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Modification of Lignins. III. Reaction of Lignosulfonates with Chlorophosphazenes*

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ABSTRACT

A new trend in flame- and heat-resistant polymers is the modification of organic by-products such as lignins. Here we continue a discussion of lignin modification; in particular, the reaction of lignosulfonates with chlorophosphazenes. The reactivity of Borregaard-type lignosulfonates toward chlorophosphazenes was studied. The properties of the products obtained, especially their flame and heat resistance, as well as SEM data, were investigated.

INTRODUCTION

Research interests have turned more and more to residues from native products manufacture, especially their polymeric forms [1-3]. A new trend in flame- and/or heat-resistant polymers is concerned with modification of organic by-products by chlorophosphazenes; among the substrates are polyaminosaccharides, lignins, and cellulose [4-8].

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In earlier papers [4, 5] we paid attention to the reaction of kraft lignin and Rauma-Repola experimental lignosulfonate with chlorophosphazenes and the properties of the product.

It is generally accepted that lignosulfonates manufactured as the residues from different wood raw materials as well as by diverse technologies differ in their properties and also in reactivity [1].

In this study the reaction of high-purity Borregaard-type lignosulfonates with chlorophosphazenes is investigated. The reactivity of these lignosulfonates toward chlorophosphazenes and the properties of products obtained, especially flame and thermal resistance, as well as SEM data, are discussed. The resulting flame- and heat-resistant products might find use by themselves or as additives or fillers for standard polymers.

EXPERIMENTAL

Materials

Commercial lignosulfonates "Borresperse" NA and "Ultrazine" NAS, donated by Borregaard Inc. Norway, characterized by the properties presented in Table 1, were used in the investigations.

Mixtures of cyclic oligomers of chlorophosphazenes [9] (mp 87-91°C, IR P=N 1 295 cm^{-1}, 1 218 cm^{-1}, ^{31}P-NMR -19.57, +6.86) were used for reaction with lignosulfonates. Reagent-grade dioxane was used as the inert dispersion medium. Reagent-grade diethylamine (n_D^{20} = 1.3860) was used for modification of the standard products.

Methods of Reaction of Lignosulfonates with Chlorophosphazenes

Modification of lignosulfonates by chlorophosphazenes was carried out according to Method A_2 of the previously described system [4].

Sodium lignosulfonate of Borregaard (1.0 g) was dispersed in dioxane (100 mL), and a corresponding amount of pyridine was introduced as a hydrogen chloride acceptor. Chlorophosphazenes dissolved in dioxane (25 mL) were added dropwise at 80°C during continuous agitation for 15 min. The mixture was allowed to react at the boiling point for a suitable time. The reaction mixture was then poured into ice water. The solid product was washed several times in dioxane and water and centrifuged at 66.6 rps for 15 min. The residual products were dried at 60°C under reduced pressure.

The reaction conditions used in these investigations are shown in Table 2.

TABLE 1. Physicochemical Properties of Lignosulfonates Used

Type of lignosulfonate	Form and color	Moisture, %	Analysis, %			Total hydroxyl group content, %	Phenol group content, %	Intrinsic viscosity, mL/g
			C	H	S			
Borresperse NA	Brown powder	5.1	56.0	4.20	4.09	14.9	3.69	5.0
Ultrazine NAS	Light brown powder	5.0	40.5	4.52	2.60	15.1	4.18	12.2

TABLE 2. Conditions of Lignosulfonate Modification by Chlorophosphazenes[a]

Sample	Time of reaction, h	Type of Lignosulfonate[b]	Type of Chlorophosphazene	Amount of Chlorphosphazene, mmol	Amount of Pyridine, mmol
1	9	NA	Mixture	4.292	9.696
2	9	NA	Mixture	12.160	7.492
3	3	NAS	Mixture	6.085	13.746
4	9	NAS	Mixture	6.085	13.746
5	3	NAS	Mixture	12.160	27.492
6	9	NAS	Mixture	12.160	27.492

[a] All reactions were carried out on lignosulfonate (1.0 g).

[b] NA, Borresperse NA; NAS, Ultrazine NAS.

Modification of the Lignosulfonate-Chlorophosphazene Reaction Product

Lignosulfonate (1.0 g) was dissolved in dioxane (100 mL) and pyridine (2.23 mL, 27.5 mmol) was introduced.

