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SPECTRAL STUDIES ON THE INTERACTIONS BETWEEN RESORCINOL-FORMALDEHYDE RESIN AND PYRIDINES

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ABSTRACT

The interactions between resorcinol-formaldehyde (RF) resin and pyridines have been studied by infrared and ultraviolet spectrometry of model compound systems. Besides the formation of hydrogen bonds and pyridinium salts, it was found that 4-ethylpyridine can react with RF resins forming cyclic amide structures. Based on the spectral studies, a possible reaction scheme is proposed.

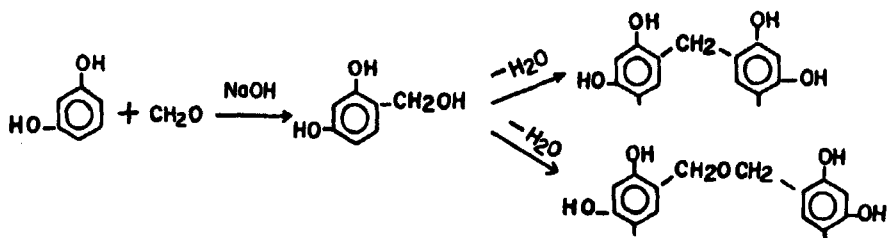
INTRODUCTION

Resorcinol-formaldehyde resins (RF) have been of great importance to the rubber industry for over 40 years. Rayon, nylon, fiberglass, polyester, steel, and aramid cords have been successfully bonded to rubber with resorcinol-based adhesives [1-6].

The development of resorcinol-based adhesive systems involves an RF mixture to which a polymer latex is added to form an "RFL" adhesive dip. When the dip is properly applied to a fabric or cord and cured by application of heat, it provides excellent adhesion of rubber to the reinforcing material. The polymeric latex is chosen for its compatibility with the rubber to be bonded. A terpolymer latex of vinylpyridine-styrene-butadiene is probably the most wide-

ly used system for tire application today. Some mechanisms have been proposed to explain the bonding of rubber and fiber filaments by RFL [7, 8]. However, the interactions between RF resin and the pyridine elements of the terpolymer lates have not been reported in detail. In this paper we report a study of physical and chemical bonding of RF resin and pyridines by the use of model systems.

It is believed that methylol groups or hydroxyl-substituted benzyl alcohol moieties are formed as intermediates during the processing of RF resin.



Two kinds of OH groups exist during the reaction, the aromatic OH groups of the resorcinol and the aliphatic OH groups of the methylol of the benzyl alcohol moieties. Since RF becomes a crosslinked thermoset resin after heat treatment, it is difficult to observe directly the reactions between RF and the pyridine elements of the terpolymer.

We used resorcinol and 2-hydroxybenzyl alcohol to model the active OH groups of the RF resin. 4-Ethylpyridine and 2-ethylpyridine were used to model the vinylpyridine components of the latex.

EXPERIMENTAL

Resorcinol, 2-hydroxybenzyl alcohol, 4-ethylpyridine, and 2-ethylpyridine were purchased and used without further purification.

The mixtures of 0.02 mol resorcinol and 0.02 mol ethylpyridines were heated at 130°C under nitrogen. Also made were mixtures of 2-hydroxybenzyl alcohol and 0.002 mol NaOH aqueous solution (25%) which were dried under nitrogen. To the mixtures, 0.02 mol ethylpyridines were added and heated under nitrogen at 130°C for 30 min, and then at 140°C for 10 min. In both cases, samples were withdrawn before and after heating, after which the unreacted ethylpyridines were evaporated under vacuum at room temperature for 3 days, then the residue was ground to a fine powder and dried for another 3 days.

The structures were determined by Fourier-transform infrared spectroscopy (Nicolet 170 SX FT-IR) and ultraviolet absorption spectroscopy (Beckman M-6 UV).

