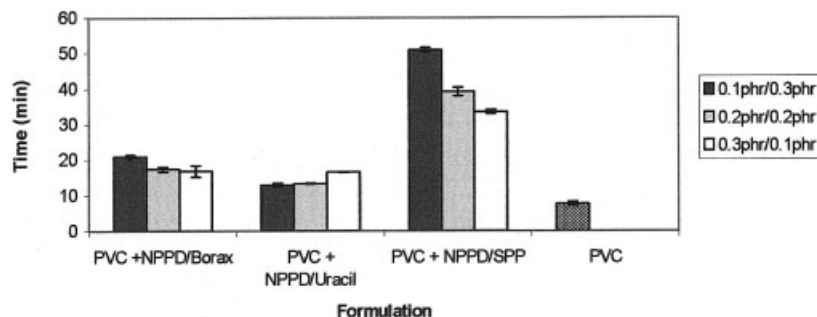


Figure 3 Ti to DHC for combinations of NPPD + (Borax, Uracil, SPP) at 3 levels of concentration.

Color measurements

To test the dynamic stability, the polymer compounds were milled at 170°C in a Collin two-roll mill to prepare sheets for oven aging. An amount of 200g was used for each run and the mill speed was 13.6 m/min.

In the case of the triple roll mill, an emulsion polymer (PVC Pevikon P14) was used. The plastisol was first mixed in a Collin Mixer for 10 min at low speed to avoid the formation of bubbles.

The sheets were cut into strips and aged in a Werner Mathis thermostester at 185°C. Samples were removed at specific times to observe discoloration. Color measurements were carried out in a HunterLab Ultrascab-XE instrument using the Yellowness Index (YI) based on ASTM E313 (2/C).

Fourier-transform nuclear magnetic resonance analysis

For the identification of the products, ^1H and ^{31}P spectra were obtained by using a Jeol 270 MHz FT-NMR spectrometer. Chemical shifts are in p.p.m. with reference to tetramethylsilane and phosphoric acid, respectively. In the case of samples run in deuterated oxide (D_2O), the reference used was the sodium salt of

2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS), $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$.

RESULTS AND DISCUSSION

Induction time to dehydrochlorination analysis

The efficiency of the system in controlling the evolution of hydrogen chloride was tested for 3 organic costabilizers at 2 different levels, as well as for their combinations with NPPD.

Figure 1 shows Ti values for formulations containing PVC + costabilizer at 2 addition levels: a low of 0.1phr and a high of 0.3phr. For comparison, the PVC control is shown on the right.

At 0.1phr, with the exception of SPP, neither of the costabilizers seemed to extend the Ti compared to the PVC control. As shown by the data, the performance of SPP was outstanding at any given level. Higher loadings resulted in both NPPD and Uracil extending their stability length compared to their values for the low level, although very much behind the performance of SPP. In the case of Borax, this costabilizer showed the poorest performance overall, with little increased length compared to the control. Finally, 0.3phr of SPP increased the Ti up to nearly 60 min.

As far as the initial DHC rate is concerned (Fig. 2), NPPD, Uracil, and Borax showed similar values com-

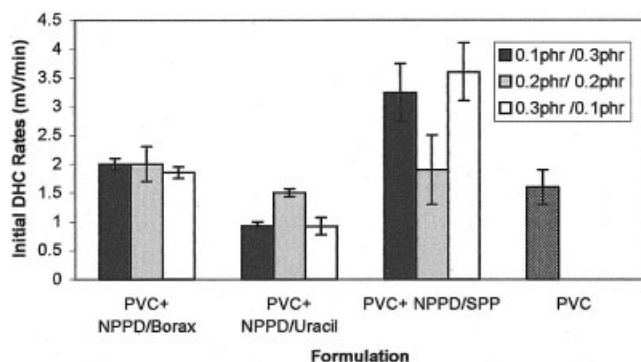


Figure 4 Initial DHC rates for combinations of NPPD + (Borax, Uracil, SPP) at 3 levels of concentration.

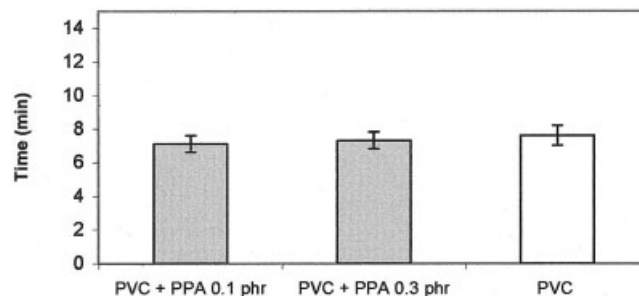


Figure 5 Effect on the Ti to DHC of phenyl phosphinic acid (PPA).

TABLE I
Model Design Summary for RSM Borax-SPP-NPPD

Study Type	Response Surface	Experiments	17
Initial Design	Central Composite	Blocks	3
Design Model	Quadratic		
Response		Unit	Transformation
Induction time		min	Natural log
Factor	Name	Units	Low Level High level
A	NPPD	phr	0.000 0.60
B	Borax	phr	0.000 2.00
C	SPP	phr	0.000 0.50

pared to the PVC control. These results seem to imply that both NPPD and Uracil, rather than inhibit HCl loss, block the growth of polyene sequences. As for Borax, the lack of increased length may be attributed to the poor dispersion within the mixture. However, on addition of SPP the degradation rate seemed to increase almost threefold, especially when 0.3phr of the costabilizer were added.

With a view to assessing possible interactions between NPPD and the rest of the costabilizers, Figure 3 shows T_i values obtained for combinations of NPPD + 3 different structures at 3 levels, relative to PVC alone (control). Keeping the overall concentration at 0.4phr, their relative levels were varied. In the case of the combination NPPD/Borax, there was an improvement in the T_i compared to their individual performances and also compared to the control. This was especially true for the combination of 0.1phr of NPPD and 0.3phr of Borax. However, from their individual values, it seemed as though there was no interaction between them and that the T_i obtained due to the combination arose from a mere sum of their individual mechanisms. According to this, Borax is likely to act as an HCl scavenger due to its basic pH (6.8–9.6, depending on the amount of boric acid) while NPPD could interact with the PVC chain.

For combinations containing NPPD/Uracil, a significant reduction in the length was observed compared to their individual performances. Although there was no substantial increase, the formulation containing NPPD 0.3phr + Uracil 0.1phr seemed to further extend the T_i . Since Uracil tends to form a two-dimensional hydrogen bonding network in the solid state,¹⁰

TABLE II
Model Summary Statistics for RSM Borax-SPP-NPPD

Source	Root MSE	Adjusted R-Squared	Predicted R-Squared	R-Square	PRESS
Linear	0.45	0.7002	0.6185	0.0786	6.80
Quadratic	0.070	0.9966	0.9906	0.6401	2.65

it is plausible that an arrangement of this type takes place on interaction with NPPD, which bears in its structure 3 different carbonyl groups. This effect would be especially detrimental if the hydrogen bonding took place through the acetyl group involved in the C-alkylation reaction,⁸ as might be the case.

In contrast, combinations of NPPD/SPP greatly extended the T_i compared to previous blends (NPPD 0.1phr/SPP 0.3phr $T_i = 50.9 \pm 1.7$ min). Despite this fact, the remarkable extension in the T_i proved to be a result of an antagonistic effect, when compared to their individual values. This effect may stem from a complexation or interaction between NPPD and SPP. However, it is believed that the addition of NPPD can improve the color control of the formulation, so it is desirable to obtain a compromise between the ratio of NPPD/SPP to optimize the length as well as the color control.

As far as the initial DHC rate is concerned (Fig. 4), except for the combinations containing Uracil, all the rest of the formulations showed higher DHC rates than the PVC control, and particularly SPP exhibited in some cases, twofold values. This fact suggests, once more, that the costabilizers block or interrupt the propagation of polyene sequences.

To assess whether the performance of SPP is related to its acid derivative, phenyl phosphinic acid (PPA) was tested. The T_i obtained for PPA alone proved to

TABLE III
Equation for the Quadratic Model for RSM BORAX-SPP-NPPD

Ln (Induction time) =	+1.56	
	+2.86	*NPPD
	+1.27	*BORAX
	+6.03	*SPP
	-1.63	*NPPD ²
	-0.18	*BORAX ²
	-3.41	*SPP ²
	-0.34	*NPPD*BORAX
	-2.52	*NPPD*SPP
	-1.23	*BORAX*SPP

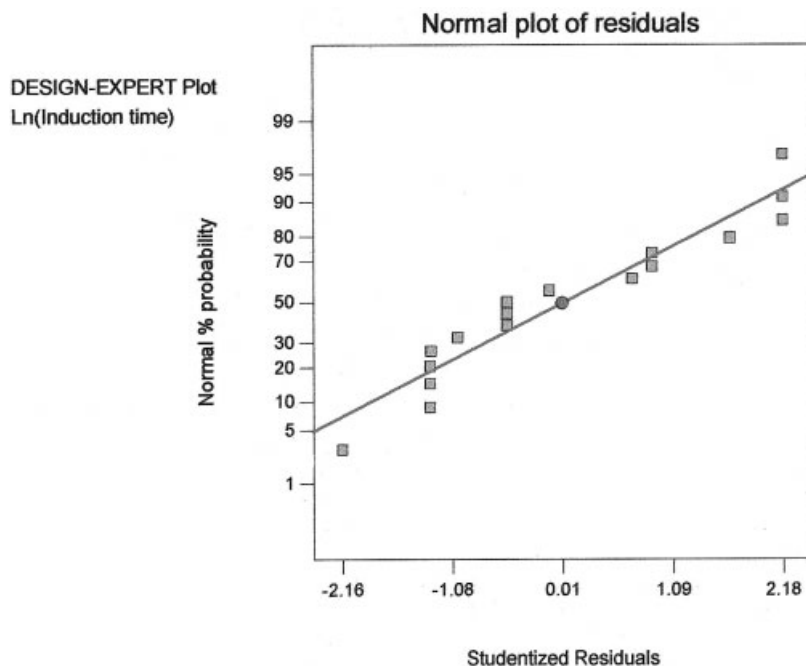


Figure 6 Normal plot of residuals for RSM of Borax-SPP-NPPD.

be similar to that of the PVC control. This fact may suggest that PPA not only did not extend the T_i , but furthermore, being an acid, promoted the DHC process. This could suggest that being a weak acid,¹¹ its counterpart would be a strong nucleophile, so explaining the high reactivity of SPP. (See Fig. 5.)

Design of Experiments (DOE)

This section deals with a study orientated towards the optimization of the levels of the costabilizers in two different formulations. The addition of several costabilizers, which can operate in different ways, is carried

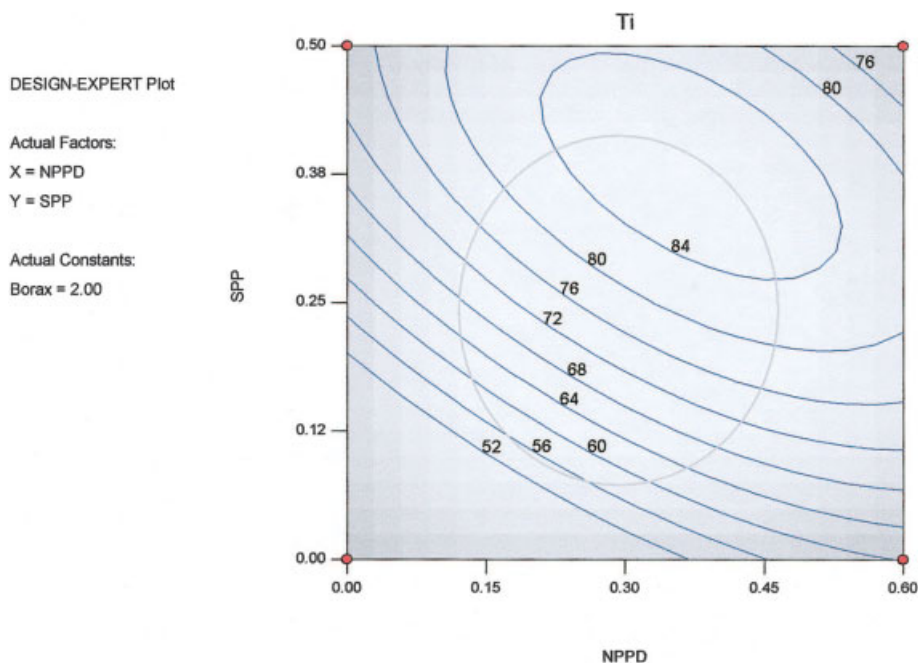


Figure 7 Contour plot for RSM Borax-SPP-NPPD.