Chlorophosphazene oligomers (1.41 g, 12.16 mmol) dissolved in dioxane (25 mL) were added during continuous agitation at 80°C for 9 h. The reaction mixture was cooled to 60°C and diethylamine (15.05 mL, 0.145 mol) dissolved in dioxane (25 mL) was added dropwise at 60°C for 15 min. The mixture was allowed to react at 60°C for 3 h. The solid reaction product was washed several times in dioxane and water to obtain a neutral reaction. It was centrifuged at 66.6 rps for 15 min. The residual product was dried at 60°C under reduced pressure.

The analytical methods used to obtain product properties were the same as reported previously [4, 5].

The hydrogen bond energy (E_H) of the phosphazenylated lignosulfonates as well as lignin raw materials was examined by infrared [10, 11]. This parameter was calculated according to

$$E_H = \frac{1}{K}\frac{\nu_0 - \nu}{\nu_0},$$

where ν_0 = the standard frequency corresponding to the vibration of free OH groups (3650 cm^{-1})
ν = the frequency corresponding to the vibration of bound OH groups
K = a constant equal to 1.6×10^{-2} $kcal^{-1}$

Differential thermal analyses (DTA) were done with a Derivatograph of Type OD-102 (MOM, Hungary), with 100 mg samples in the temperature range 20-600°C and at a heating rate of 10°C/min. Differential thermogravimetry (DTG) and thermogravimetry (TG) were done with a Du Pont thermal analyzer of Type 990 with 10 mg of samples in air. The weight of samples was recorded against temperature in the range of 20-600°C at a heating rate of 10°C/min. The appearance of sodium lignosulfonates raw materials and products was studied by scanning electron microscopy. SEM microphotographs were produced on a scanning electron microscope of the Jeol M50A type at a magnification of 1 000×.

RESULTS AND DISCUSSION

Modification of various types of lignosulfonates by chlorophosphazenes allows manufacture of products characterized by 1) different

TABLE 3. Properties of the Products of Reaction between Lignosulfonates of the Borregaard Type and Chlorophosphazenes

Sample	Type of lignosulfonate	Color of solid product	Yield of product,[a] g	Analysis, %			Infrared frequency of units, cm^{-1}	
				P	S	Cl	P=N	P–O–C
1	Borresperse NA	Brown	0.015	2.80	4.50	2.15	1210	1165,[b] 1040
2	Borresperse NA	Dark brown	0.185	5.90	3.90	1.46	1210	1170, 1050
3	Ultrazine NAS	Dark brown	0.038	3.86	2.60	1.10	1200	1170, 1045
4	Ultrazine NAS	Dark brown	0.300	4.25	4.54	2.60	1250, 1195	1165, 1045
5	Ultrazine NAS	Black	0.192	8.76	3.43	1.31	1250, 1200	1160, 1025
6	Ultrazine NAS	Black	0.500	6.40	3.58	1.62	1255, 1210	1140, 1030
-	Borresperse NA	Brown	-	-	4.09	-	-	-
-	Ultrazine NAS	Light brown	-	-	2.60	-	-	-

[a] All reactions were carried out on sodium lignosulfonate (1.0 g).

[b] Slight.

properties in practical application; and 2) flame and thermal resistance due to the lignin-phosphazene polymer structure as well as to the flame-retardant elements content, such as phosphorus, nitrogen, and sulfur.

Table 3 shows the effect of reaction conditions on the resulting properties. As the concentration of chlorophosphazenes and the reaction time increase, the yield of products as well as their phosphorus content tends to grow. Lower chlorine concentration in the products, indicating incomplete substitution of chlorine in the phosphazene rings, changed with increasing chlorophosphazene content as well as with longer reaction time. Modification by diethylamine (Table 4) reduced chlorine content in the products and improved their useful properties (Fig. 1).

The products formed by the discussed reaction are not as soluble in typical solvents as the previously described products [4]. This seems to confirm the crosslinked structure of ligninlike modified

