Reaction of Tall Oil Pitch with Desmodur N Isocyanate

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ABSTRACT

The reaction between six tall oil pitch (TOP) grades and Desmodur N Isocyanate was followed by IR spectroscopy by decrease of NCO absorption in the film cast from the reaction mixture. Time-conversion curves show that the reactivities of three TOP grades are of the same magnitude up to 50% conversion, while in the other grades considerably slower reaction rates were observed. In most catalyzed reactions 90% conversion was completed during 14 days. Development of tensile properties of the films during the reaction sequence indicates the formation of polymers. Hypothetical routes for the reaction are presented.

INTRODUCTION

Tall oil pitch (TOP) is obtained as a nonvolatile residue in the fractional distillation process of crude tall oil. The yield of TOP in the refining process amounts to 15-40% depending primarily on the quality of the crude tall oil. The total world production of TOP is over 200,000 tons/yr.

The utilization of this by-product is still an unsolved problem. Recently it has been discovered that TOP possesses film-forming properties in combination with Desmodur N Isocyanate, and therefore it may be used as a starting material for polyurethane lacquers (1).

The object of this work was to extend the knowledge on the reaction between TOP and Desmodur N. IR spectroscopy was used both for the characterization of TOP grades and evaluation of their reactivities toward Desmodur N. Formation of polymers was studied by measuring tensile properties of the films during the reaction sequence.

EXPERIMENTAL PROCEDURES

The investigated samples were of ordinary grades of tall oil pitch as received from the distillation plants.

The reactive isocyanate was Desmodur N 100, a biuret type of aliphatic tri-isocyanate, manufactured by Bayer. Its NCO content was 20.9% as determined by titration method (2). Desmorapid PP, a tertiary amine from Bayer, was used as a catalyst. Ethyl acetate, employed as a solvent, was of analytical grade.

The infrared spectra were measured with a Perkin-Elmer Model 457 spectrophotometer using KBr pellets on which a drop of TOP and Desmodur N mixture in ethyl acetate solution was deposited. After evaporation of the solvent, a homogeneous film was formed on the KBr tablet.

RESULTS AND DISCUSSION

Characterization of Samples

General characteristics of TOP samples are given in Table I. Table II gives the composition of TOP grades as determined previously (3).

Infrared Spectroscopic Investigations

Typical infrared absorption bands (cm^{-1}) of TOP were found to be as follows: 2950, *2930*, 2870, *2855*, *1735*, *1705*, *1695*, 1605, 1515, *1465*, *1380*, 1270, 1245, 1175. Very strong bands are italicized. These characteristic vibrations were found in all investigated TOP grades.

The infrared absorption bands (cm^{-1}) of Desmodur N were found to be as follows: 3670, 3470, *3385*, *3270*, *2940*, *2860*, *2270*, 1765, *1690*, *1640*, *1515*, *1470*, 1355, 1275, 1215, 1100, 865, *770*, 730, 585. The vibrations found in Desmodur N agree with those reported in the literature (4).

TABLE I

Properties of Tall Oil Pitch Grades

Properties	Grade 1	2	3	4	5	6
Acid number, mg KOH/g	38	39	34	49	30	27
Saponification number, mg KOH/g	111	105	94	115	106	101
Equivalent weight for free acids	716	642	648	591	873	719
Resin acids, %[a]	15.5	10.8	12.6	16.9	8.8	10.6
Insoluble in petroleum ether, %	10.0	9.5	2.4	7.4	8.5	0.4

[a] Linder-Persson method.

TABLE II

Component Group Composition of Tall Oil Pitch (wt % of pitch)

Constituents	1	2	3	4	5	6
Free acids, total	48.6	44.6	39.3	51.6	46.7	34.6
Fatty acids	1.3	0.8	1.4	1.8	1.3	2.4
Resin acids	9.7	6.1	10.6	12.5	3.3	6.5
Other acids	37.6	37.7	27.3	37.3	42.4	25.7
Esterified acids, total	23.3	26.8	30.6	32.2	27.9	37.8
Fatty acids	13.3	15.2	8.2	12.9	13.8	12.4
Resin acids	1.2	0.9	1.7	0.9	1.6	1.9
Other acids	8.8	10.7	20.7	9.4	12.5	23.5
Unsaponifiables, total	28.2	28.6	30.1	25.3	25.4	27.6
Low molecular	14.1	17.7	14.6	14.6	15.8	15.1
High molecular	14.1	10.9	15.5	10.6	9.6	12.5