RESULTS AND DISCUSSION

The Interactions between Resorcinol and 4-Ethylpyridines

The interactions between resorcinol and 4-ethylpyridine were studied by IR spectra (Fig. 1). Spectrum A of the residue after evaporating the initial mixture shows bands in the region of 2600-3100 cm^{-1} that are broadened because of hydrogen bonding. Spectrum B is due to the residue after evaporation of the

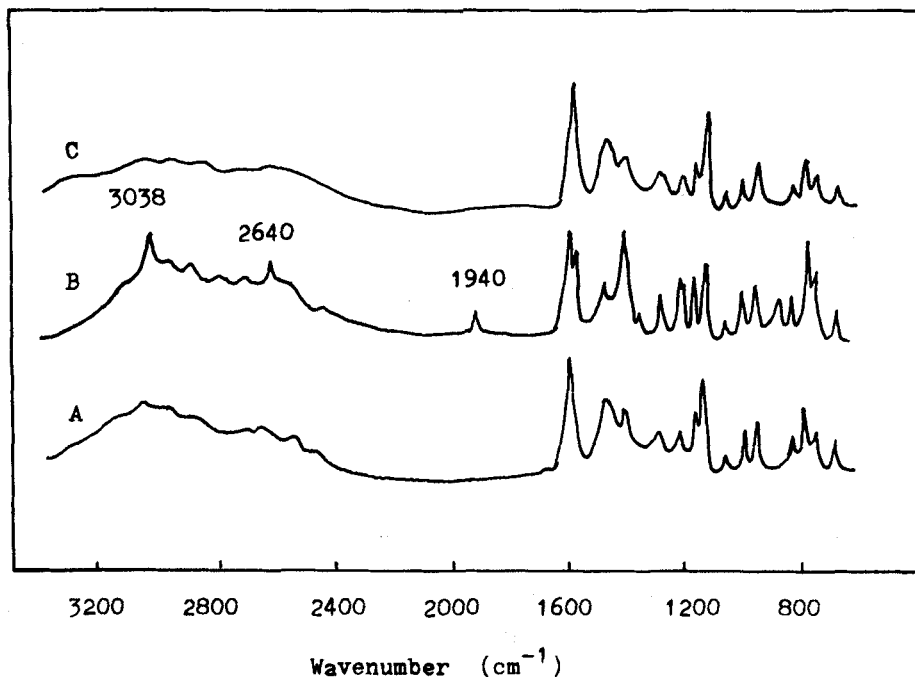
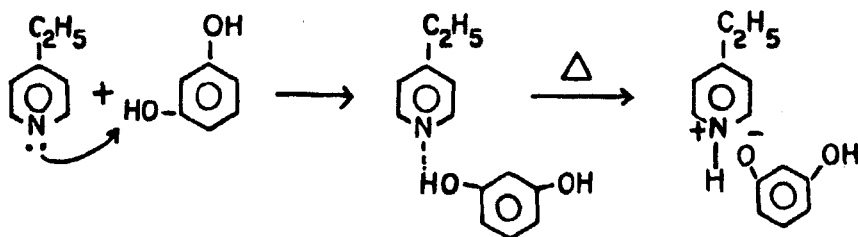


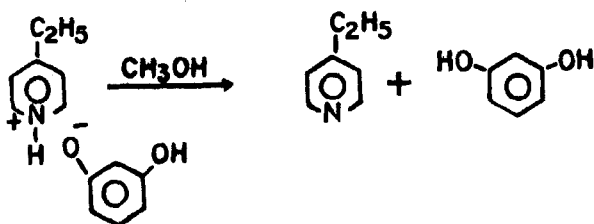
FIG. 1. IR spectra of (A) the residue after evaporating the mixture of 4-ethylpyridine and resorcinol, (B) the residue after evaporating the mixture which had been previously heated, and (C) the methanol-treated residue in B.

mixture which had been heated previously at 130°C for 60 min. The band at 2640 cm^{-1} is assigned to the N–H stretching mode, and the 1940 cm^{-1} band is due to the N–H bending mode. The band at 3038 cm^{-1} is due to C–H stretching, while the bands at 1595 and 1450 cm^{-1} are due to the ring stretching modes of pyridinium salt [9]. Apparently, the 4-ethylpyridine formed a salt with resorcinol upon heating.