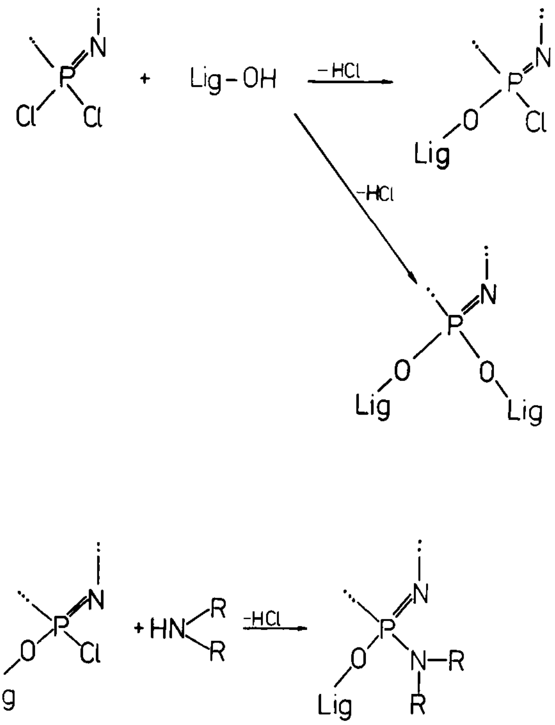

FIG. 1. Assumed course of reaction between lignins and chlorophosphazenes.

TABLE 4. Properties of the Modified Lignosulfonate-Chlorophosphazene Reaction Products[a]

Sample	Type of lignin	Symbol of initial product	Modifier	Yield of solid product,[b] g	Analysis, %			Infrared frequency of units, cm^{-1}		
					P	S	Cl	P=N	P–O–C	P–N–C
7	Borresperse NA	2	Diethylamine	0.142	4.10	4.73	0.65	1240, 1220	1155, 1030	930
8	Ultrazine NAS	6	Diethylamine	0.650	3.35	4.73	0.88	1265, 1225	1150, 1025	930

[a] All products were dark brown.

[b] All reactions were carried out on sodium lignosulfonate (1.0 g).

TABLE 5. Hydrolytic Resistance of the Lignosulfonate-Chlorophosphazene Reaction Products[a]

Sample	Type of lignosulfonate	KOH consumed, mg/g reaction product
2	Borresperse NA	80.0
3	Ultrazine NAS	70.0
8	Ultrazine NAS	50.0
NA	-	85.0
NAS	-	85.0

[a] Hydrolysis for 24 h at 50°C in 0.4 N KOH solution.

products. In comparison to other lignosulfonates [4], the Borregaard type seems to be more useful for reaction with chlorophosphazenes (Table 3). One improvement of the studied lignosulfonates, in comparison to Ultra B002 [4], is increased phosphorus content in the modified products. Moreover, the reactivity of Ultrazine NAS toward chlorophosphazenes is distinctly greater than that of Borresperse NA. This is probably related to the structure of the lignosulfonate and its susceptibility to reaction with chlorophosphazenes. It may be that the yield of products obtained from the lignosulfonate base made by both producers is lower than for kraft lignin.

Table 5 contains hydrolytic resistance data. Based on these results, it can be concluded that the present products have roughly the same base resistance, which corresponds to that for the Ultra B002 [4] or lignin raw materials. At the same time, a product modified by diethylamine (No. 8) is characterized by greater hydrolytic resistance, derived undoubtedly from its structure. Analogous results were obtained for acid resistance. No difference was observed between the acid-resistance parameter of the raw materials and the products derived from them.

Table 6 shows a summary of semiquantitative tests of fire resistance. The results do not differ from the results for other lignin-chlorophosphazene polymers. The modificates are flame resistant and do not glow completely, whereas lignosulfonate raw materials glow very fast under these conditions.

Interesting results were obtained from scanning electron microscope studies (Figs. 2-5). The appearance of lignosulfonates (Figs. 2 and 3) presented at 1 000× showed the characteristic cylindrical shape of these raw materials. The SEM photographs of lignosulfonate-phosphazene polymers showed nonregular particles with smaller dimensions but with porous surfaces compared to the raw materials (Figs. 4 and 5).