TABLE IV
Model Design Summary for RSM Uracil-SPP-NPPD

Study Type	Response Surface	Experiments	17
Initial Design	Central Composite	Blocks	3
Design Model	Quadratic		
Response		Unit	Transformation
Induction time		min	Natural log
Factor	Name	Units	Low Actual High Actual
A	NPPD	phr	0.000 0.60
B	SPP	phr	0.000 0.50
C	Uracil	phr	0.000 0.50

out with a view to improving both the Ti and the extent of discoloration, always bearing in mind that the combination does not affect the processing conditions a great deal. Similar attempts have been recorded in the literature¹² to combine the different mechanisms of action of different costabilizers.

Response Surface Method (RSM): Borax-SPP-NPPD

In this case, an RSM was carried out to optimize the response for the formulation containing Borax, SPP, and NPPD. Table I shows the main characteristics of the design.

The following summary (Table II) describes the statistics for the proposed model. Provided that the most suitable model should give low "Root MSE," high "Predicted R-Squared," and low "PRESS," it is quite clear that the model that best adjusts to the system is the quadratic model.

The ANOVA (analysis of variance) section provided an equation (Table III) for the proposed quadratic model. In order that the quadratic model fitted the system, transformation of the natural log was taken.

The first term in the equation, 1.56, refers to the Ti for PVC control. According to this, the most important factor contributing to the system is SPP, followed by NPPD and Borax. Furthermore, all the combinations showed negative coefficients, that is, a detrimental effect in the system. It is important to note that none of the combinations with SPP showed a synergistic effect.

This supports the results obtained in terms of the dehydrochlorination times, which showed that in

spite of the outstanding performance of SPP extending the induction time of the system, this effect was reduced when combined with other costabilizers and attributed to an antagonistic effect.

Figure 6 presents the normal plot of the residuals with a view to elucidating if all the errors are equally scattered. No significant curvature in the line was observed, suggesting that the model was valid.

The contour plot in Figure 7 indicates that, as a result of the optimization of the system, a formulation achieving a Ti of 80 min could be obtained, adding 2phr of Borax, 0.3phr of NPPD, and 0.25phr of SPP. If we were to obtain a value of 84 min, 0.45phr of NPPD should be added and, probably, the increase in the Ti would not justify an increase of 1/3 in the concentration of NPPD. The gray circle indicates the area where the error for the response values is diminished.

Response Surface Method (RSM): Uracil-SPP-NPPD

Table IV is the design summary obtained in the optimization of the above formulation.

Table V shows the statistics for the models proposed. Provided that the most suitable model should give low "Root MSE," high "Predicted R-Squared" and low "PRESS," the model that best adjusts to the system is, again, the quadratic model.

TABLE VI
Equation for the Quadratic Model for RSM Uracil-SPP-NPPD

Ln(Induction Time) =	+1.75
	+2.53 *NPPD
	+6.07 *SPP
	+2.47 *Uracil
	-1.30 *NPPD ²
	-4.41 *SPP ²
	-2.52 *Uracil ²
	-2.62 *NPPD *SPP
	-1.26 *NPPD *Uracil
	-0.77 *SPP *Uracil

TABLE V
Model Summary Statistics for RSM Uracil-SPP-NPPD

Source	Root MSE	Adjusted R-Squared	Predicted R-Squared	R-Squared	PRESS
Linear	0.38	0.7443	0.6746	0.3178	4.26
Quadratic	0.076	0.9953	0.9869	0.6115	2.43

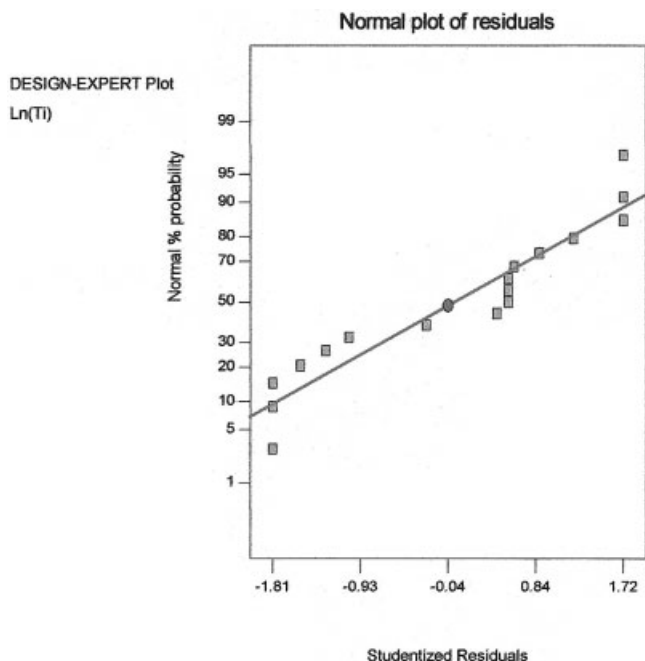


Figure 8 Residuals versus Predicted for RSM Uracil-SPP-NPPD.

The ANOVA (analysis of variance) section in Table VI gives the equation for the proposed quadratic model.

The first term of the equation, 1.75, refers to the T_i of PVC alone, with no costabilizers. The three costabilizers have positive coefficients; therefore, they contribute to increase the length of the system, with SPP having the most important effect. High concentrations of any of the costabilizers induced a detrimental effect in the system. Similarly, combinations of NPPD and

TABLE VII
Details of Formulation for PVC + BORAX + SPP + NPPD

BASE FORMULATION (SPREAD SHEET)	
Base formulation:	
Pevikon P14 (emulsion polymer)	100 phr
DOP	80 phr
Sample 1: blank	
Sample 2: BORAX 2 phr	
Sample 3: SPP 0.5 phr	
Sample 4: NPPD 0.6 phr	
Sample 5: BORAX 2 phr + SPP 0.5 phr + NPPD 0.6 phr	
Sample 6: BORAX 1.45 phr + SPP 0.5 phr + NPPD 0.3 phr	
Sample 7: BORAX 2 phr + SPP 0.25 phr + NPPD 0.3 phr	
Sample 8: BORAX 1 phr + SPP 0.5 phr + NPPD 0.3 phr	
Sample 9: BORAX 1.4 phr + SPP 0.3 phr + NPPD 0.6 phr	

Uracil produced antagonism in the system, and so did the combination of NPPD and SPP.

To validate the model, the diagnostics section (Fig. 8) presented a normal plot of the residuals with a view to elucidating if all the errors are equally scattered. A straight line in the plot confirmed that there was no evidence of problems with the model.

In the contour graph of the model (Fig. 9), the T_i for different values of the factors is depicted. According to this, it would be possible to obtain a formulation that extended the T_i up to 50 min with 0.5phr of Uracil, 0.4phr of SPP, and 0.4phr of NPPD.

Color measurements

This section is complementary to the above section on Design of Experiments, where a statistical design was applied to two different formulations. All the values of

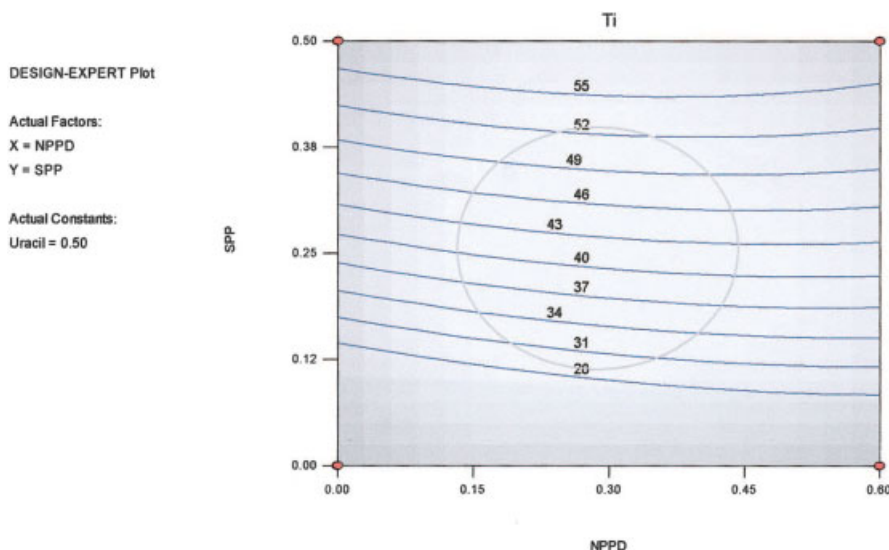


Figure 9 Model contour for RSM Uracil-SPP-NPPD.

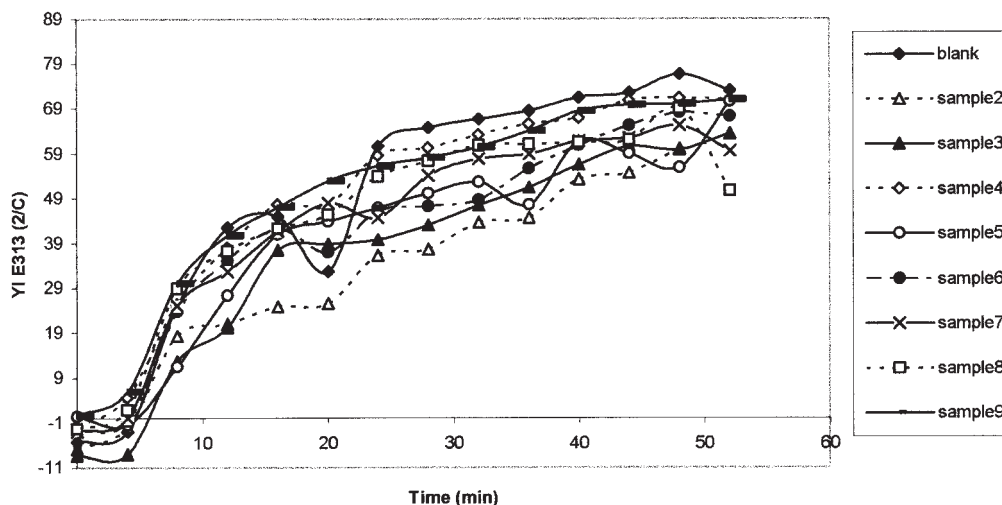


Figure 10 Yellowness values for spread sheet combinations of PVC Pevikon P14 + Borax + SPP + NPPD.

the Ti obtained need to be contrasted with their color measurements, since ultimately the latter is the critical factor in industry to decide about its possible implementation.

The formulations selected to perform the color measurements for each formulation corresponded to combinations whose Ti was high. Two sets of color measurements (yellowness index) were obtained:

1. PVC sheets were produced using a Collin two-roll mill at 170°C for about 2 min. Stearic acid was added to provide lubrication and prevent the formulation from sticking to the mill.
2. The formulation was mixed in a triple roll mill, and then spread in a sheet. In this case, an emulsion polymer was required. In addition, 80phr of dioctyl-phtalate (DOP) were added, compared to 45phr in the milled formulation. This was done with a view to improving the

flow, since the milling was carried out at room temperature.

The dynamic stability of the plasticized formulations in terms of color control was tested. It can be defined as the time elapsing until the sample has turned completely black.

The mechanical shear suffered in the triple roll mill was higher than that undergone in the two-roll mill and, therefore, the color developed by the formulations was expected to be stronger. Furthermore, this shear-stress reduced the differences among the formulations, so the yellowness values were within a short range.