Spectrum C in Fig. 1 is the methanol-treated sample. All volatile materials had been evaporated by vacuum before the IR spectrum was taken. The N–H vibrational absorption bands and the ring absorption bands of pyridinium salt disappeared. The major part of Spectrum C is similar to Spectrum A, except for slight changes in the broad bands in the 2800–3400 cm^{-1} region, which are probably due to changes in hydrogen bonding. Based on these spectra, we propose that, when resorcinol is mixed with 4-ethylpyridine, the unshared electron pair of nitrogen forms a hydrogen bond with the proton of the phenolic hydroxyl group. On heating, the nitrogen and hydrogen atoms form an ionic structure.



This ionic structure dissociates in methanol and then reverts to resorcinol and 4-ethylpyridine.



The changes in the 3260 cm^{-1} band and other broad bands in the 2800–3400 cm^{-1} region in Fig. 2 indicate that inter- and intramolecular hydrogen bonds of resorcinol have been disrupted and that a variety of types of hydrogen bonding are present [11–14]. Spectrum D shows no ionic absorption

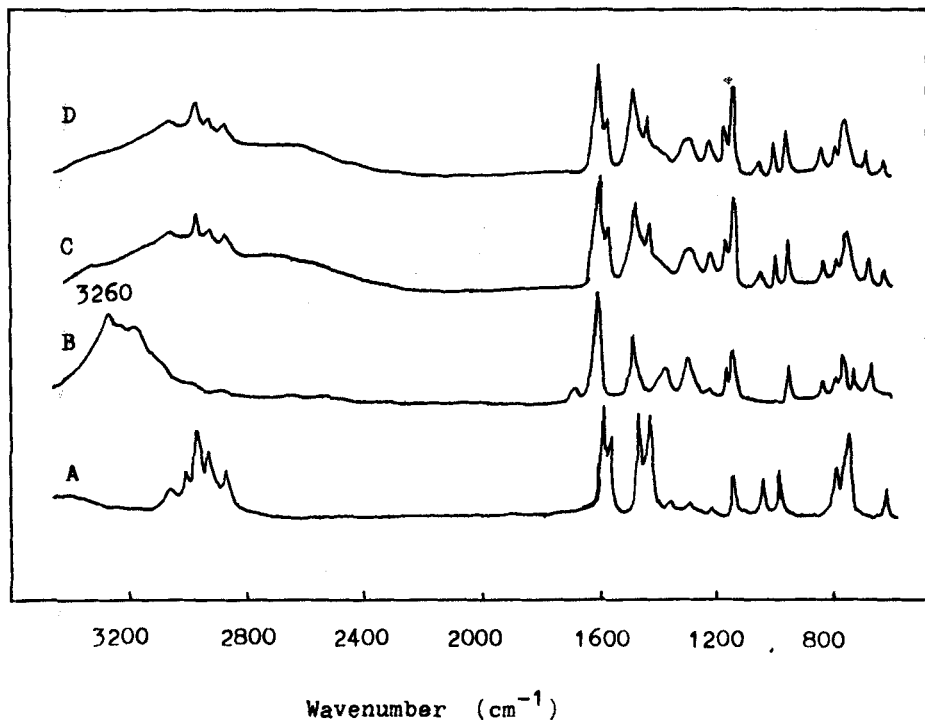


FIG. 2. IR spectra of (A) 2-ethylpyridine, (B) resorcinol, (C) the initial mixture of 2-ethylpyridine and resorcinol, and (D) the heated mixture.

bands. Because of the steric effect of the ethyl group, it is difficult for nitrogen to approach the hydroxyl group. The hydrogen bond between 2-ethylpyridine and the hydroxyl group is expected to be weaker than for 4-ethylpyridine [15].

Interactions between 2-Hydroxybenzyl Alcohol and Ethylpyridines

During the processing of RF resin, hydroxyl-substituted benzyl alcohol moieties are supposed to form as intermediates. The activity of the methylol is influenced by the OH groups attached to the benzene ring. In order to study the interactions between the intermediates of RF resin and the pyridine components of the terpolymer latex, we used the commercially avail-

