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The Dissolution of Heat-treated Acenaphthylene Pitch

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Synopsis. About half of the pyridine insolubles in heat-treated acenaphthylene pitch was dissolved into hydrogenated pitch. Observation with optical and scanning electron microscopes showed that the components dissolved consisted of small mesophase spherules with an optically isotropic texture.

An optically anisotropic mesophase texture appears from isotropic pitch when the pitch is carbonized. Once the mesophase texture is formed, most of the anisotropic structures are insoluble, even in such powerful solvents as pyridine and quinoline.[1-3] In this study we attempt to dissolve the mesophase texture formed at an early stage of carbonization by using a hydrogenated pitch and a pyridine-soluble fraction containing molecular species near the mesophase constituent.

Experimental

A pitch (683-4) containing 15.2 wt% of pyridine insolubles (PI) and 8.6 wt% of quinoline insolubles (QI) was obtained by heat-treating acenaphthylene at 683 K for 4 h in a nitrogen atmosphere. The process of preparing the additives used for dissolution is shown in Fig. 1. Acenaphthylene was heated at 703 K for 2 h in a nitrogen stream and then evacuated at 623 K for 2 h to remove any volatile materials. The pitch (703-2) was hydrogenated with Li-ethylenediamine,[4] *i.e.*, by BenKeser reduction, and the product thus obtained was treated under a vacuum at 623 (703-2BK(623)) or 648 K (703-2BK(648)) for 2 h. On the other hand, the pyridine-soluble fraction from the pitch of 703-2 was evacuated at 623 (703-2PS(623)) or 648 K (703-2PS(648)) for 2 h.

The pitch of 683-4 was mixed with an equal portion of each additive, and the mixture was transferred into an ampule connected to a vacuum line to degas and seal it. After the sealed ampule had been heat-treated at 623 K for 1 h in a fluidized sand bath, all the product in the ampule was used to estimate the solubility. The amounts of PI and QI were determined by soxhlet extraction and the JIS-K2425 method respectively.

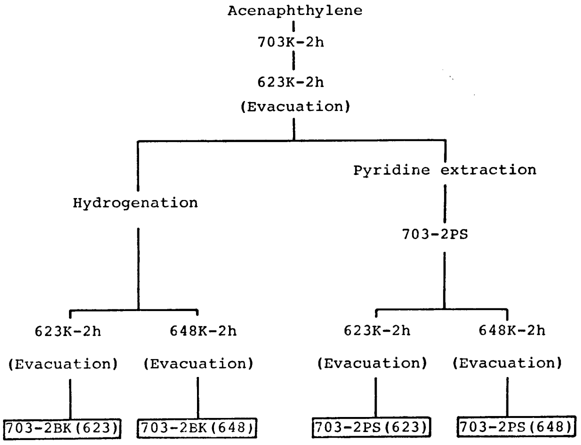

Fig. 1. Preparation of additives.

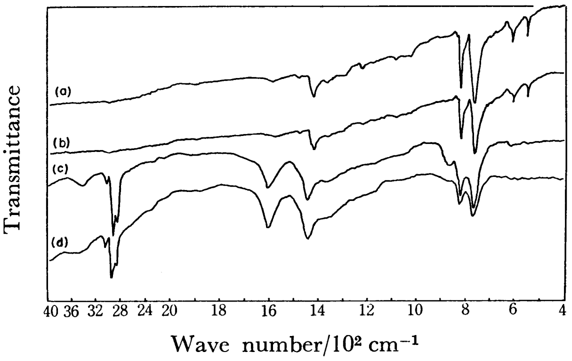

Fig. 2. Infrared spectra of additives, (a): 703-2PS (623), (b): 703-2PS(648), (c): 703-2BK(623), (d): 703-2BK(648).

Table 1. Elemental analysis of additives

Additive	C (wt%)	H (wt%)	H/C (atomic ratio)
703-2	96.68	4.27	0.526
703-2BK (623)	92.63	6.67	0.858
703-2BK (648)	93.44	5.92	0.745
703-2PS (623)	95.49	4.37	0.545
703-2PS (648)	95.66	4.30	0.536

Results and Discussion

The infrared spectra of 703-2BK and 703-2PS are shown in Fig. 2. The peaks at 2850 and 2900 cm^{-1} due to aliphatic CH symmetric and antisymmetric stretching are largely enhanced by the hydrogenation of the pitch of 703-2. Since condensed aromatic hydrocarbons are mainly converted to saturated or partially saturated ring compounds by BenKeser reduction,[4] in this case also some naphthenic hydrocarbons are considered to be present in 703-2BK. The results of elemental analyses and the hydrogen-to-carbon atomic ratio of the additives are given in Table 1, along with that of 703-2. The hydrogen content increases with the BenKeser reduction, but some of the hydrogens added are eliminated by treatment *in vacuo* at these temperature ranges. The extent of dehydrogenation for 703-2BK is much higher than that for 703-2PS. This was confirmed by the analysis of the gas evolved on the heat-treatment of these samples. This suggests that the hydrogens in naphthenic rings formed by the saturation of the aromatic molecules are unstable. The average molecular weight for 430-2BK is comparable to that for 703-2PS at the same treatment temperature (Table 2). However, an increase in the temperature tends to raise the molecular weight and, at the same time, to form PI, although the QI are negligibly small for all the samples except for 703-2. The formation of PI may be considered to