PVC + Borax + SPP + NPPD

In this instance, only the spread sheet formulation was available, due to problems encountered during

TABLE VIII
Details of Formulation for PVC + Uracil + SPP + NPPD

BASE FORMULATION (MILLED)		BASE FORMULATION (SPREAD SHEET)	
Solvic 271 (suspension polymer) GC	100 phr	Pevikon P14 (emulsion polymer)	100 phr
DOP	45 phr	DOP	80 phr
Stearic acid	0.5 phr		
Sample 1: blank			
Sample 2: NPPD 0.6 phr			
Sample 3: SPP 0.5 phr			
Sample 4: Uracil 0.5 phr			
Sample 5: NPPD 0.6 phr + SPP 0.5 phr + Uracil 0.5 phr			
Sample 6: NPPD 0.3 phr + SPP 0.5 phr + Uracil 0.2 phr			
Sample 7: NPPD 0.6 phr + SPP 0.25 phr + Uracil 0.5 phr			
Sample 8: NPPD 0.3 phr + SPP 0.35 phr + Uracil 0.5 phr			
Sample 9: NPPD 0.35 phr + SPP 0.5 phr + Uracil 0.35 phr			

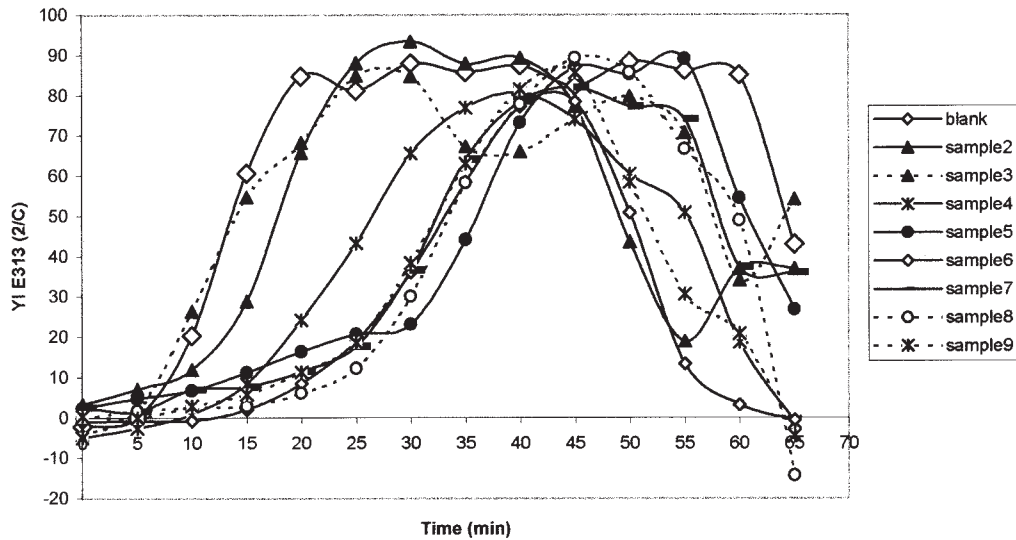


Figure 11 Yellowness values for milled combinations of PVC Solvic 271 GC + Uracil + SPP + NPPD.

the two-roll milling process. The addition of 2phr of Borax to the formulation made impossible to mill it, since the additive never melted and, therefore, the formulation was not stabilized enough and stuck to the mill.

Details of the different samples are summarized in Table VII.

From the yellowness values obtained (Fig. 10), it can be inferred that the addition of 2phr of Borax (sample 2) provides excellent color control compared to the rest of the formulations. Although not shown here, the color strips presented small lumps due to the fact that Borax never melted completely during the mixing,

reducing its effect. Slightly higher values were obtained by SPP (sample 3), but its performance alone was nevertheless better than that of the mixture of the 3 costabilizers. This may indicate that the addition of high levels of Borax might be a breakthrough towards an excellent color control of the formulation, once the problems encountered during the milling are solved. This could be achieved by grinding the costabilizer before adding it into the mixture or by changing its grade. Pulverization is suggested as a more effective method as opposed to grinding. This method was already tried to overcome the problems during milling but all efforts proved unsuccessful.

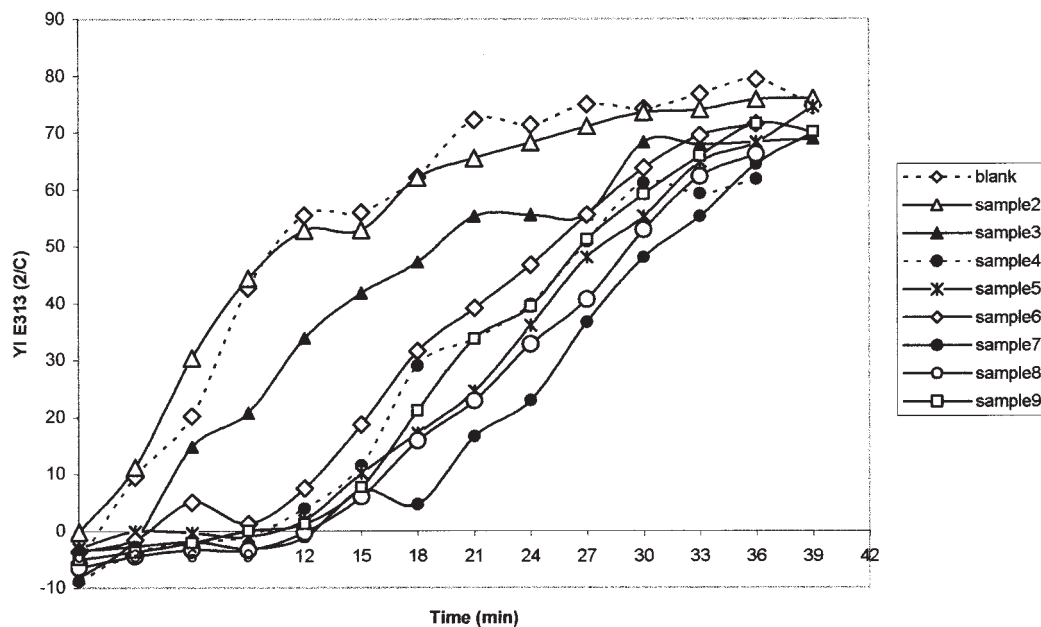


Figure 12 Yellowness values for spread sheet combinations of PVC Pevikon P14 + Uracil + SPP + NPPD.

PVC + Uracil + SPP + NPPD

Table VIII summarizes the index of formulations and levels of the costabilizers added for both milled and spread sheet formulations.

The yellowness values obtained for the milled samples (Fig. 11) indicated that the formulation that best controlled the discoloration in later stages was sample 5, which corresponded to the highest levels of the 3 costabilizers. It is worth noting that, initially, a better color control was provided by sample 8, but after the onset of the discoloration, sample 5 seemed to delay the blackening of the polymer. In later stages, it becomes quite clear that, due to fast chain propagation, all samples undergo a sudden blackening owing to the formation of conjugated polyene sequences. Notwithstanding this, the results obtained by sample 8 can be considered comparable to those of sample 5, bearing in mind that NPPD is at half the concentration and that the level of SPP is about a third lower.

Comparing their individual performances, Uracil seemed, again, to reduce discoloration more effectively than NPPD.

In the case of the spread sheet formulations (Fig. 12), the evolution of discoloration started earlier than in the milled combinations. Samples 7 and 8 achieved the lowest discoloration, although comparing the concentration of the costabilizers, sample 8 having half the concentration of NPPD, it seems to indicate a better color control, which confirms the results obtained for the milled formulation.

Model compound studies

With a view to elucidating the type of interactions that occur between PVC and SPP, a model compound for PVC was synthesized. This model was 4-chloro-2-hexene (4C2H), which simulates the in-chain allylic chlorine impurities present in PVC.

Since SPP is only soluble in water, the reaction was carried out in a mixture of H₂O/THF (1 : 3). In addition,

REACTION 2

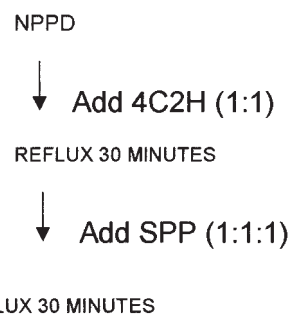


Figure 14 Flow chart of Reaction 2.

tion, the FTnmr analysis for the starting material was carried out in D₂O, whereas in the case of the reaction samples it was carried out in d₈-THF. The flow charts shown in Figures 13, 14, and 15 represent the three reactions carried out to assess the type of interactions that take place between SPP, NPPD, and the model compound. Since the results obtained in the second reaction failed to add any significant information, they won't be shown.

The ¹H-FTnmr spectrum of SPP (Fig. 16) in D₂O shows two singlets at 6.5 and 8.5ppm assigned to the -H and -OH protons, respectively. The peaks between 7 and 8ppm are attributed to the three kinds of protons in the aromatic ring. The same chemical shifts were observed for PPA (Fig. 17). In the case of the ³¹P spectrum of SPP (Fig. 18), two strong singlets are observed. This is attributed to the fact that being a hydrated salt, the acid form is also present. From comparison with the ³¹P spectrum of PPA (Fig. 19), the signal at 22ppm was assigned to the acid, whereas the signal at the lower chemical shift was attributed to the salt.

In reaction one, the addition of NPPD to a solution containing SPP did not result in any interaction occurring, according to the ¹H-FTnmr spectra, even after heat treatment (Figs. 20 and 21). On addition of 4C2H

REACTION 1

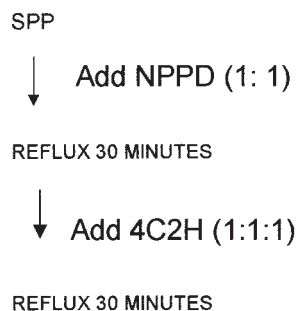


Figure 13 Flow chart of Reaction 1.

REACTION 3

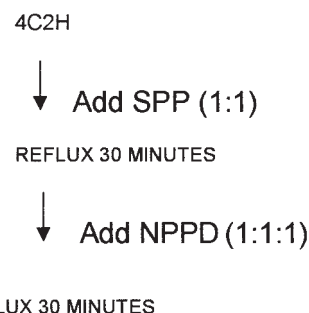


Figure 15 Flow chart of Reaction 3.

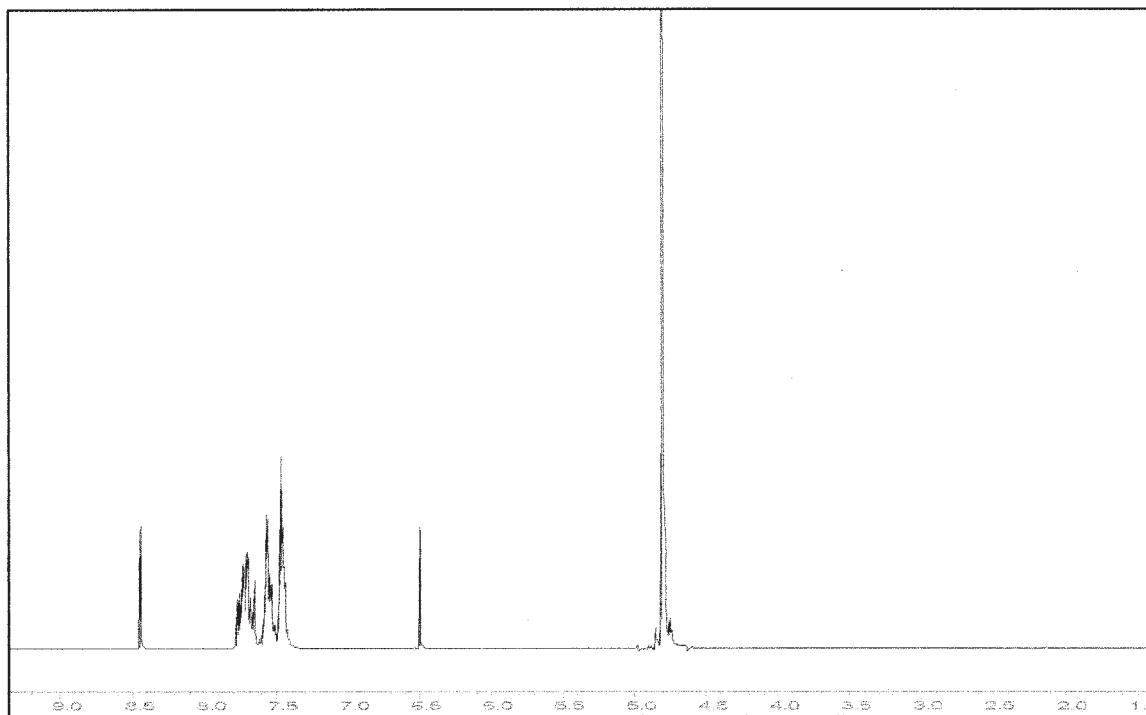


Figure 16 ^1H -FTNmr of SPP in D_2O .