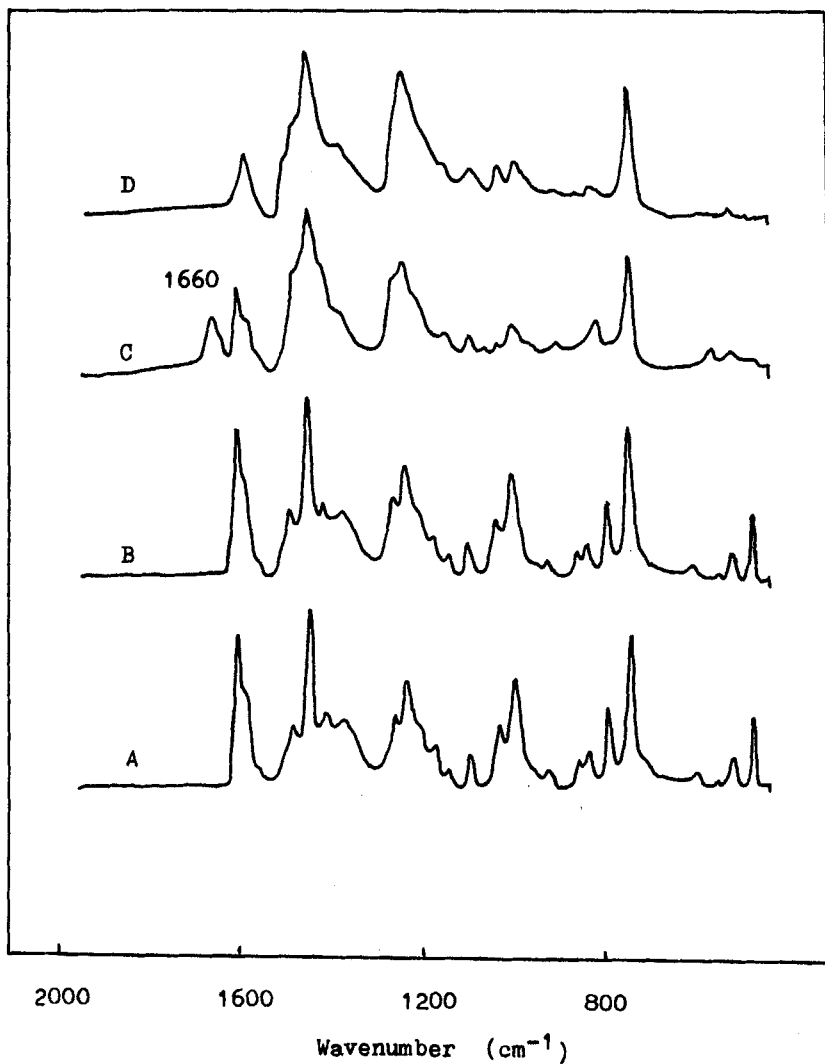


FIG. 3. IR spectra of (A) the initial mixture of 4-ethylpyridine and 2-hydroxybenzyl alcohol, (B) the mixture heated at 140°C for 40 min, (C) the reaction products heated in the presence of NaOH, and (D) the NaOH-catalyzed self-condensation products of 2-hydroxybenzyl alcohol.

able 2-hydroxybenzyl alcohol as a model of the intermediates. The IR studies of the reaction of 2-hydroxybenzyl alcohol and 4-ethylpyridine are shown in Fig. 3. Little difference can be observed between Spectra A and B. As sodium hydroxide was added to the reactants mixture, a brown solid material formed on heating. After evaporation of the unreacted pyridine it gave Spectrum C in Fig. 3. Spectrum D is due to the reaction product of 2-hydroxybenzyl alcohol and sodium hydroxide without 4-ethylpyridine. The intense bands of Spectra C and D in the 1400-1500 cm^{-1} region are due to the self-condensation products of 2-hydroxybenzyl alcohol. The bands in the 1590-1610 cm^{-1} region are due to the aromatic structures. There is a broad new band at 1660 cm^{-1} in Spectrum C, which is possibly due to a carbonyl or C=C absorption, or a combination of them. Since no bands appear in this region of Spectrum D, we concluded that the 1660 cm^{-1} band is due to the reaction product between pyridine and hydroxybenzyl alcohol in the presence of sodium hydroxide.

Figure 4 shows the IR study of the reaction of resorcinol, 4-ethylpyridine, and sodium hydroxide. We did not observe absorption changes in the 1400-1500 and 1640-1670 cm^{-1} regions. The hydroxyl group directly connected to the benzene ring neither underwent self-condensation nor reacted with pyridine to form a carbonyl group.