Table 2. Molecular weight, PI, and QI of additives

Additive	Average molecular weight[a)]	PI (wt%)	QI (wt%)
703-2	—	18.6	10.3
703-2BK (623)	780	0.0	0.0
703-2BK (648)	1005[b)]	2.6	0.1
703-2PS (623)	670[b)]	4.7	0.4
703-2PS (648)	1025[b)]	5.6	0.4

a) Measured in pyridine by means of a vapor-pressure osmometer. b) Obtained on the sample without PI.

Table 3. Effect of addirives on PI and QI contents of 683-4

Additive	PI (wt%)	QI (wt%)
—	15.2	8.6
703-2BK (623)	8.1	7.1
703-2BK (648)	9.4	8.1
703-2PS (623)	14.0	8.0
703-2PS (648)	15.4	8.9

result from the condensation of large molecules and from a decrease in the fluidity due to the elimination of the molecules with comparatively low molecular weight on evacuation. No appreciable amount of PI could be detected when these additives were treated in a sealed ampule at 623 K for 1h.

Table 3 show the data for pyridine and quinoline insolubility when the mixture of the pitch of 683-4 and additives was treated at 623 K for 1 h. Since the insoluble fractions are already involved in 703-2BK (648), 703-2PS(623), and 703-2PS(648) (Table 2), the values of PI were corrected for the mixture with these additives. When the pitch hydrogenated was used as an additive, about half of the PI in the pitch of 683-4 was dissolved and converted to a component soluble in pyridine. On the contrary, when 703-2PS(623) and (648) were added and treated, no effect could be observed on the values of PI and QI. It can be presumed, on the basis of these results, that hydrogen transfer is needed to dissolve the pyridine-insoluble component, for the additives of 703-2BK contain the labile naphthenic hydrogens described above.

A microscopic observation of the whole sample of the 683-4 alone shows that the pitch contains both mesophase spherules with a wide range of distribution in terms of diameter and a flow texture which settles at the bottom of the sample tube. Also, the pyridine-insoluble fraction of this pitch consists of isotropic and anisotropic phases, whereas the QI fraction is composed of almost anisotropic textures where both large mesophase spherules and a partially coalesced flow domain are present. In the case of the mixture of 683-4 and 703-2BK, anisotropic components were predominantly observed in the PI of the mixture treated. These observations may indicate that the isotropic part and the small spheres in the PI of 683-4 are dissolved upon the addition of 703-2BK. The rough agreement between PI and QI values upon the addition of 703-2BK in Table 3 might be qualitatively consistent with the optical observations; both PI and QI are mainly composed of anisotropic textures with large spheres and flow domain.

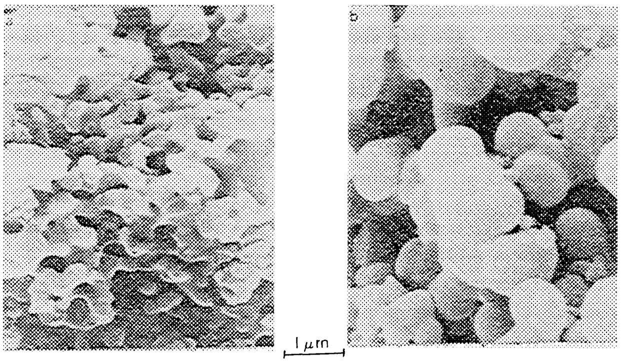

Fig. 3. Scanning electron microphotographs. (a): pyridine insoluble component from 683-4, (b): pyridine insoluble component from the mixture of 683-4 and 703-2BK(623).

The size and the shape of particles in PI were observed with a scanning electron microscope. While in the PI from the 683-4 pitch small spheres (0.3 μm) are partially fused and linked with each other in spherules of about 1 μm, spherical bodies of about 1 μm in size are agglomerated, and each body has round shape near a true sphere, in the case of the PI from the mixture of 683-4 and 703-2BK(623), as can be seen in Fig. 3.

It can be considered, therefore, that the hydrogenated pitch used as an additive dissolves small spherules and the optically isotropic texture connecting these spherules.

References

1) M. Ihnatowicz, P. Chiche, J. Deduit, S. Pregermain, and R. Tounant, *Carbon*, **4**, 41 (1966).

2) H. Honda, H. Kimura, Y. Sanada, S. Sugawara, and T. Furuta, *Carbon*, **8**, 181 (1970).

3) Chwastiak and I. C. Lewis, *Carbon*, **16**, 156 (1978).

4) J. D. Brooks and H. Silberman, *Fuel*, **41**, 67 (1962).