(Figs. 22 and 23), there is the evolution of a new singlet at 7.95ppm. Since the peak due to the water overlaps with the peaks assigned to CHCl of $4\text{C}2\text{H}$, nothing conclusive can be inferred as far as the substitution of

the allylic chlorine is concerned. However, the strong coloration of the samples degraded in section 3 seemed to indicate that the mechanism by which SPP stabilizes PVC does not involve the interaction with

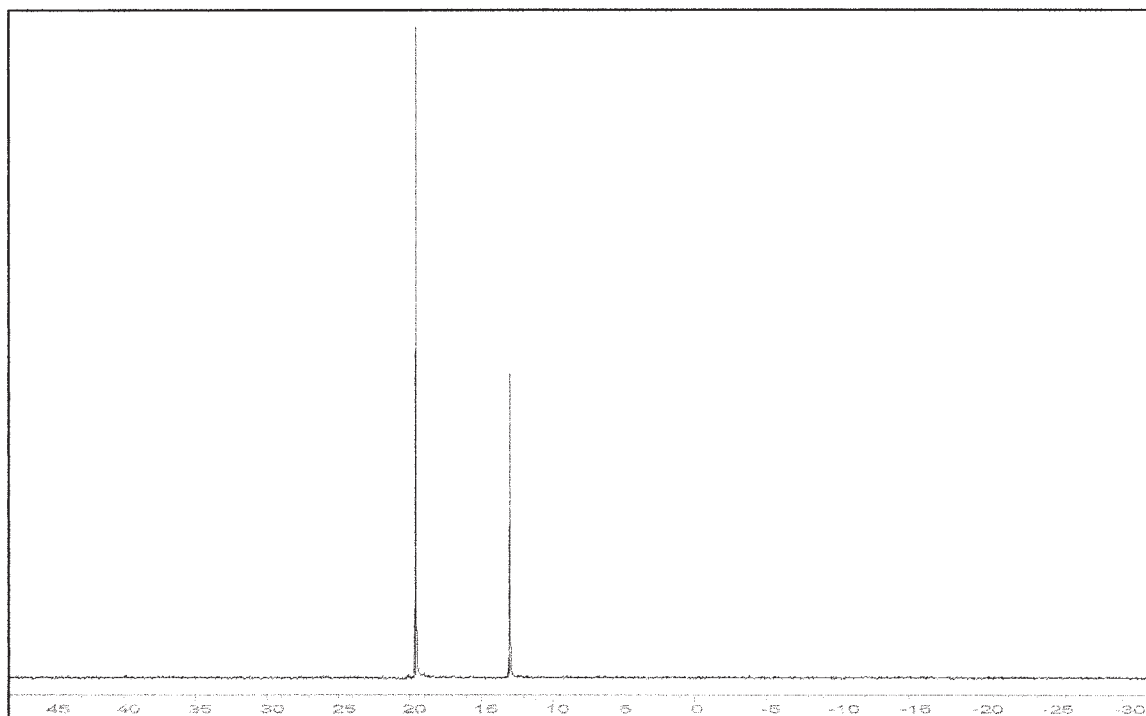


Figure 17 ^1H -FTNmr of PPA in D_2O .

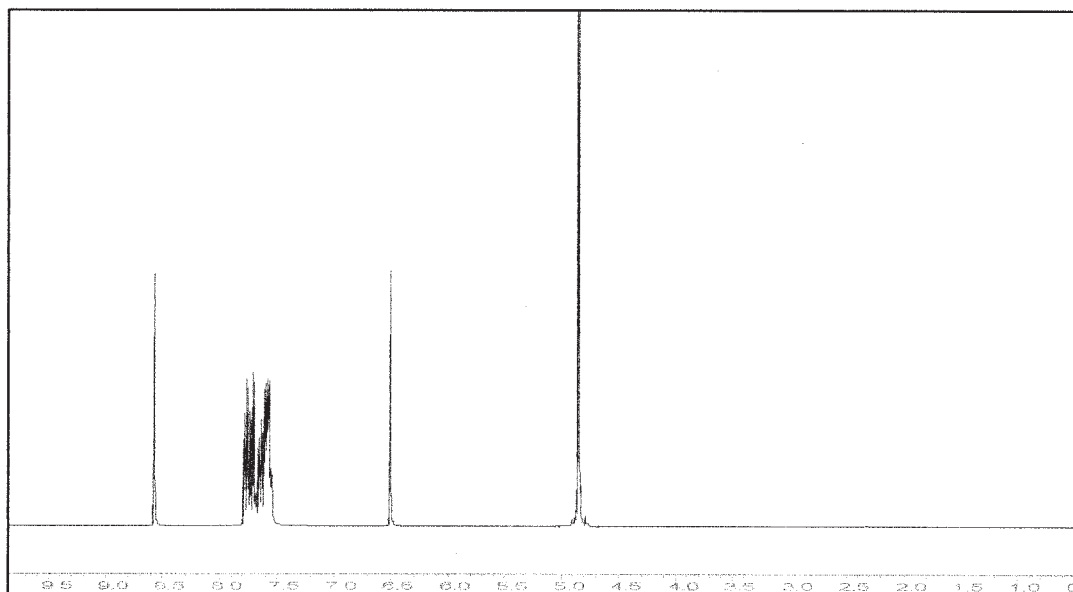


Figure 18 ^{31}P -FTNmr of SPP in D_2O .

the PVC chain. Certainly, the appearance of the band just below 8ppm can be attributed to the formation of the hydrolysis product. After refluxing, the peaks attributed to P-H and P-OH at 6.3ppm and 8.4ppm, respectively, become coupled. This seems to indicate that the H of OH can couple with the H and *vice versa*. However, the band at 7.9ppm remains a singlet. The peaks as-

signed to NPPD remained unchanged, which implies that there is no interaction between SPP and NPPD.

^{31}P -FTNmr spectra of the same samples were also carried out. In reaction one, the ^{31}P analysis in Figure 24 shows before heating two peaks at 14.74 and 13.72ppm, which are attributed to the acid and salt forms, respectively. Figure 25 shows similar bands

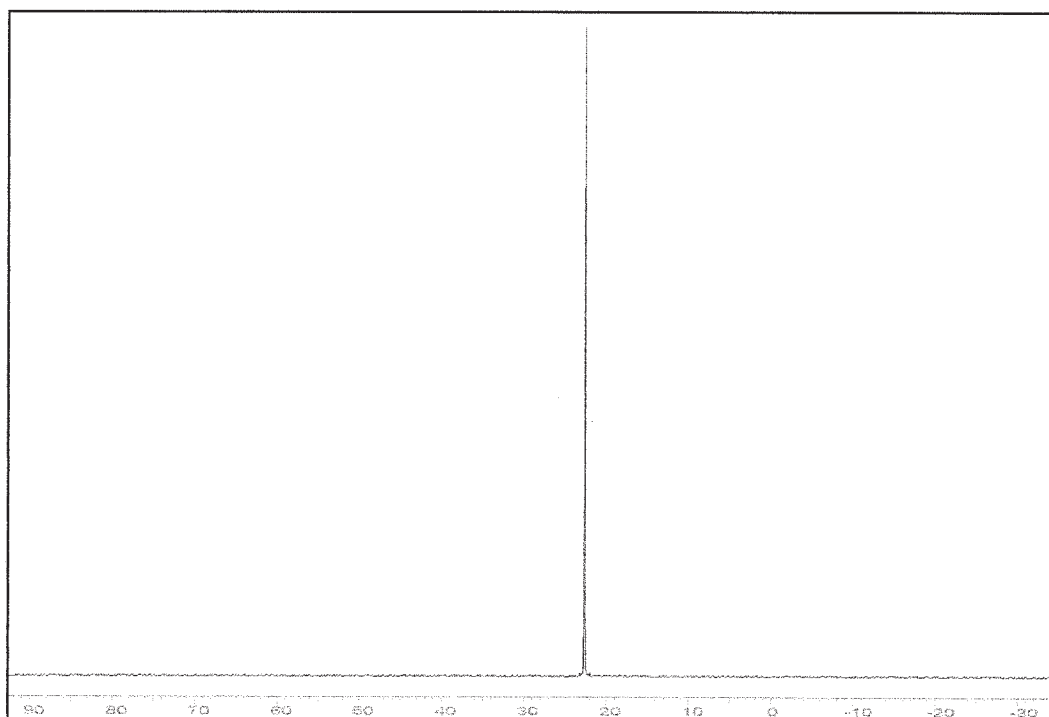


Figure 19 ^{31}P -FTNmr of PPA in D_2O .

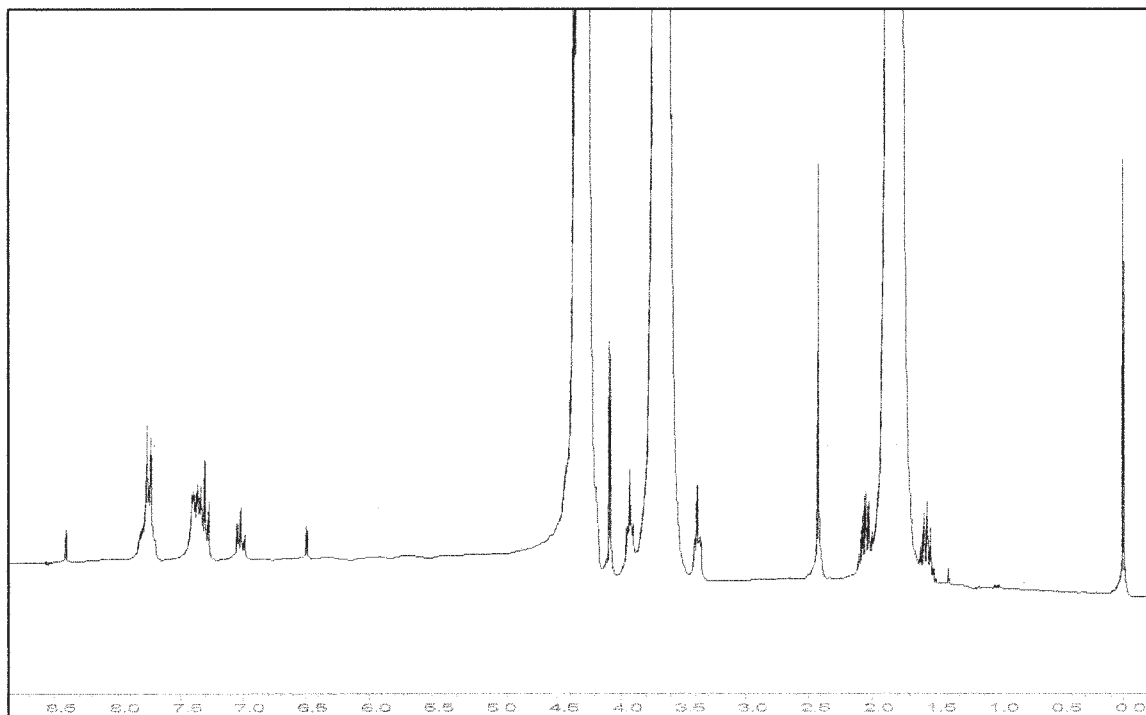


Figure 20 ^1H -FTNmr spectrum of sample SPP + NPPD before heating.

after heating, although at slightly lower chemical shifts. The differences among the spectra may be due to steric hindrance or electrostatic interaction between NPPD and SPP (as was suggested earlier), since the

solvent¹³ has a very small affect on ^{31}P chemical shift values. On addition of the model compound (Figs. 26 and 27), two new species seem to evolve at lower chemical shifts. The presence of the starting material seems to