G. Xue et al. observed new bands in the carbonyl region during a study of the reaction of pyridine and epoxy compounds [15]. They assigned the bands at 1670 cm^{-1} to the carbonyl of a cyclic amide structure which formed during the reaction [16]. We propose that the reaction of 4-ethylpyridine and 2-hydroxybenzyl alcohol proceeds in a similar way in the presence of sodium hydroxide.

Pyridine and its derivatives show full aromatic properties. The similarity of pyridine to benzene with respect to their aromatic stability is well known. Pyridine also behaves as a weak monoacidic tertiary base, so it can react with acidic protons to form pyridinium salts. As mentioned already, 4-ethylpyridine and resorcinol can form salts upon heating. If the acidic proton of the hydroxyl group connected with benzene of 2-hydroxybenzyl alcohol is neutralized by NaOH, the hydrogen atom of the methylol group may bond with the nitrogen atom of pyridine. Further heating may induce the formation of a salt. We propose pyridinium salt formation as the first step of the reaction scheme.

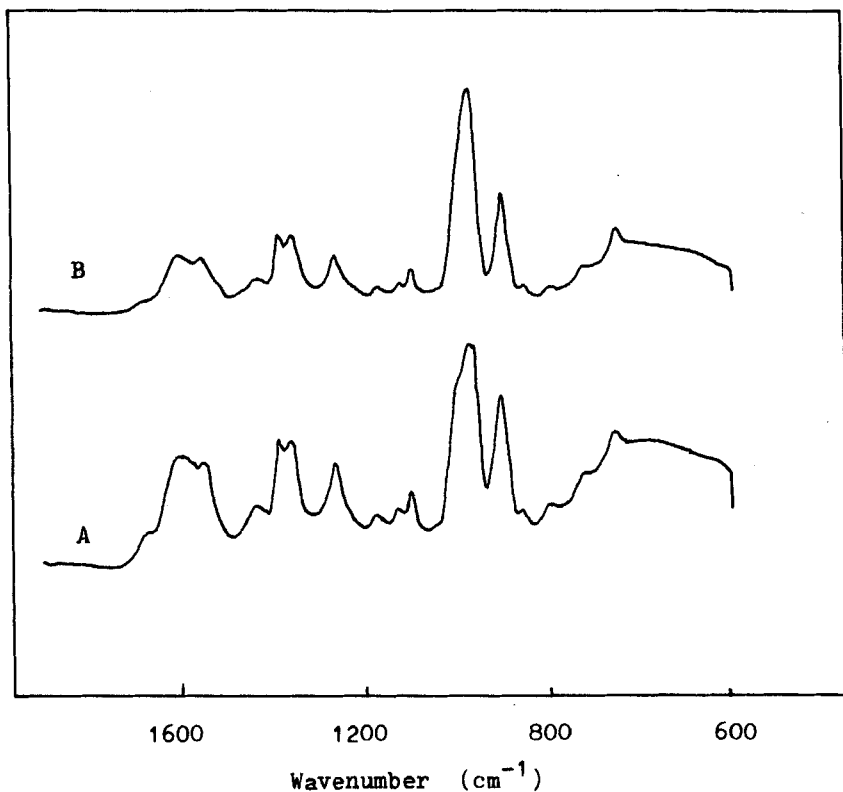
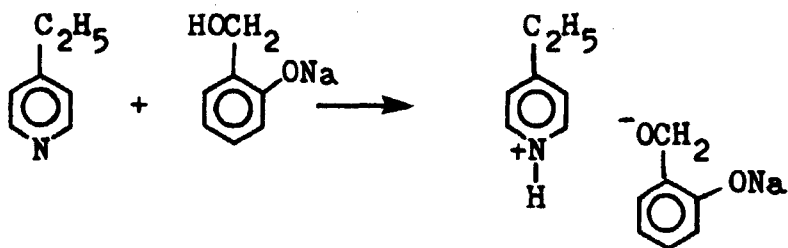
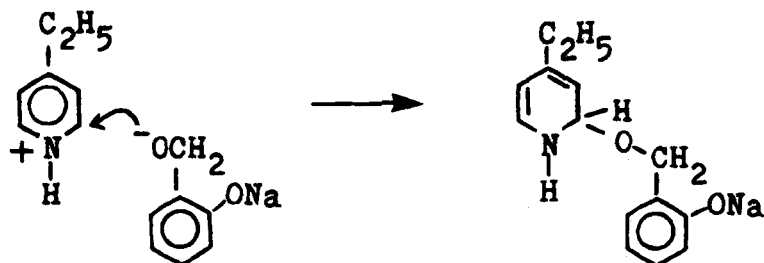