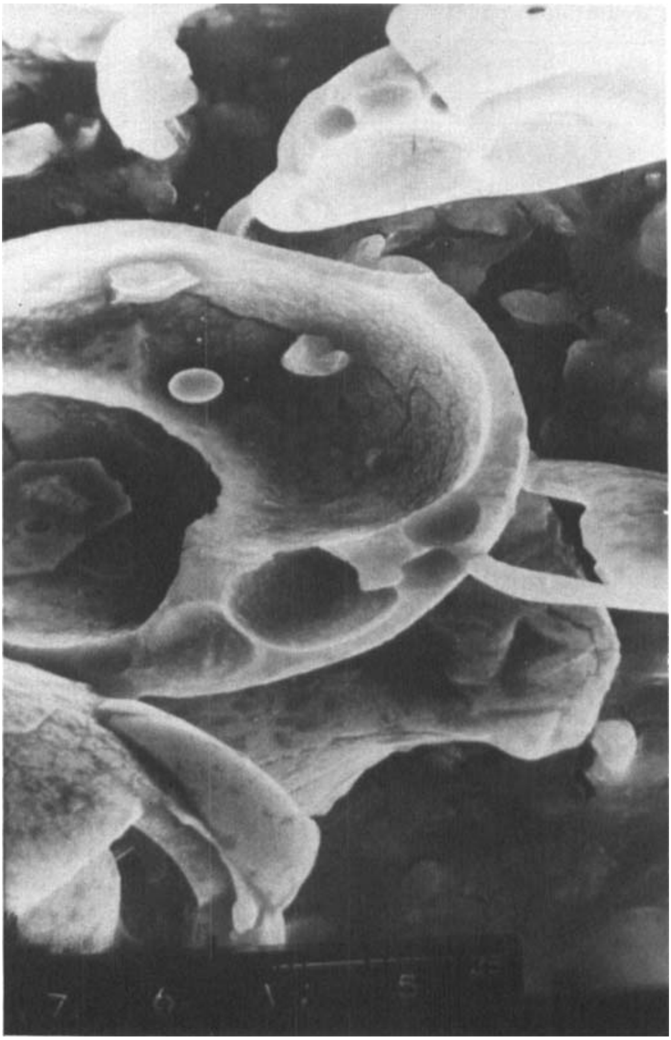

FIG. 2. SEM photograph (1 000×) of Borresperse NA lignosulfonate.

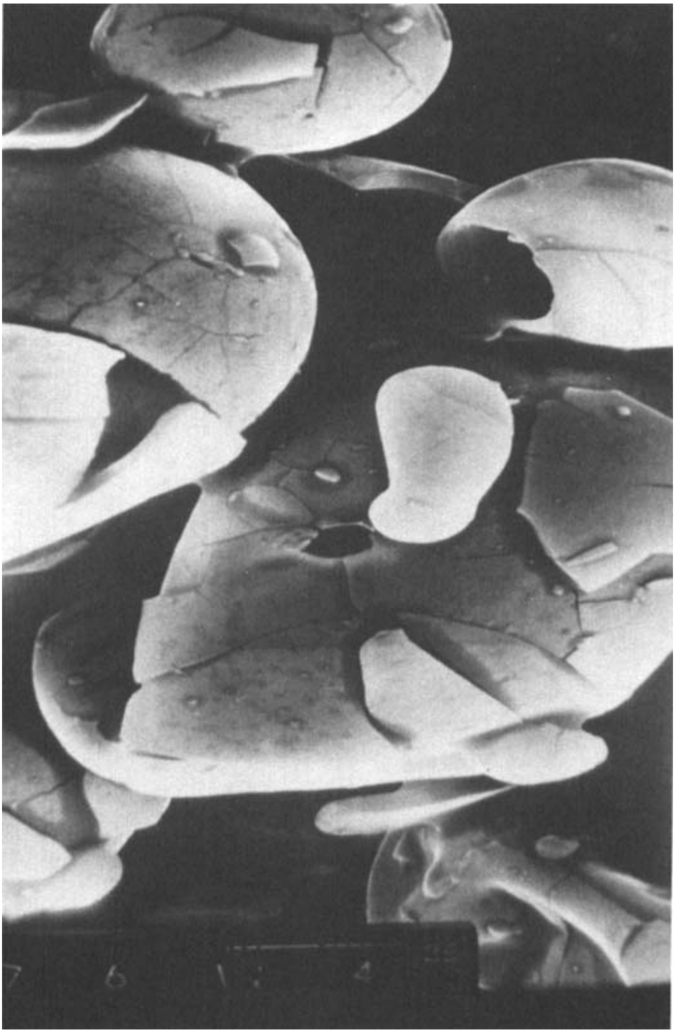

FIG. 3. SEM photograph (1 000×) of Ultrazine NAS lignosulfonate.

FIG. 4. SEM photograph (1 000×) of chlorophosphazene-Ultrazine NAS reaction product (No. 6).