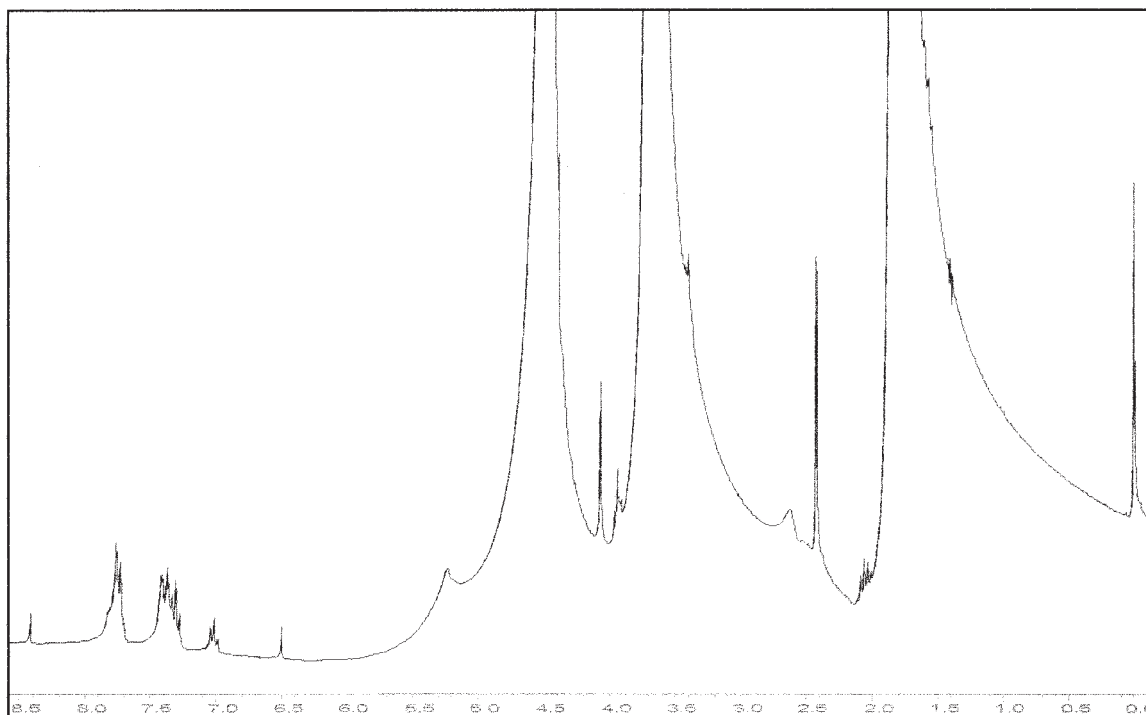


Figure 21 ^1H -FTNmr spectrum of sample SPP + NPPD after heating.

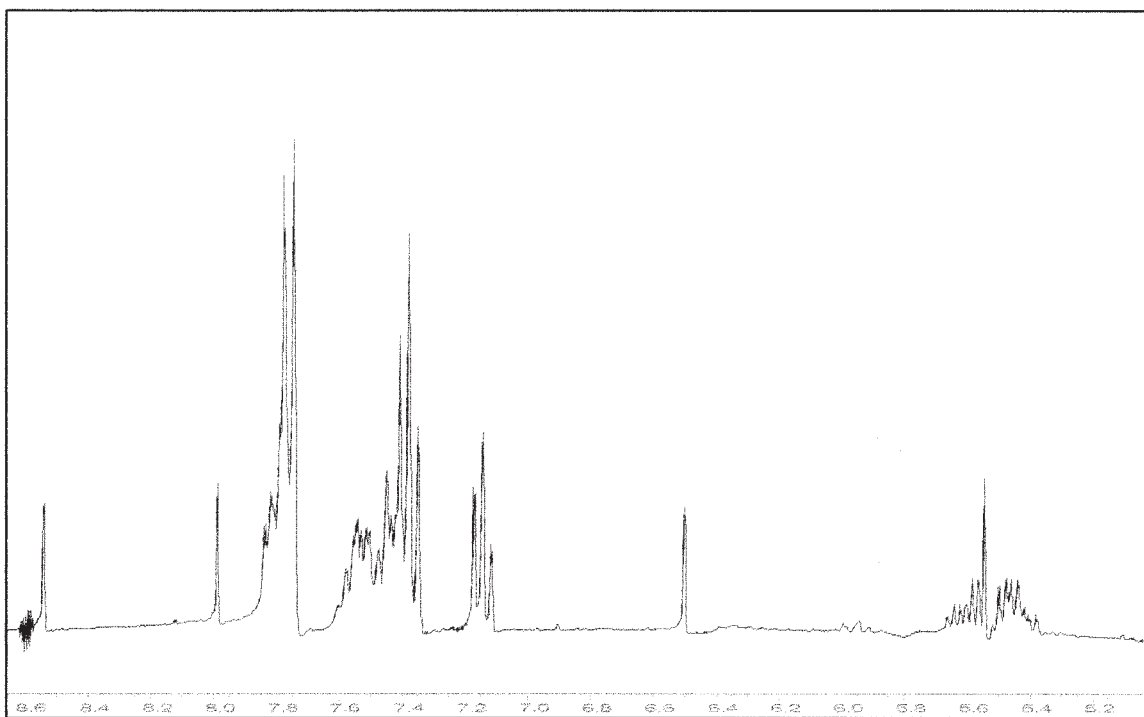


Figure 22 ^1H -FTNmr spectrum of sample SPP + NPPD + 4C2H before heating.

imply that although two new species are formed, the conversion is not total and there is a mixture of SPP and the corresponding acid is still unreacted.

In reaction three, the addition of SPP to a solution containing 4C2H led to the evolution of a singlet be-

low 8ppm (Fig. 28), which was attributed to the hydrolyzed product. There is an indication of bands due to CHCl at around 4ppm, which imply that there is no substitution of the allylic chlorine by SPP. No changes were observed after the refluxing (Fig. 29), and no other

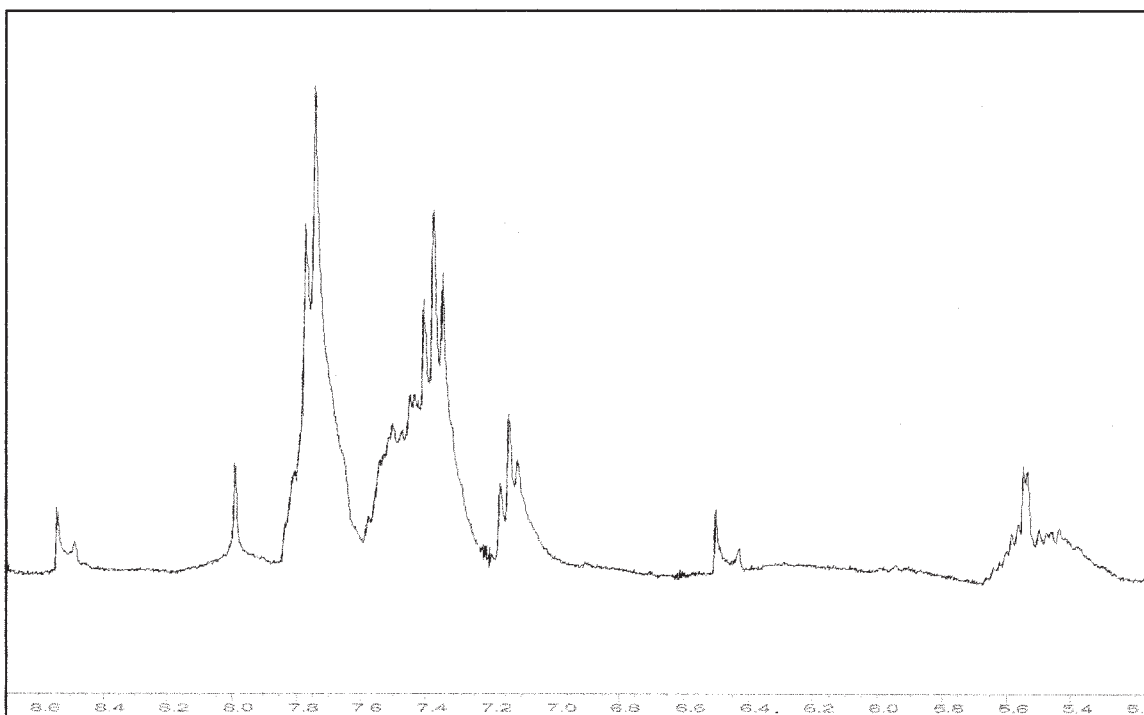


Figure 23 ^1H -FTNmr spectrum of sample SPP + NPPD + 4C2H after heating.

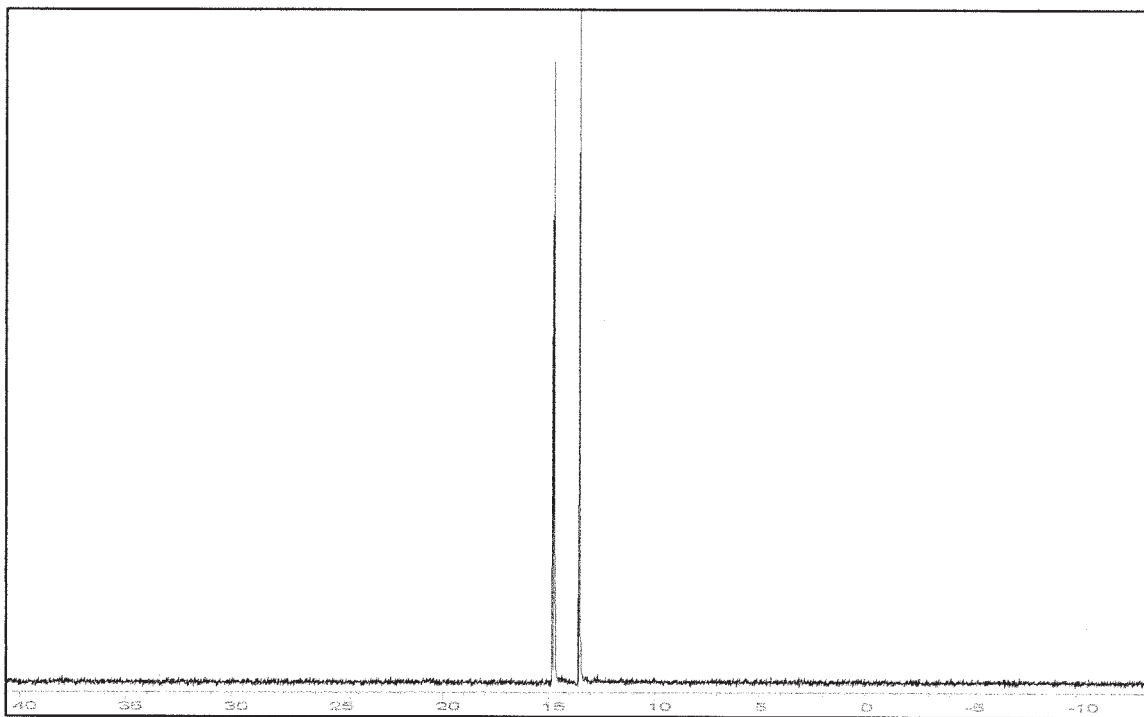


Figure 24 ^{31}P -FTNmr spectrum of sample SPP + NPPD before heating.

interactions were observed after the addition of NPPD (Figs. 30 and 31).