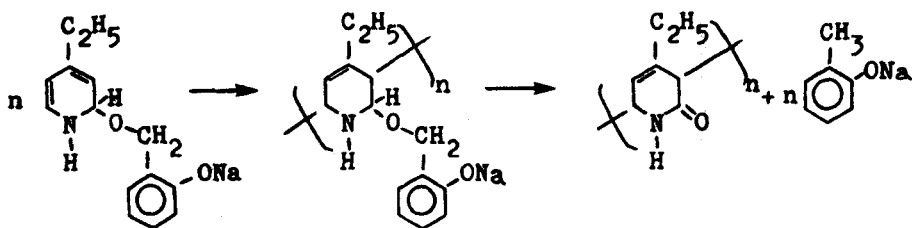
FIG. 4. IR spectra of (A) the initial mixture of resorcinol, 4-ethylpyridine, and NaOH, and (B) the heated mixture.



Pyridinium salt differs from pyridine in its stability toward nucleophilic attack [17, 18]. The second step is proposed as a nucleophilic attack at the α -position of the ring, forming an $-N-C-O-$ structure.



It should be noted that so far there is a conjugated 3,5-diene in the six-membered ring instead of whole-ring aromatic conjugation. The diene undergoes Diels-Alder reaction upon heating. As a result, the molecular weight increases [19]. The $-N-C-O-$ structure formed is unstable and rearranges to an amide structure upon heating [20, 21]. Finally, a product with a carbonyl group is formed.



The other bands in Spectrum C of Fig. 3 overlap and are difficult to assign. With the help of UV spectra, we learned that there is a complex in the reaction products besides the cyclic amide structure. We shall discuss this below.

Figure 5 shows a comparison of 4- and 2-ethylpyridine in the reaction with 2-hydroxybenzyl alcohol and sodium hydroxide. Spectrum A is due to the self-condensation products of 2-hydroxybenzyl alcohol catalyzed by sodium hydroxide. Spectrum B corresponds to the reaction products of 2-ethylpyridine, while Spectrum C is due to the reaction products of 4-ethylpyridine and is the same as Spectrum C in Fig. 3. In Spectrum B we could only see the self-condensation products, meaning that little 2-ethylpyridine had reacted.

The difference in reactivity of 4- and 2-ethylpyridine supports the reaction scheme proposed above. The ethyl group in the α -position on the pyridine ring sterically hinders salt formation. Also, as one of the *o*-positions was occupied by the alkyl group, nucleophilic attack would proceed slowly. For these two reasons the reaction of 4-ethylpyridine was much faster than that for 2-ethylpyridine.

