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Carbon Products Prepared from Variant Pitch Materials. VI. Pitch Carbon Prepared from Naphtha Cracking Pitch

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It was previously reported that a carbon rod or tablet could be prepared from specific variant pitch materials alone instead of from coke powder and a pitch binder.[1-5] The carbon-shaped articles prepared by this method were referred to as Pitch Carbon, and coal-tar pitch was used as the raw pitch material in the previous experiments. In this case, some special, very trouble some pre-treatments[1-3,5] were required in preparating the pitch carbon in order to elevate the softening point of the raw coal-tar pitch and/or to increase its reactivity in the heating process.

This work was undertaken in order to search for better raw pitch materials for the preparation of pitch carbon, it was found that the pitch produced in the naphtha cracking process is an interesting raw material for pitch carbon.

Experimental

The raw pitch material used here was naphtha cracking pitch (Ligare-N) supplied by the Kureha Chemical Ind. Co., this pitch had a softening point of 193—196°C and had the elemental composition shown in Table 1. The raw pitch was crushed to under 100 mesh and then pressed with 400 kg/cm² into tablets of 20 mm in diameter and about 4 mm thick. The tablets were pre-heated in air up to 300°C over a 7-hr period. When the heating rate of this process was too fast, the tablets fused or blistered. Consequently, in the range of temperatures from 180° to 230°C, the heating rate was controlled to 0.3°C/min. The resulting tablets were heated under a stream of N_2 gas at the desired temperatures below 2600°C for 10 min. The heating rate was 5°C/min up to 1000°C and 50°C/min at temperatures higher than 1000°C. The measurement of the properties of the resulting pitch carbon was carried out according to the procedures previously described.[2]

Table 1. Changes in elemental compositiions of naphtha cracking pitch and coal-tar pitch by heating in air

Kind of pitch		C(%)	H(%)	diff.(%)[b]
Naphtha	Raw	94.3	4.5	1.2
	After pre-heating	79.4	3.8	16.8
Coal	Raw	91.5	4.6	3.9
	After pre-treatment[a]	92.0	3.9	4.1

a) Raw pitch was distilled at 400°C for 80 min by bubbling air, powdered after cooling, and then heated in air up to 200°C.[3]

b) diff. (%)=100 −C(%) −H(%)

Results

Four characteristic phenomena were observed in the present experiments compared with the case of using coal-tar pitch.

(1) The pre-treatment on the raw pitch material as reported in the previous papers[2-3,5] could be eliminated from the process of preparing pitch carbon without any trouble.

1) S. Ōtani, G. Kubota, A. Ōya, and T. Koitabashi, *Tanso*, No. 52, 13 (1968).
2) S. Ōtani, A. Ōya, and T. Fukabori, *Kogyo Kagaku Zasshi*, **72**, 317 (1969).
3) S. Ōtani, A. Ōya, I. Nakagawa, and T. Fukabori, *ibid.*, **72**, 323 (1969).
4) S. Ōtani and A. Ōya, *ibid.*, **73**, 1110 (1970).
5) S. Ōtani, A. Ōya, and T. Nagashima, *ibid.*, **73**, 2095 (1970).

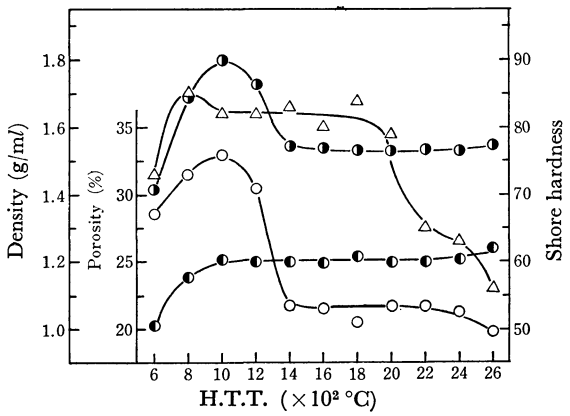
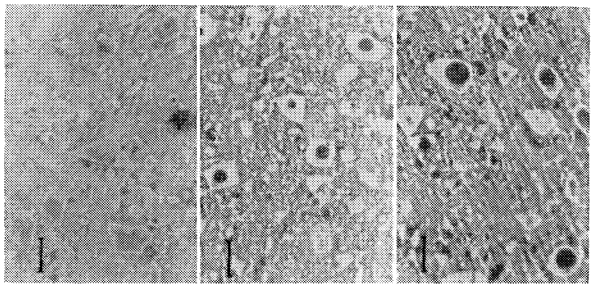


Fig. 1. Changes of density, porosity, and hardness with H.T.T. (—○— Apparent porosity, —◐— Bulk density, —◑— Apparent density, —△— Shore hardness)

(2) As is shown in Fig. 1, the most characteristic feature of the pitch carbon obtained here was its much greater hardness for its low-bulk density as compared with that of the pitch carbon prepared from coal-tar pitch[2-3] or conventional artificial graphite.[6] The pitch carbon finally obtained was non-graphitizable.

(3) Considerable amounts of oxygen were incorporated into the pitch by pre-heating up to 300°C. This phenomenon was not observed at all in the case of coal-tar pitch, as is shown in Table 1. From its infrared spectra and elemental analysis, it was found that the oxygen incorporated is in the form of C=O (1700 cm^{-1}) and C–O (1200 cm^{-1}) and is eliminated during the further heating process under a N_2 gas atmosphere.

6) M. Ichinose, *Tanso*, **1**, 7 (1949).



(a) After heating up to 300°C in air (b) 800°C (c) 1600°C

Fig. 2. The microscopic textures of the pitch carbon. (|——| 100μ)

(4) In the tablets heated above 600°C, the closed pores formed in most of the larger particles, as is shown in Fig. 2.

Discussion

The fact described in (3) indicates that the naphtha cracking pitch has a higher reactivity to oxygen in air than does coal-tar pitch. This reactivity accelerates to sinter or bridge among the pitch particles and/or molecules. The high softening point and this reactivity of the pitch may it possible to eliminate the pre-treatment required in the case of coal-tar pitch. It seems that the rigid layers from at the surface of the particle at an early stage of heating and result in the closed pores in the large particles during the subsequent carbonization process. The characteristic feature pointed at in (2) is probably due to those closed pores.