The ^{31}P analysis for reaction three shows that the addition of SPP to the model compound resulted in

the appearance of four peaks, with chemical shifts very similar to those shown in reaction one (Fig. 32). The first two signals were assigned to the acid and salt forms of SPP, respectively, and the signals at lower

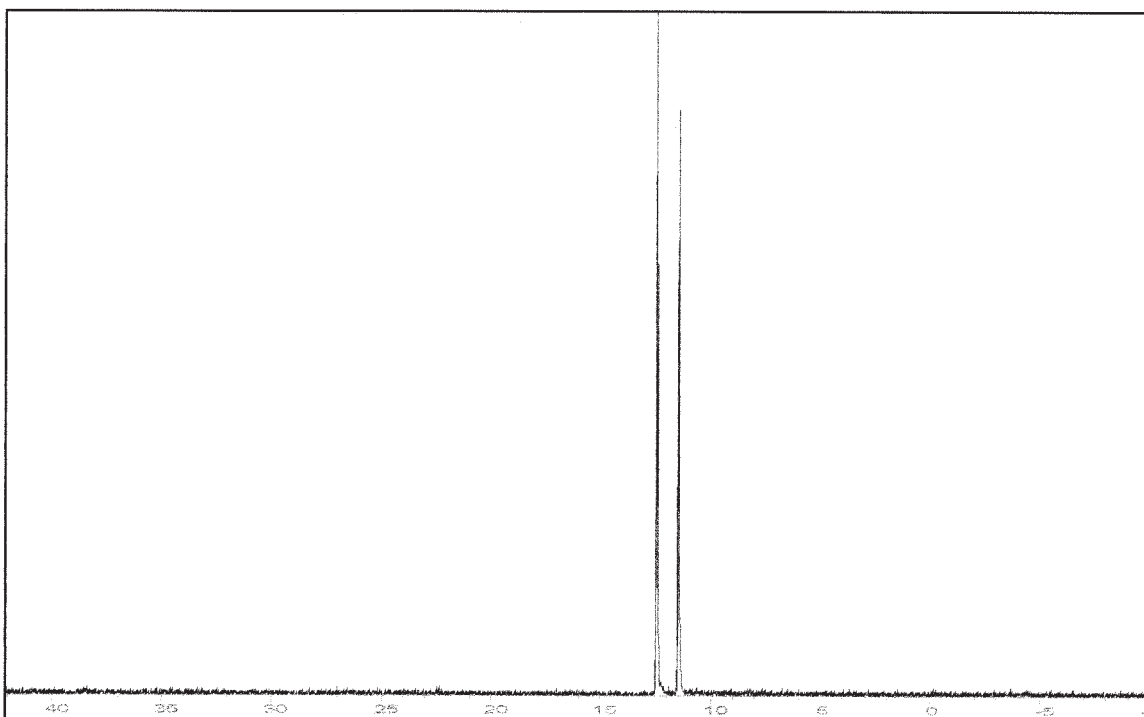


Figure 25 ^{31}P -FTNmr spectrum of sample SPP + NPPD after heating.

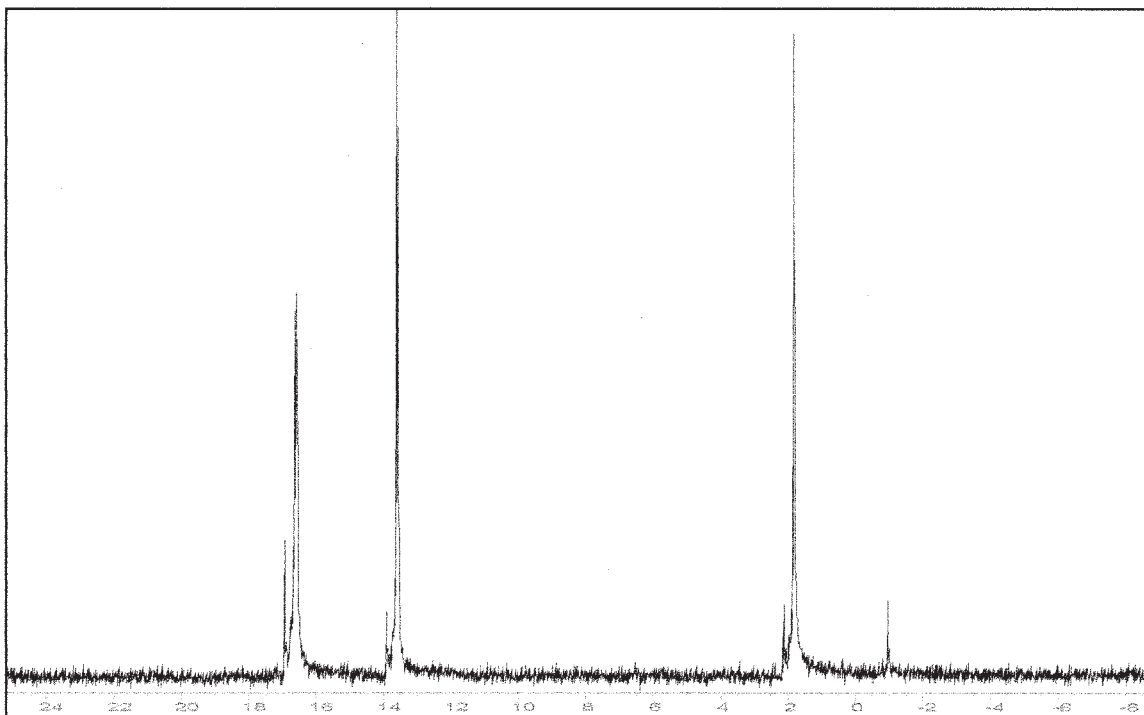


Figure 26 ^{31}P -FTNmr spectrum of sample SPP + NPPD + 4C₂H before heating.

chemical shifts were attributed to two new different species formed. Since from the ^1H -FTNmr spectra, no evidence for the interaction with the model compound was observed, the formation of two new species can

be associated to the reaction of HCl with SPP. After refluxing (Fig. 33), coupling between P-H could be observed. On addition of NPPD (Figs. 34 and 35), the chemical shifts of the two newly formed species seem

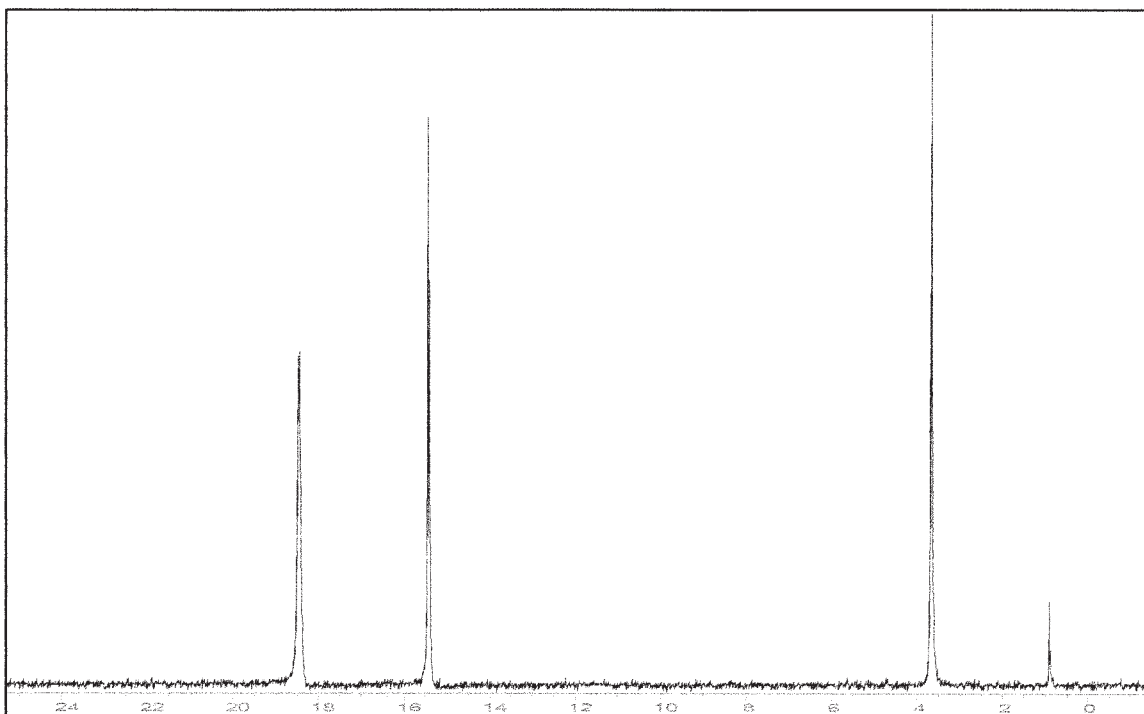


Figure 27 ^{31}P -FTNmr spectrum of sample SPP + NPPD + 4C₂H after heating.

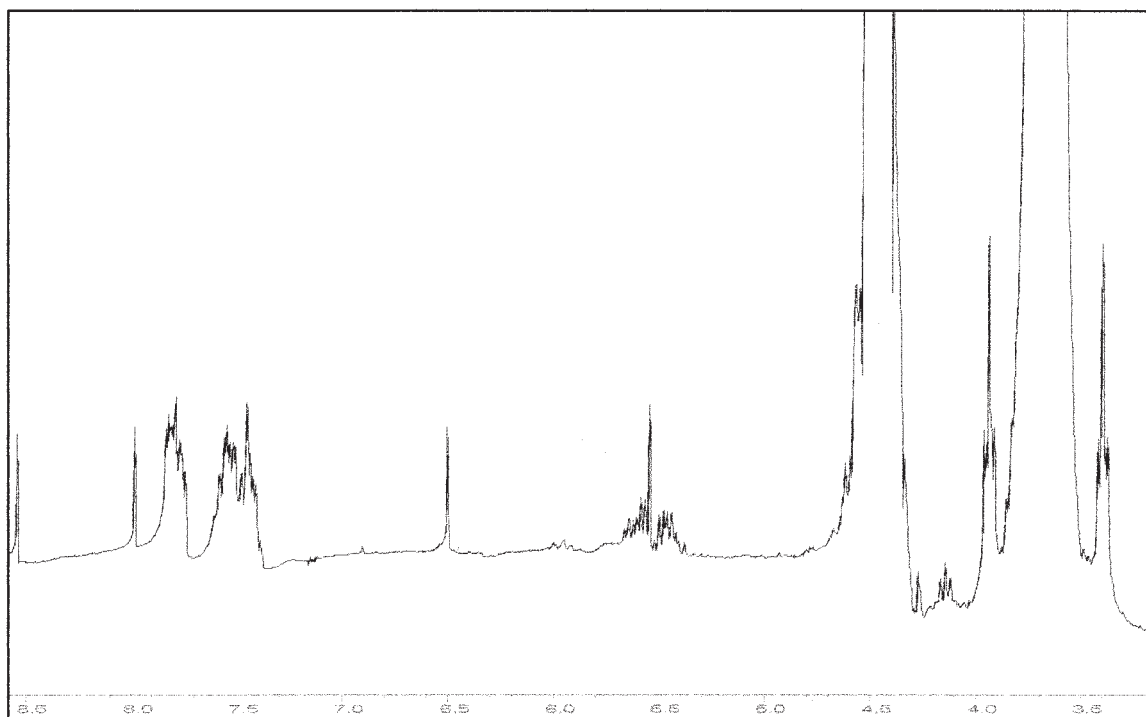


Figure 28 ^1H -FTNmr spectrum of sample 4C2H + SPP before heating.

slightly shifted towards higher values, which could be caused by an electrostatic interaction taking place through the $-\text{OH}$ groups.

Therefore, the results shown above indicate that SPP does not interact with NPPD under the present conditions. However, the addition of the model

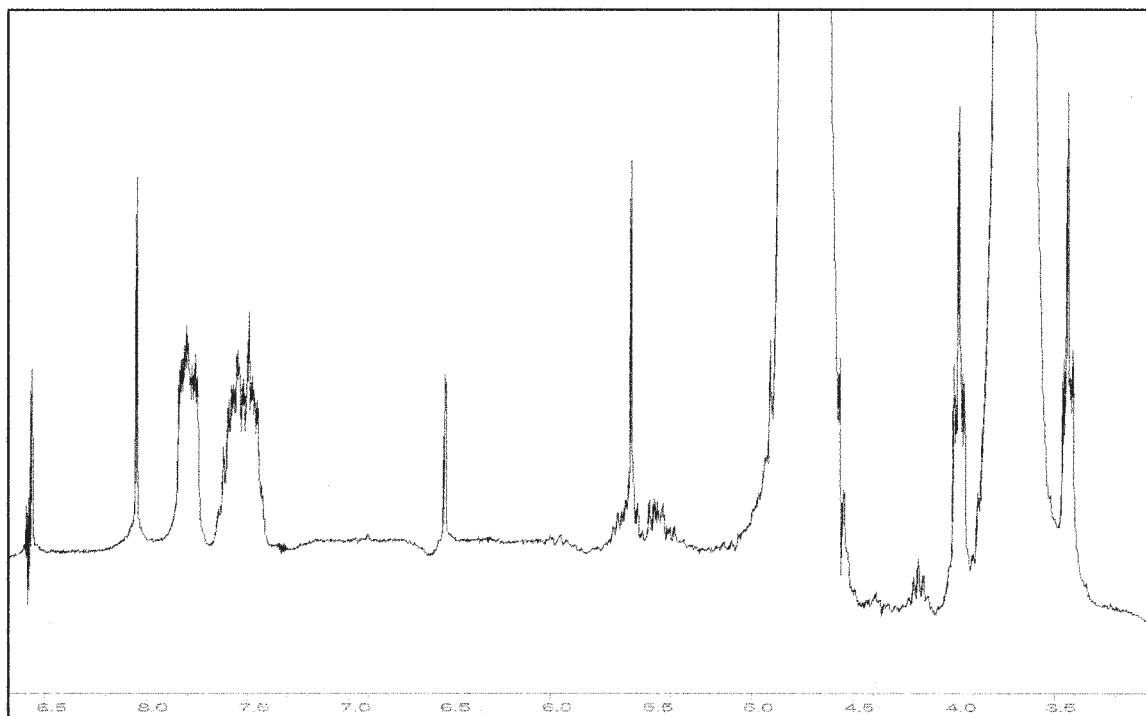


Figure 29 ^1H -FTNmr spectrum of sample 4C2H + SPP after heating.