Spectroscopic Studies of Phosphazenylated Lignosulfonates

Infrared studies of phosphazenylated Borregaard lignosulfonates showed, in comparison to modified Ultra B002 [4], a small displacement to higher frequency of the absorption band characteristic of asymetric vibration of P=N groups of cyclic trimer and tetramer (Fig. 6, Tables 4 and 5). Infrared investigation also showed two characteristic absorption bands typical of the stretching vibration of P–O–C groups in the frequency range 1170-1140 cm^{-1} for P–O–C (aromatic) and in the frequency range 1050-1025 cm^{-1} for P–O–C (aliphatic).

FIG. 5. SEM photograph (1 000×) of chlorophosphazene-Ultrazine NAS reaction product modified by diethylamine (No. 8).

The characteristic absorption band at 1210-1200 cm^{-1} can be assigned to symmetric vibration of the S=O group of lignosulfonates (Fig. 6). The modification induced a small displacement of this band to 1250-1220 cm^{-1}.

A small but meaningful difference in the infrared spectra for the sodium lignosulfonates used was observed (Fig. 6 [4]). This is undoubtedly related to the diverse structure of the lignin raw materials. The difference in the infrared spectra of the Borregaard lignosulfonates was related mainly to variations in their characteristic groups.

Table 7 presents the hydrogen bond energy as obtained by the infrared method of the lignosulfonates and their modification products. It is apparent that the modification of lignosulfonates increases the

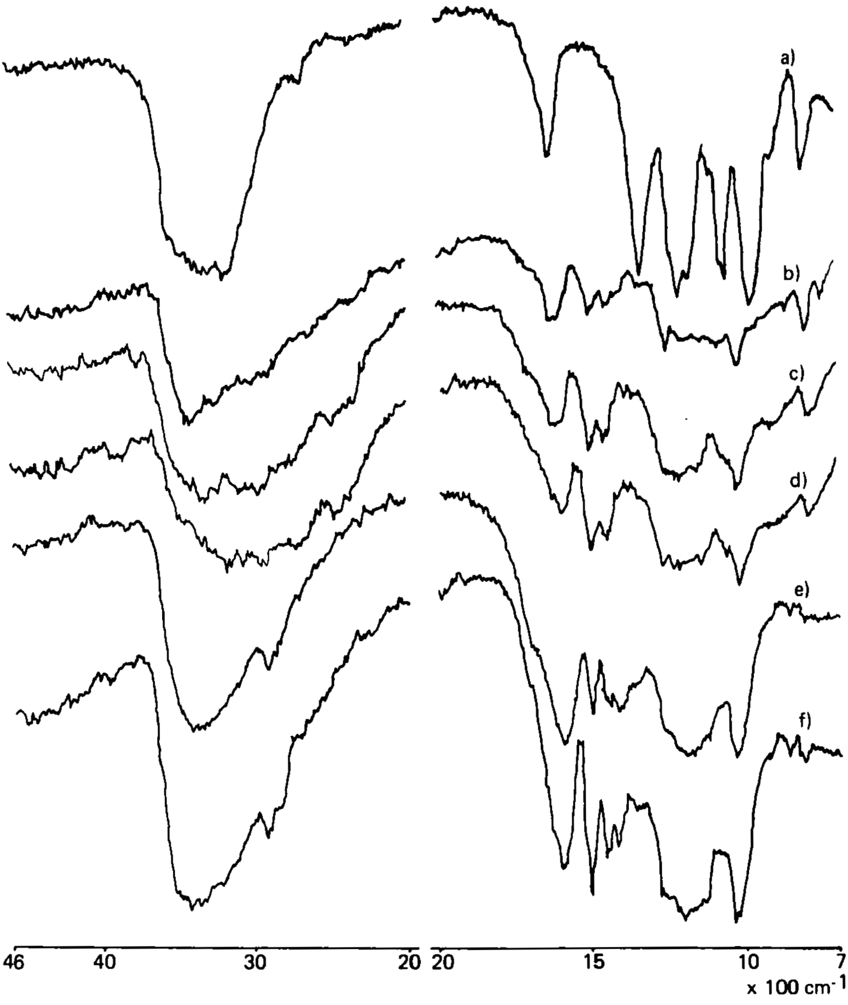

FIG. 6. Infrared spectra of the reaction products of (a) Borresperse NA with chlorophosphazene oligomers (No. 2), (b) Ultrazine NAS with chlorophosphazene oligomers (No. 6), (c) Borresperse NA-chlorophosphazene oligomers reaction product modified by diethylamine (No. 7), (d) Ultrazine NAS with chlorophosphazene oligomers reaction product modified by diethylamine (No. 8), (e) Borresperse NA lignosulfonate, and (f) Ultrazine NAS lignosulfonate.