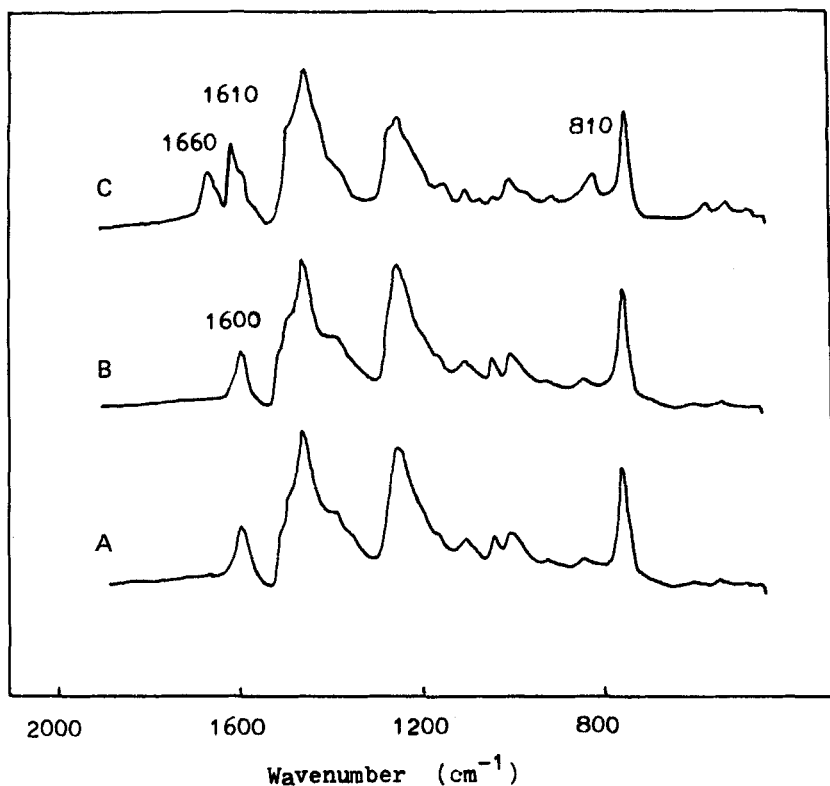


FIG. 5. IR spectra of the reaction products of (A) NaOH-catalyzed self-condensation of 2-hydroxybenzyl alcohol; (B) NaOH, 2-ethylpyridine, and 2-hydroxybenzyl alcohol; and (C) NaOH, 4-ethylpyridine, and 2-hydroxybenzyl alcohol.

Figures 6 and 7 are UV spectra of the reaction products which had been dried under vacuum for 6 days before determination. Spectrum A in Fig. 6 is due to the NaOH-catalyzed 2-hydroxybenzyl alcohol. Spectrum B corresponds to the reaction products of 2-ethylpyridine, 2-hydroxybenzyl alcohol, and NaOH. Spectra A and B are essentially the same. It means that only self-condensation products of 2-hydroxybenzyl alcohol were observed. This result agrees with the IR study. Spectrum C, which is due to the reaction products of 4-ethylpyridine, shows noticeable differences. A weak band at 302 nm appeared, which is assigned to the absorption of one kind of cyclic

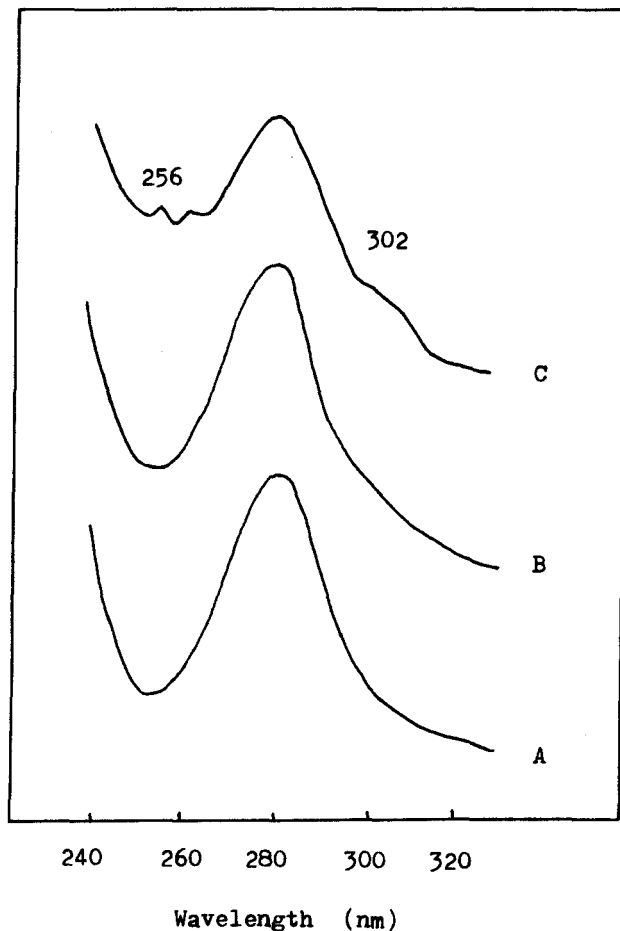


FIG. 6. UV spectra of the reaction products of (A) NaOH, 2-ethylpyridine, and 2-hydroxybenzyl alcohol; (B) NaOH-catalyzed self-condensation of 2-hydroxybenzyl alcohol; and (C) NaOH, 4-ethylpyridine, and 2-hydroxybenzyl alcohol.

