

# Characterization of Charge-Transfer Adducts of Coal-Tar Pitches

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**Abstract** Benzene soluble and trichlorobenzene soluble fractions of coal-tar pitch were divided into two fractions each according to their ability to form charge-transfer adducts with picric acid. Each fraction was characterized by ESR, GC-MS and NMR, and studied their thermal reactivities. In the case of the fractions which readily formed adducts with picric acid, the study by ESR showed that these fractions had more unpaired electrons than the others, and the study by GC-MS showed that the fractions consisted of large amounts of heterocycles, containing nitrogen atoms, and high molecules. In addition, these fractions reacted rapidly when heat-treated. Azacompounds, such as acridine, can serve as catalysts for polymerization of pitch because of their hydrogen acceptability.

## Introduction

The degree of polymerization is one of the key properties of binder or impregnant pitch. It is very important to know what kinds of compounds in pitch react readily during polymerization. As pitch consists of a variety of compounds, it is very difficult to study all of these compounds simultaneously. Though pitch is divided into several fractions using solvents, these fractions have similar properties. Gemmenke et al., proposed fractionation of pitch according to chemical reactivity, such as an ability to form charge-transfer adducts.<sup>1)</sup> They reported that, in the case of  $\gamma$ -resin (benzene soluble) of pitch, the compounds which readily form picrate with picric acid can be readily polymerized. However, they did not specify the compounds which can form picrate.

This paper reports a study undertaken to determine what kinds of compounds in  $\gamma$ -resin readily form picrate. Pitch is fractionated into  $\beta$ -resin (benzene insoluble but quinoline soluble) and  $\alpha$ -resin (quinoline insoluble) in addition to  $\gamma$ -resin.  $\gamma$ -resin is a valuable fraction of pitch for the electrode industry, because it has a high coking value and a high joining ability with a filler. It is, however, difficult to determine the properties of  $\beta$ -resin because of its poor solubility in solvents other than quinoline. Unfortunately, quinoline is not a suitable solvent for studies in which picric acid is used. Accordingly, trichlorobenzene (TCB) was chosen as a solvent for  $\beta$ -resin, because TCB is inert to picric acid, though it dissolves only half of  $\beta$ -resin. The TCB soluble fraction of  $\beta$ -resin was also investigated using picric acid. Based on the results of these studies, acridine and phenazine were added to improve the reactivity of pitch.

## Experimental section

Commercially available coal-tar hard pitch with a

softening point (SP) of 91.6°C (pitch A) and quinoline insoluble free coal-tar soft pitch with a SP of 36.2°C (pitch B) were used.

$\beta$ -resin was separated from the pitch A using benzene and quinoline. This  $\beta$ -resin was dried in vacuo and dissolved in TCB. The TCB soluble fraction of  $\beta$ -resin was filtered and used as a TCB solution. The picric acid dissolved in TCB was added to the TCB solution, and the mixture was stirred at 80°C for 1.5 hours. The resultant precipitate was separated from the solution by filtration. An ammonium hydrate solution was added to the precipitate and filtrate to wash off picric acid as ammonium picrate, and pitch was recovered in the form of  $\beta$ -pic and  $\beta$ -n-pic from the precipitate and filtrate, respectively. The recovered pitches were dried in vacuo.

$\gamma$ -resin was separated from the pitch A using benzene. The  $\gamma$ -resin dissolved in benzene was added with the picric acid dissolved in benzene, and the mixture was stirred at 60°C for 2 hours. The resultant precipitate and filtrate were washed with an ammonium hydrate solution, and pitch was recovered in the form of  $\gamma$ -pic and  $\gamma$ -n-pic from the precipitate and filtrate, respectively. The recovered pitches were dried in vacuo.

The separated pitches were examined by ESR (JEOL JES-FE3X), GC-MS (JEOL DX-300), and NMR (JEOL FX90Q and Varian XL-200). They were also heated at 430°C for 1.5 hours in an autoclave, and their TI (toluene insoluble fraction) and QI (quinoline insoluble fraction) were measured before and after heat treatment.

Three different kinds of pitch B were prepared by adding 10% acridine, phenazine and anthracene, respectively. These pitches and the pitch B which did not contain such additives were heated in a nitrogen atmosphere, and their TI, QI and FC (fixed carbon) were measured.

## Results and discussion

The recoveries of the separated pitches are shown in Fig. 1. It will be noted that the ratio of  $\beta$ -pic to  $\beta$ -n-pic is 1:2.3, while that of  $\gamma$ -pic to  $\gamma$ -n-pic is 1:3.6. The TI and QI of  $\gamma$ -pic are shown in Table 1 in comparison with those of  $\gamma$ -n-pic. Both the TI and QI are increased by heat treatment. Increases in TI and QI of  $\gamma$ -pic are greater

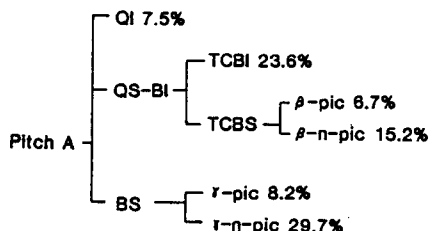


Figure 1. Recoveries of separated pitches.