TABLE 6. Flame Resistance of the Lignosulfonate Modificates

Sample	Type of lignosulfonate	Flame resistance[a]	Glow resistance[a]
1	Borresperse NA	NF	NG
2	Borresperse NA	NF	NG
3	Ultrazine NAS	NF	NG
7	Ultrazine NAS	NF	NG
-	Borresperse NA	NF[b]	G
-	Ultrazine NAS	NF[b]	G

[a] NF = nonflammable, G = glowing, NG = nonglowing.
[b] Sample burned by intensive glowing.

TABLE 7. Hydrogen Bond Energy of Lignosulfonates and Modification Products

Sample	Type of lignosulfonates	E_H, kcal
2	Borresperse NA	4.11, 5.48
6	Ultrazine NAS	5.14
7	Borresperse NA	4.18, 5.30
8	Ultrazine NAS	5.02
-	Borresperse NA	4.11, 4.62
-	Ultrazine NAS	3.68, 4.88
-	Ultra B002	3.42, 3.94

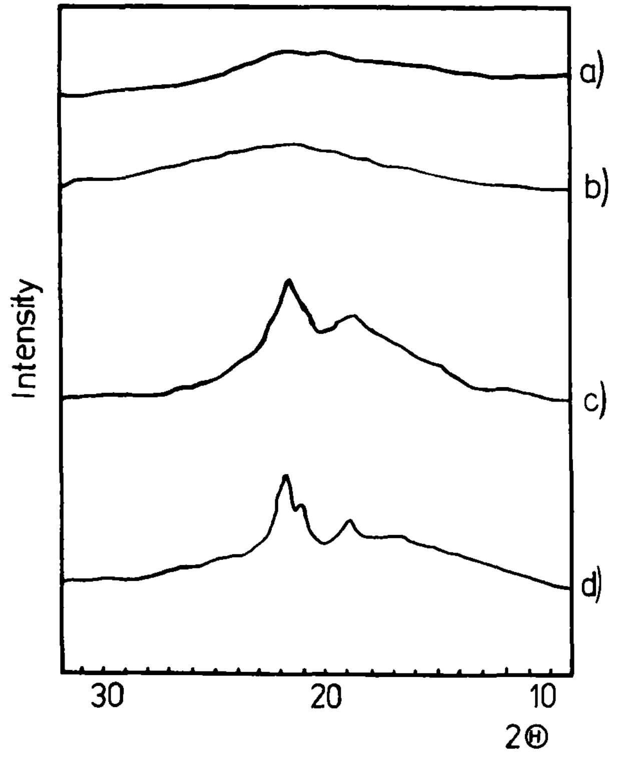

FIG. 7. X-ray diffractograms of (a) Borresperse NA, (b) Ultrazine NAS lignosulfonates, (c) the lignosulfonate-chlorophosphazene reaction products of No. 2, and (d) No. 6.

hydrogen bond energy. At the same time, the E_H of Ultra B002 lignosulfonate is a little lower than that of Ultrazine NAS and Borresperse NA.

Analogous to previous investigations [4], x-ray measurements demonstrated that modifications of the Borregaard lignosulfonates base showed crystalline patterns, whereas the original lignosulfonates were typically amorphous (Fig. 7).

Thermal Behavior of Phosphazenylated Lignosulfonates

The preparation of new types of flame- and/or heat-resistant polymers from the lignins seems to be one way for utilization of these accessible and relatively cheap by-products of the wood pulping process. Interest in these polymers is concerned with their thermal behavior; hence, the best method for their characterization is thermal analysis.

Table 8 summarizes the data of TG and DTG studies of the lignosulfonates as well as examples of their derivatives. The Borregaard lignosulfonates, especially Ultrazine NAS, were found to be somewhat more thermally stable than Ultra B002 (Table 8, [5]). The modified materials were also found to be considerably more thermally stable than the lignosulfonate raw materials and the Ultra B002 modifications [5].

The thermal stability of the modified materials can probably be connected to their crosslinked structure and the aromatic units in them. Degradation of the lignosulfonate derivatives followed by pyrolysis of the fragments yielded volatile, nonflammable products. A relatively small amount of these flame-inhibiting products from Borregaard lignosulfonate modification (Table 8) stifled a flame effectively. This seems to be mainly the result of cooperation of the phosphorus, nitrogen, and sulfur contained in the products.