amide [22]. The pyridine absorption occurs in the region of 250-265 nm in Spectrum C. We tried to eliminate pyridine from the reaction products by heat or solvent treatment. One sample of the products which had previously been vacuum treated was heated at 130°C for 2 h with a flow of nitrogen. Another

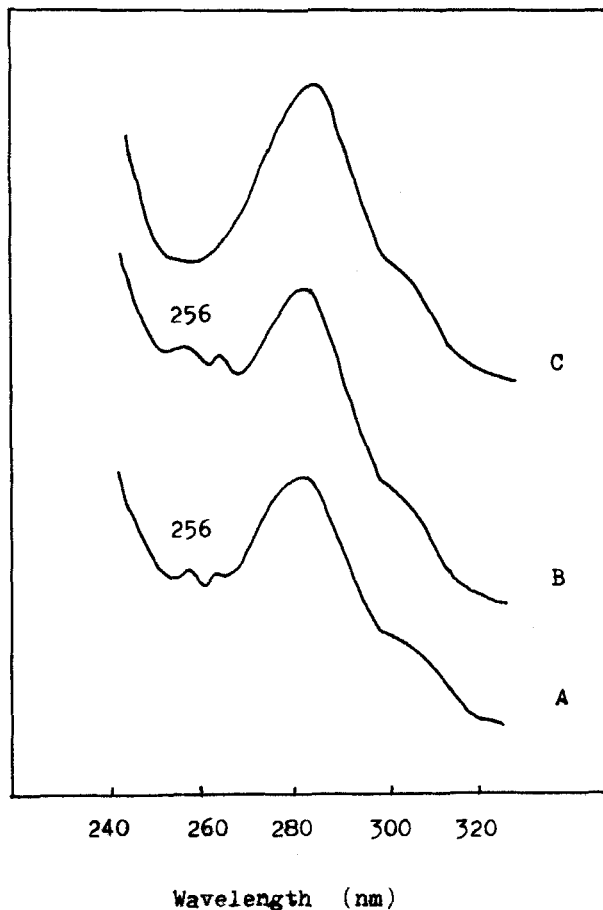


FIG. 7. UV spectra of (A) reaction products of 4-ethylpyridine, 2-hydroxybenzyl alcohol, and NaOH; (B) heat-treated reaction products; and (C) solvent-treated reaction products.

sample of the products was dissolved in ethanol and dried at 80°C . This procedure was repeated 3 times, and Fig. 7 shows the UV spectra. The pyridine absorption bands in the $250\text{--}265\text{ nm}^{-1}$ region appear in Spectra A and B, but not in Spectrum C. From the UV spectra in Figs. 6 and 7, we found that there was a complex which was stable upon heating in the reaction products. We could not evaporate the 4-ethylpyridine which was involved in the complex

by simple vacuum or heat treatment. But once the complex was dissolved and dried, it gave off 4-ethylpyridine.

Now we can assign the IR absorption at 1610 and 810 cm^{-1} in Spectrum C of Figs. 3 and 5 to 4-ethylpyridine involved in a complex. From the IR spectral studies in Fig. 5 and the UV spectral studies in Fig. 6, we can see that 2-ethylpyridine did not form a complex with 2-hydroxybenzyl alcohol.

CONCLUSIONS

The interactions between resorcinol-formaldehyde (RF) resin and ethylpyridines have been studied by model compounds. Their interactions are complicated. When they are mixed together, different kinds of hydrogen bonds will form. The resorcinol can react with 4-ethylpyridine upon heating to form an ionic structure. The interactions between the intermediates of RF resin and 4-ethylpyridine may form a cyclic amide structure and a complex. The formation of the cyclic amide structure disrupts the aromatic nature of the heterocyclic ring of 4-ethylpyridine. Further study concerning the structure and properties of the materials formed in this reaction may yield interesting results.

2-Ethylpyridine can only form hydrogen bonds with the functional groups of RF resin, and it is less reactive due to the steric effect of the ethyl group as the neighbor of the nitrogen atom of the pyridine ring.

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