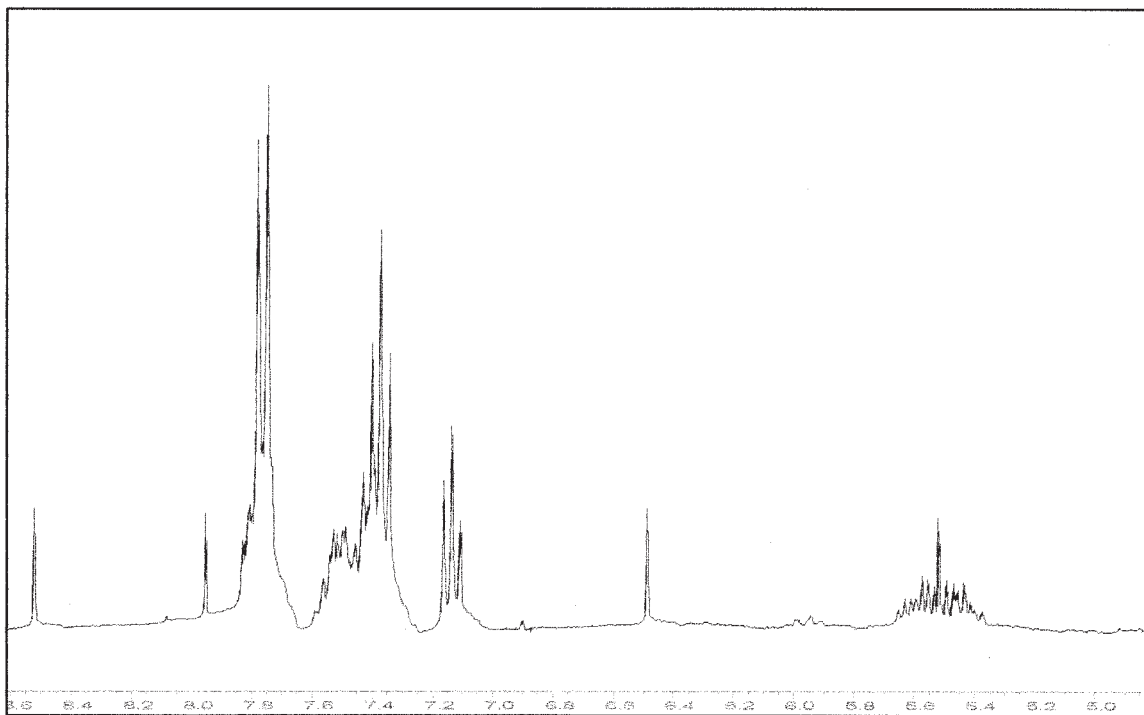


Figure 30 ^1H -FTNmr spectrum of sample 4C2H + SPP + NPPD before heating.

compound leads, on the one hand, to the evolution of a singlet below 8ppm in ^1H -FTNmr and to the associated formation of 2 new species, as was ob-

served in the ^{31}P . Since there is no evidence to suggest that the interaction with the model compound occurs, the changes observed may be attrib-

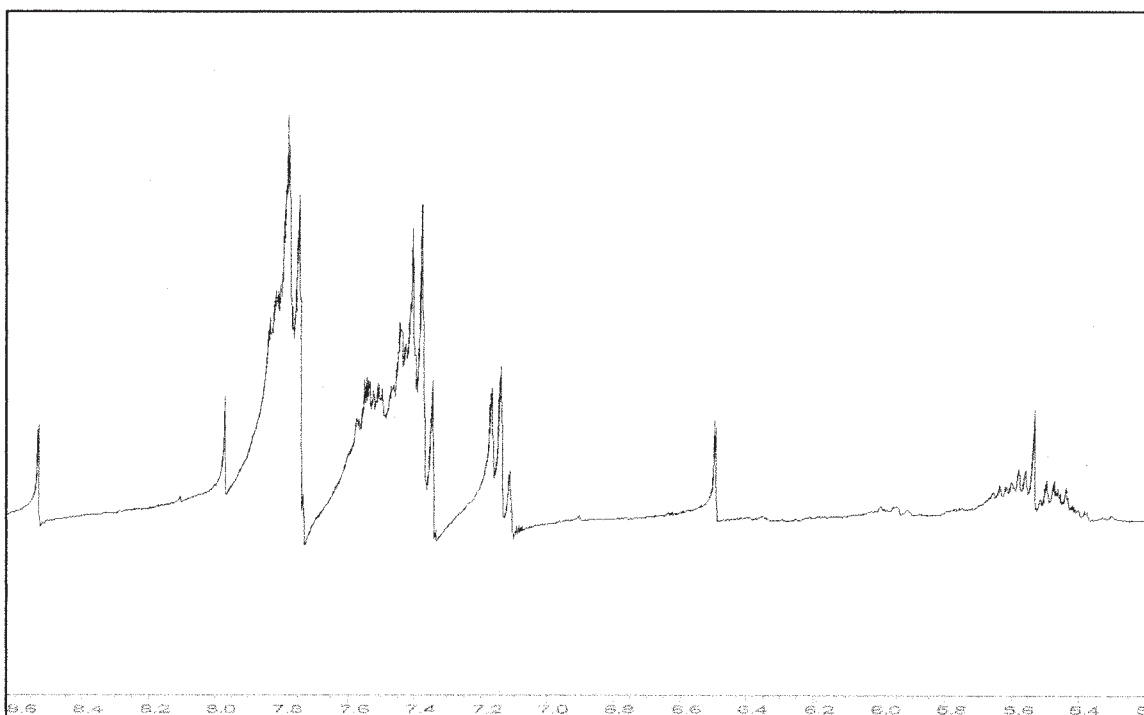


Figure 31 ^1H -FTNmr spectrum of sample 4C2H + SPP + NPPD after heating.

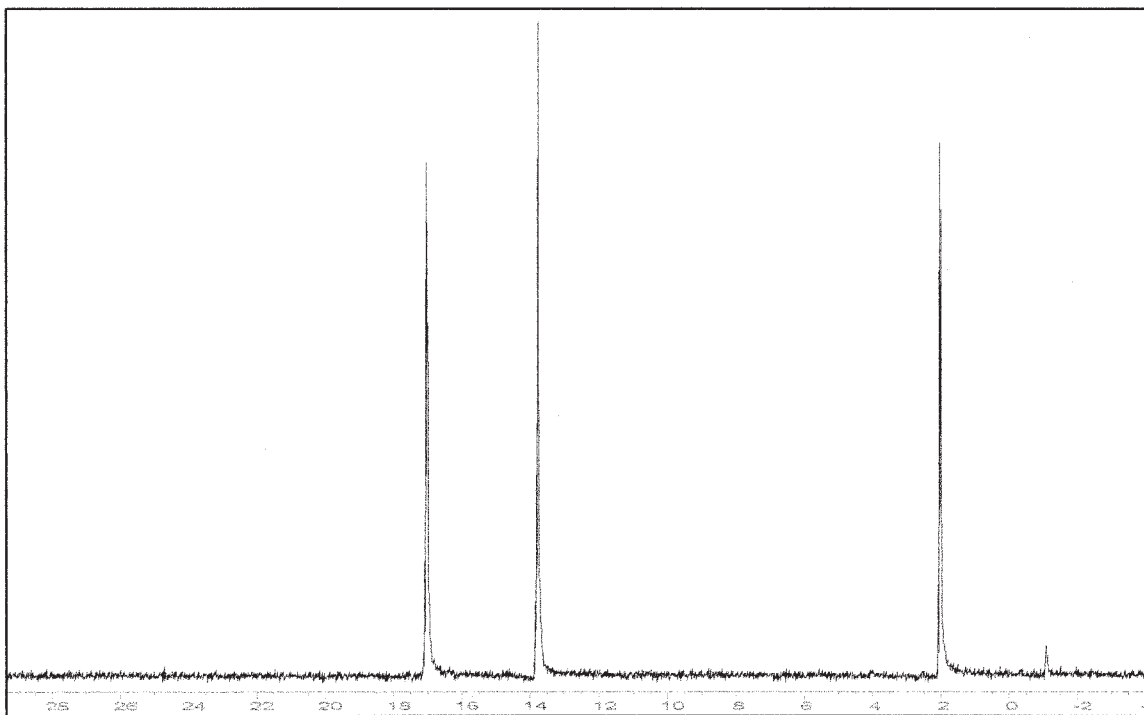


Figure 32 ^{31}P -FTNmr spectrum of sample 4C2H + SPP before heating.

uted to the interaction with HCl. Scheme 2 is an attempt to correlate the FTNmr signals with the species formed.

In the first step, $-\text{OH}$ being a good leaving group, the nucleophilic attack by the chlorine takes place to form the monochlorinated species. Evidence to sug-

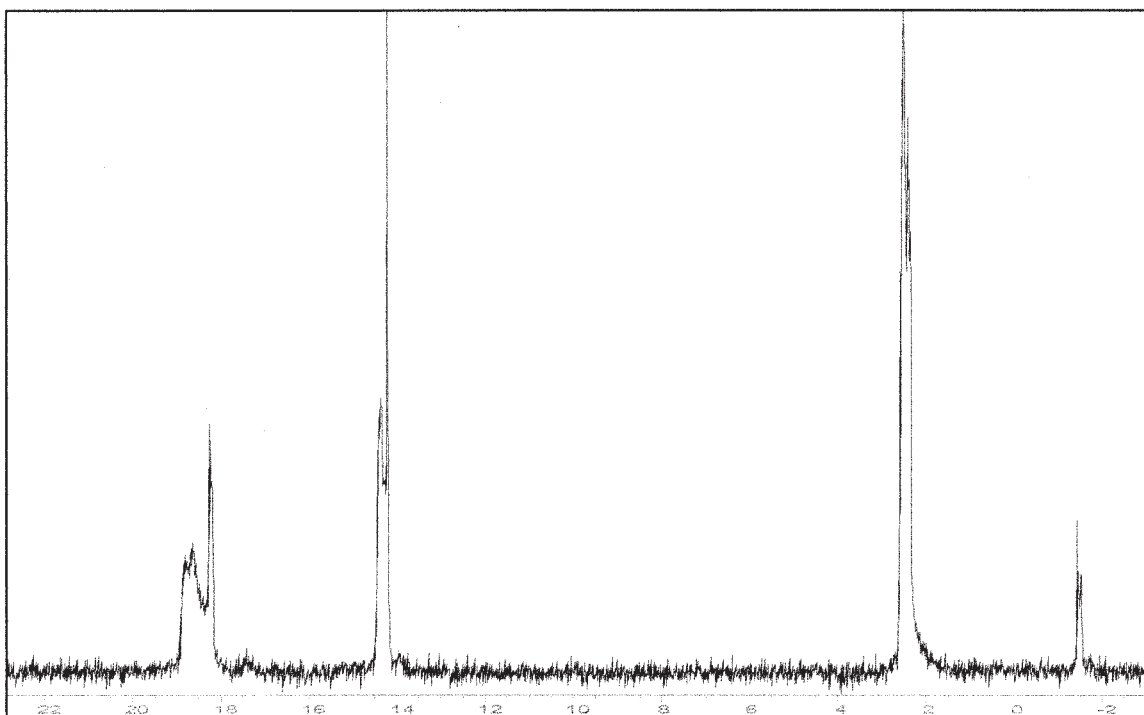


Figure 33 ^{31}P -FTNmr spectrum of sample 4C2H + SPP after heating.