Figure 8 compares the DTA curves of lignosulfonates modified by chlorophosphazenes as well as the raw materials. In the presence of air, the Borresperse NA and Ultrazine NAS showed an exothermic peak at 322 and 370°C, corresponding to their pyrolysis. In Ultra B002 lignosulfonate this occurred at 330°C [5]. The pyrolysis of the derivatives at 400-500°C indicates several exothermic effects due, apparently, to secondary degradation of obtained fragments. The phosphazenylated lignosulfonate based on Borresperse NA modified by diethylamine was characterized by an exothermal peak at 410°C related to pyrolysis and a mass loss at 500°C of only 28.6%. In both types of modifications, a relatively low amount of inhibiting volatile products were formed during degradation by an exothermic process. At the same time, it can be noted that the phosphorus concentration in the modified materials affects their thermal analysis curves.

CONCLUSION

The modification of Borregaard lignosulfonates by chlorophosphazenes seems to be a satisfactory way to form new products with heat and flame resistance as well as base and acid hydrolytic resistance. The future should bring practical exploitation of the new ligninlike polymers.

TABLE 8. Thermogravimetric and Differential Thermogravimetric Analysis of the Lignosulfonates Modified by Chlorophosphazenes

Sample	Type of lignin	Phosphorus content, %	Temperature of maximum rate of mass loss, °C	Range of temperature of maximum rate of mass loss, °C	Percentage of mass loss at differential temperatures, °C					
					100	200	300	400	500	600
2	Borresperse NA	5.90	-	-	6.0	9.0	10.5	13.0	16.0	20.0
6	Ultrazine NAS	6.40	-	-	4.1	7.5	16.3	24.5	28.6	-
7[a]	Borresperse NA	4.10	-	-	4.0	7.0	8.5	12.0	15.0	16.0
-	Borresperse NA	-	325	250-350	4.5	7.1	28.2	44.9	51.3	-
-	Ultrazine NAS	-	280, 370	240-430	3.5	5.0	12.1	26.1	31.5	45.0

[a] Product modified by diethylamine.

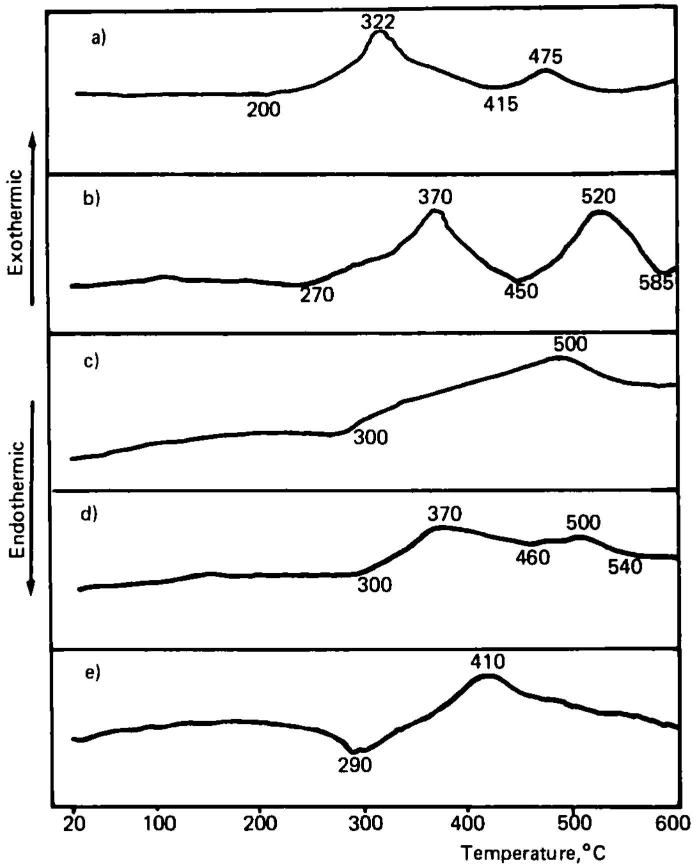

FIG. 8. DTA curves of (a) Borresperse NA type, (b) Ultrazine NAS type, (c) Ultrazine NAS-phosphazene (No. 4), (d) Ultrazine NAS-phosphazene (No. 6), and (e) Borresperse NA-phosphazene (No. 7) modified by diethylamine.

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