Table 1. Differences in Heat Sensibility of Separated  $\gamma$ -Resin (%)

		TI	QI
Pic	a	13.4	0.1
	b	51.8	36.3
N-pic	a	0.1	tr.
	b	26.8	17.4

a: before heat-treatment  
b: after heat-treatment

than those of  $\gamma$ -n-pic. Fig. 2 shows the spin concentrations in  $\gamma$ -pic and  $\gamma$ -n-pic during heat treatment which were measured by the ESR spectrometer with a variable temperature probe. It will be noted that the spin concentrations of  $\gamma$ -pic are higher than those of  $\gamma$ -n-pic and increase more rapidly.

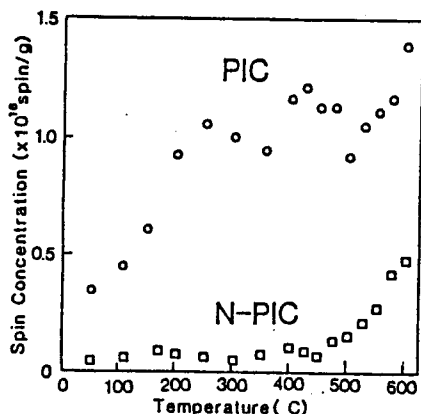


Figure 2. Dependence of Spin Concentrations on Temperature.

The results of elemental analysis of  $\gamma$ -resin are shown in Table 2.  $\gamma$ -pic has more heteroatoms than  $\gamma$ -n-pic. The GC-MS was employed to clarify the state of existence of these heteroatom in pitch. The spectra of  $\gamma$ -resin are shown in Fig. 3. It will be noted that  $\gamma$ -n-pic consists mainly of relatively small three- or four-ring hydrocarbon compounds, while  $\gamma$ -pic consists of over four aromatic ring compounds, containing nitrogen atoms, in addition to large hydrocarbons.

Table 2. Elemental Analysis of  $\gamma$ -Resin (%)

	C	H	N	O
Pic	89.3	3.6	2.5	1.9
N-pic	91.8	4.3	0.7	1.0

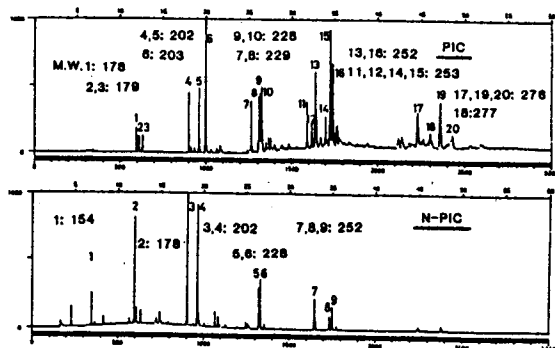


Figure 3. GC-MS spectra of  $\gamma$ -resin.

Gemmenke et al. reported that  $\gamma$ -pic was more reactive than  $\gamma$ -n-pic. This high reactivity is attributed to highly conjugated compounds and/or heterocycles. However, it is unknown which one plays the principal role. If heterocycle compounds containing nitrogen atoms play the main role, the reactivity of pitch can be increased by adding an azacompound which is one of the heterocycles containing nitrogen atoms. The effects of addition of acridine and phenazine are shown in Tables 3 and 4, respectively. It will be noted that the pitches added with these azacompounds show higher reactivity than the pitch which is not added with azacompounds. As these compounds are thermally stable, increases in TI, QI and FC are not attributed to the polymerization of these compounds. However, these compounds accelerate the polymerization of pitch. According to the results of elemental analysis, nitrogen atoms are not increased during heat treatment even if an azacompound is added to the pitch.

Table 3. Effect of Additives (%)

Additive	TI	QI	FC
Acridine	32.1	2.6	60.6
Anthracene	22.7	tr.	51.8
none	25.1	0.2	54.2

415°C, 1.5 hrs

Table 4. Effect of Additives (%)

Additive	TI	QI	FC
Phenazine	28.6	0.1	52.0
none	22.4	0.2	46.7

406°C, 4 hrs

Azacompounds serve as catalysts for pitch polymerization. Though the mechanism is not clear, it is supposed that a Lewis base, such as acridine, strips the pitch of its proton and produces active intermediates, thus increasing the reactivity of pitch.

## References

- 1) W. Gemmenke et al., *Light Metal*, 355 (1978); J. Stadelhofer et al. *ibid*, 1211 (1983).