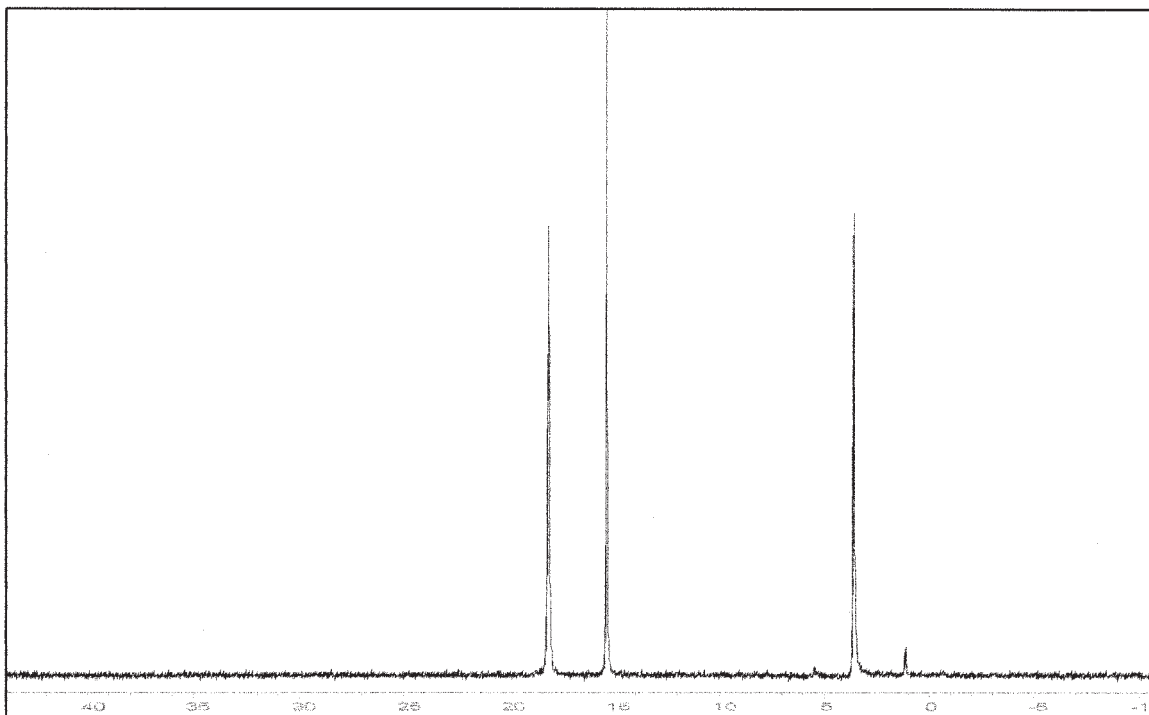


Figure 34 ^{31}P -FTNmr spectrum of sample 4C2H + SPP + NPPD before heating.

gest the formation of this structure comes from the ^{31}P spectra, with a signal based at 2ppm. Since the P-Cl bond is very weak, this leads to the hydrolysis of the

product. In addition, under acid-catalyzed conditions, the P-C bond of phenyl can be broken (step b). This hydrolysis product is shown by the appearance of the

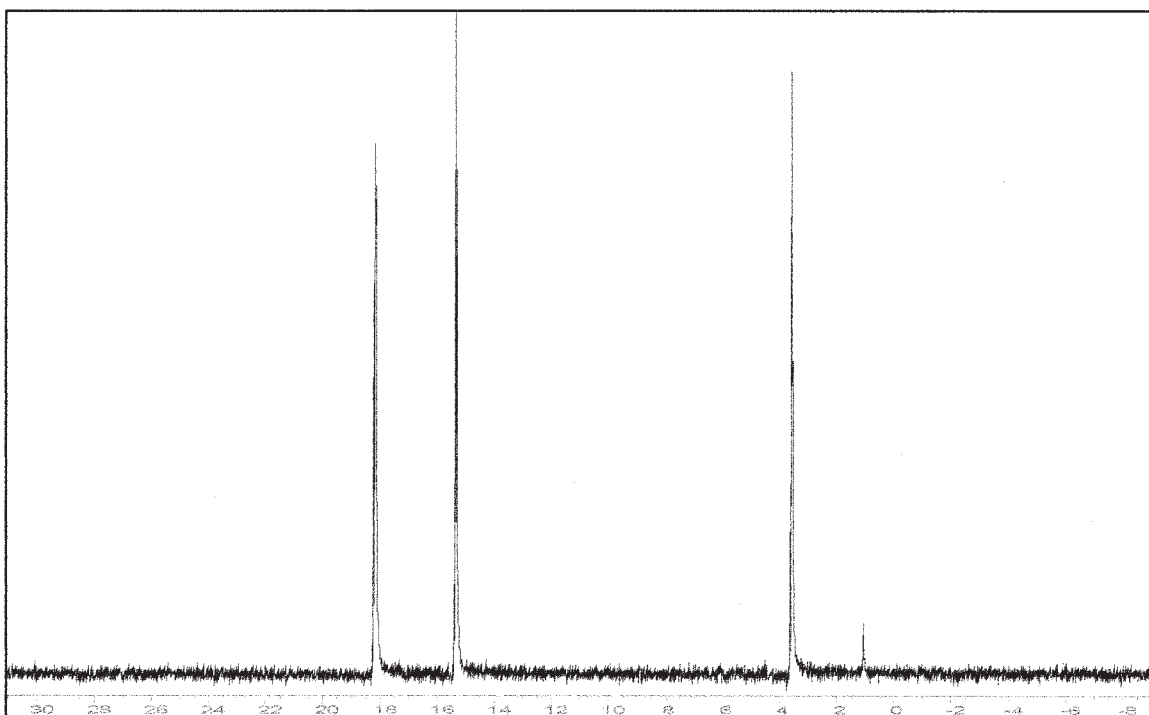
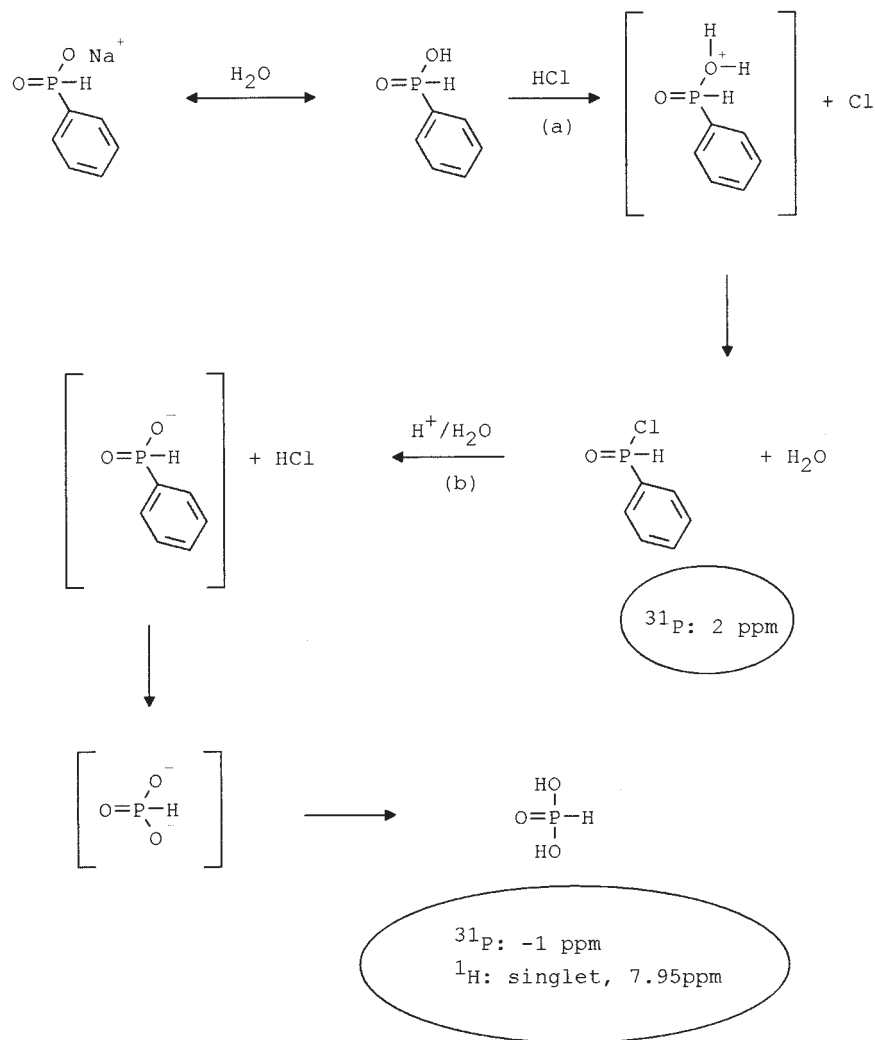


Figure 35 ^{31}P -FTNmr spectrum of sample 4C2H + SPP + NPPD after heating.



Scheme 2 Hydrolysis of SPP in HCl catalyzed conditions.

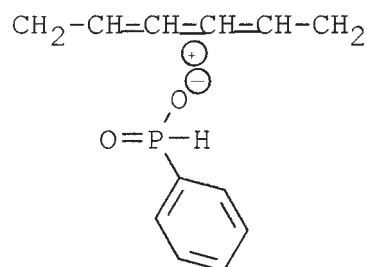
singlet below 8ppm in the ^1H -FTNmr spectra and the signal based at -1ppm in the ^{31}P -FTNmr. The singlet at 8ppm is due to the formation of a new -OH group.

Moreover, since the H is not a good leaving group, it is unlikely that any changes take place through this atom, especially in tetracoordinated phosphorous compounds. This implies that SPP cannot act as a peroxide decomposer in the conventional sense. Therefore, the great extension in the stability length observed in PVC formulations implies that it must be inhibiting chain propagation and it may do this by stabilizing the carbocation generated during the dehydrochlorination process (Scheme 3), along with its acid scavenging activity (Scheme 4).

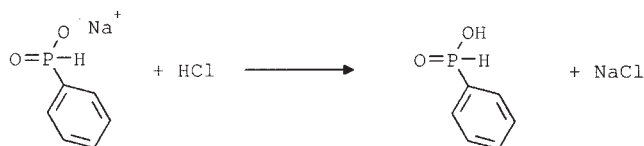
CONCLUSIONS

This paper deals with the possible implementation of Heavy Metal Free Systems (HMFS) due to the addition

of different costabilizers (i.e., 6-amino-1,3 dimethyluracil (Uracil), sodium tetraborate (Borax), sodium phenyl phosphinate (SPP), and NPPD (*N*-phenyl-3-acetylpyrrolidin-2,4-dione), and their combinations) to PVC. The experimental design carried out with a view to optimizing the levels of the costabilizers in terms of dehydrochlorination revealed that a formulation con-



Scheme 3 Stabilization of the carbocation by SPP.



Scheme 4 Scheme 4. HCl scavenging by SPP.

taining Uracil + SPP + NPPD could extend the induction time up to 50 min. Moreover, an induction time of more than 80 min could be obtained with the combination of the costabilizers Borax + SPP + NPPD. In terms of color, the addition of 2phr of Borax to the formulation showed an excellent color control, overshadowing even a mixture of the three costabilizers at their highest levels (Borax + SPP + NPPD). For a formulation containing Uracil + SPP + NPPD, the best results were obtained by the combination of the highest levels of the three costabilizers. SPP showed an outstanding performance in controlling the HCl evolution. However, its poor color control stability implied that, rather than acting as a peroxide decomposer as previously thought, it must be inhibiting chain propagation and it may do this by stabilizing the carbocation generated during the dehydrochlorination process.

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