TABLE III

The Advancement of the Reaction between TOP and Desmodur N

Catalyzed reaction			Uncatalyzed reaction		
A_{2270} cm^{-1}	Conversion, % based on A_{2270} cm^{-1}	Time, days	A_{2270} cm^{-1}	Conversion, % based on A_{2270} cm^{-1}	Time, days
1.157	0	0	1.157	0	0
0.866	25.2	1	0.982	15.1	1
0.636	45.0	2	0.852	26.4	2
0.465	59.8	3	0.714	38.3	3
0.291	74.8	6	0.431	62.7	6
0.248	78.6	7	0.345	70.2	7
0.208	82.0	8	0.303	73.8	8
0.176	84.8	10	0.245	78.8	10
0.148	87.2	13	0.207	82.1	13
0.105	90.9	14	0.185	84.0	14

The reaction of TOP towards Desmodur N was followed by IR spectra taken from the film deposited from ethyl acetate solution on the KBr tablet. In the reaction mixtures, the TOP/Desmodur N ratio was 2:1. Desmorapid PP was used as a catalyst, and its content in the catalyzed mixture was 0.5%. Measurements were carried out at room temperature, and the disappearance of NCO band at 2270 cm^{-1} indicated the advancement of the reaction.

Table III presented the data on the absorbances A_{2270} cm^{-1}, the conversion % calculated from the decrease of NCO absorption at 2270 cm^{-1}, and the reaction time in days respective to the reaction between TOP grade 2 and Desmodur N.

From the data in Table III, it can be seen that during the interval of 6 days considerably lower reaction rates are observed in the uncatalyzed reaction than in the catalyzed one, respectively. After that, the reaction shows a tendency to level off in both cases. This indicates that the reaction between TOP and Desmodur N occurs at least in two steps.

Figure 1 shows the advancement of the catalyzed reactions of the investigated TOP grades toward Desmodur N in terms of conversion and time data. On the basis of 50% conversion data, it can be concluded that this stage of the reaction can be attained in TOP grades 1, 2, and 3 during 2-2.5 days. In TOP grades 4, 5, and 6, the reaction is slower and takes 4-5 days to reach this point. In most reaction, 90% conversion was completed during 14 days.

Polymer Formation

The isocyanates react with compounds containing reactive hydrogen to give addition products:

$$\mathrm{R.\,NCO + R'\,H \rightarrow R.\,NH.\,CO.\,R'} \qquad \text{(I)}$$

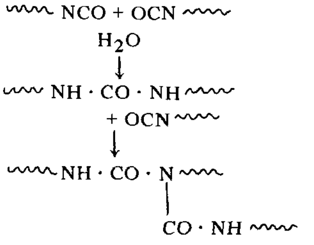
In more specific terms isocyanates react with hydroxyl groups to give urethanes:

$$\mathrm{R.\,NCO + R'\,OH \quad R.\,NH.\,CO.\,OR'}\ \text{(urethane)} \qquad \text{(II)}$$

The reaction with carboxylic acids give mixed anhydrides which break down to form amide group:

$$\mathrm{R.\,NCO + R'\,COOH \rightarrow R.\,NH.\,CO.\,O.\,CO.\,R'} \qquad \text{(III)}$$
$$\downarrow$$
$$\mathrm{R.\,NH.\,CO.\,R' + CO_2}$$
(amide)

The isocyanate groups react with atmospheric moisture at ordinary temperature leading to chain branching through biuret formation:



(IV)

$$\begin{gathered}\sim\!\sim\,\mathrm{NCO + OCN}\,\sim\!\sim \\ \downarrow \mathrm{H_2O} \\ \sim\!\sim\,\mathrm{NH \cdot CO \cdot NH}\,\sim\!\sim \\ +\ \mathrm{OCN}\,\sim\!\sim \\ \downarrow \\ \sim\!\sim\,\mathrm{NH \cdot CO \cdot \underset{\displaystyle |\atop \displaystyle CO \cdot NH\,\sim\!\sim}{N}}\,\sim\!\sim\end{gathered}$$

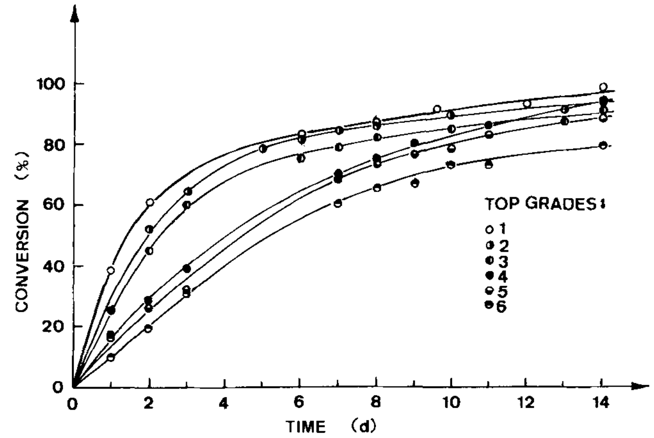


FIG. 1. Time-conversion curves on the reaction of TOP towards Desmodur N 100.

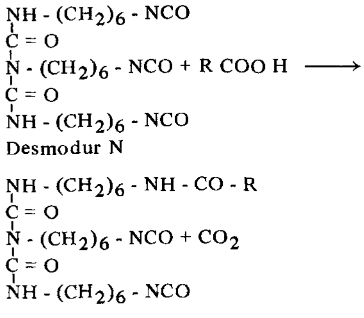
TABLE IV

Strength Properties of the Films[a] Prepared from TOP and Desmodur N Mixtures (1:1)

	Tensile strength, psi		Elongation, %	
TOP grade	5 day	30 day	5 day	30 day
1	1843	2714	2.9	2.8
6	1357	1700	3.9	1.5

[a] The films were cast from 50% ethyl acetate solution using 0.5% Desmorapid PP as a catalyst.

Considering the composition of the weight fractions in TOP grades (Table II) one can see that 34.6-51.6% of the components contained free acids. The presence of high molecular free acids is evident from the high equivalent weights in the range of 591-873 obtained for the acids. Therefore, it may be postulated that the acidic groups in TOP react with Desmodur N according to route (III) forming amide bonds:

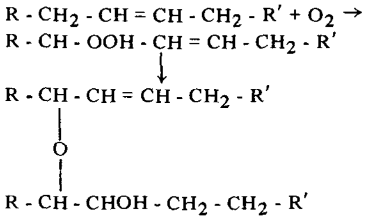


(V)

$$\begin{array}{l}\mathrm{NH - (CH_2)_6 - NCO} \\ \mathrm{|} \\ \mathrm{C = O} \\ \mathrm{|} \\ \mathrm{N - (CH_2)_6 - NCO + R\,COO\,H} \longrightarrow \\ \mathrm{|} \\ \mathrm{C = O} \\ \mathrm{|} \\ \mathrm{NH - (CH_2)_6 - NCO} \\ \text{Desmodur N} \\[1ex] \mathrm{NH - (CH_2)_6 - NH - CO - R} \\ \mathrm{|} \\ \mathrm{C = O} \\ \mathrm{|} \\ \mathrm{N - (CH_2)_6 - NCO + CO_2} \\ \mathrm{|} \\ \mathrm{C = O} \\ \mathrm{|} \\ \mathrm{NH - (CH_2)_6 - NCO}\end{array}$$

Since the product of the latter reaction possesses free NCO groups, it may react on exposure to atmospheric moisture to undergo further extension through reaction route (IV).

The esterified acids liberated from the neutral components by saponification were composed mainly of fatty acids and high molecular modified acids (Table II). The main fatty acid components in tall oil and TOP are oleic and linoleic acids which contain unsaturated double bonds. These are the sites for the oxidation by air and polymerization reactions which may be illustrated as follows (5):



$$\begin{array}{l} R-CH_2-CH=CH-CH_2-R' + O_2 \rightarrow \\ R-CH-OOH-CH=CH-CH_2-R' \\ \qquad\qquad\qquad\quad \downarrow \\ R-CH-CH=CH-CH_2-R' \\ \quad\;\; | \\ \quad\;\; O \\ \quad\;\; | \\ R-CH-CHOH-CH_2-CH_2-R' \end{array} \qquad (VI)$$

It can be assumed that in the free film, oxidation by air leads to these intermediates containing hydroxyl groups which may react further with isocyanate groups forming urethane bonds according to route (II).

Tensile Strength of the Films

The formation of polymers from TOP and Desmodur N can be proved by the evaluation of strength properties of the films during the reaction sequence. Table IV presents data on tensile strength and elongation of the films made from TOP and Desmodur N mixtures. The measurements were carried out after 5 and 30 days from the beginning of the reaction.

The results show that considerably higher tensile strength was developed in the film prepared from the faster reacting TOP grade 1 (Fig 1) than in that made from slower reacting grade 6, respectively. The ultimate tensile value of 2714 psi obtained for the former film compares well with the literature values of 2028 psi and 3100 psi reported for urethane oil coatings (6). Table I shows that the faster reacting TOP grade 1 possesses higher acid number than the slower reacting grade 6, respectively. The development of higher tensile value for the film made from the former grade indicates that there are more reactive sites in the backbone of TOP, e.g., acidic groups for the addition reaction according to route (III).

CONCLUSIONS

Considering the reaction between TOP and Desmodur N, one can conclude that higher reaction rates at the initial stages may be due to the ready availability of carboxyl groups in the backbone of TOP. Once these carboxyl groups have been utilized in forming amide bonds, the slower reactions take place, namely air oxidation leading to reactive hydroxyl groups and addition reactions of free NCO groups with atmospheric moisture. The reactions are diffusion controlled owing to their occurrence in the solid state. The differences in the reactivities of TOP grades toward Desmodur N are mainly due to the variations in their composition, e.g., the amount of reactive sites, and to steric factors developed during the reactions.

ACKNOWLEDGMENTS

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