

INFLUENCE OF SULFUR AND METALS ON MESOPHASE FORMATION

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Introduction

When petroleum residue containing the large amounts of sulfur is heat-treated, mesophase formed in this residue shows the fine mosaic texture. By addition of inorganic sulfur to the pitch which showed the fibrous texture, the texture of mesophase turns the fine mosaic. Marsh et al(1) reported that the size of the mesophase spheres formed in anthracene was about 25 μ m, and the size of the mesophase spheres formed in anthracene and 10wt% of ferrocene was 10 μ m. It is considered that the mesophase texture formed in the petroleum residue is the fine mosaic because sulfur and metals in the petroleum residue prevent two processes of the mesophase spheres growth and of smoothly proceeded molecular rearrangement in the coalesced mesophase. This report describes the influence of sulfur and metals containing the pitch on the mesophase texture.

Experimental

Cracked oil used is thermal cracked oil which is obtained from Khafji asphalt heat-treated at 420°C for 70 min, contains about 3 wt% sulfur and is free from metals. This oil is mixed with vanadium acetylacetonate, nickelocene, ferrocene and copper phthalocyanine, and the mixtures are heat-treated at 430°C for a certain period and were observed by using a polarized-light microscope.

Results and Discussion

Khafji asphalt, cracked oil and the mixtures of cracked oil and organometallic compounds are heat-treated at 430°C for 180 min. The sulfur and metal contents in those samples are shown in Table 1. The sulfur content is about 6wt% for all the samples. The metal contents are 420 ppm for Khafji asphalt, 32 ppm for cracked oil and from 802 to 2840 ppm for the mixtures. Micrographs of those samples are shown in Fig.1. Mesophase formed in Khafji asphalt shows the fine mosaic texture and that in cracked oil shows the fibrous texture in spite of 6wt% sulfur content (Fig.1-a). Mesophase shows the fibrous texture for the mixture of cracked oil with Cu, the coarse mosaic texture for cracked oil with Fe and the fine mosaic texture for cracked oil with Ni and V (Fig.1-b). Thus, the mesophase textures are different with kinds of metal added in cracked oil and influence of metals on the

growth process of the mesophase spheres is stronger than sulfur.

It is clear that the texture of mesophase do not be influenced by existence of organic sulfur compounds in cracked oil. The mesophase texture in coal-tar pitch free from sulfur with 1wt% Fe (Ferricene) (2) showed the coarse mosaic and turned to the fine mosaic with increase of Fe. Amount of Fe in cracked oil, which cause transformation from the fibrous texture to the coarse mosaic texture, correspond to about 0.1 times amount of Fe in coal-tar pitch. Therefore, the change of the mesophase texture occurs easily with coexistence together sulfur and metals.

On the other hand, Fig.2 shows amounts of quinoline-insolubles in cracked oil heat-treated at 430°C as a function of residence time. Amounts of quinoline insolubles correspond to the amounts of mesophase transformation. The amounts of mesophase transformation increased in order of Fe, Ni and V in cracked oil for a definite time. This result indicates that the mesophase transformation is accelerated by organic sulfur compounds and Ni, V in cracked oil during heat treatment. In other words, Ni and V in cracked oil function as the catalyst which accelerate mesophase.

Also, from comparison of Fig.1 and 2, it is considered that the mesophase texture is related to the increase rate of the mesophase transformation, that is, in the case of the mixture of cracked oil with Ni or V, those mesophase spheres coalesce with each other after growth up little and the coalesced mesophase shows the fine mosaic texture because the large amounts of mesophase in the cracked oil are formed at the same time by the catalytic action of Ni or V.

Dickie et al (3) reported that the asphaltene containing petroleum residue form the micelle structure, and these micelles are containing organic sulfur compounds and metal compounds. When the asphaltene in petroleum residue was heat-treated, mesophase formed in the asphaltene showed the fine mosaic texture. Therefore, it is suggested that organic sulfur compounds and Ni, V in cracked oil change into molecules constructing mesophase with the thermal decomposition and polymerization, form the micelle structure and the formed micelles nucleate the fine mosaic texture of mesophase.

References

1. Marsh, H., Foster, J. M., Hermon, G. and Hey, M., Fuel, Lond. 52, 234 (1973)
2. Oi, S., Yamada, Y. and Honda, H., Tanso No. 85, 47 (1976)
3. Dickie, J. P. and Yen, T. F., Anal. Chem., 39, (14), 1847 (1967)

Table 1 Metal contents and sulfur content

Sample	Metals (ppm)				S (%)
	V	Ni	Fe	Cu	
Cracked oil	10	12	8	0	6.0
Cracked oil+V	802	-	-	-	-
Cracked oil+Ni	-	1200	-	-	6.0
Cracked oil+Fe	-	-	913	-	5.3
Cracked oil+Cu	-	-	-2840	-	5.4

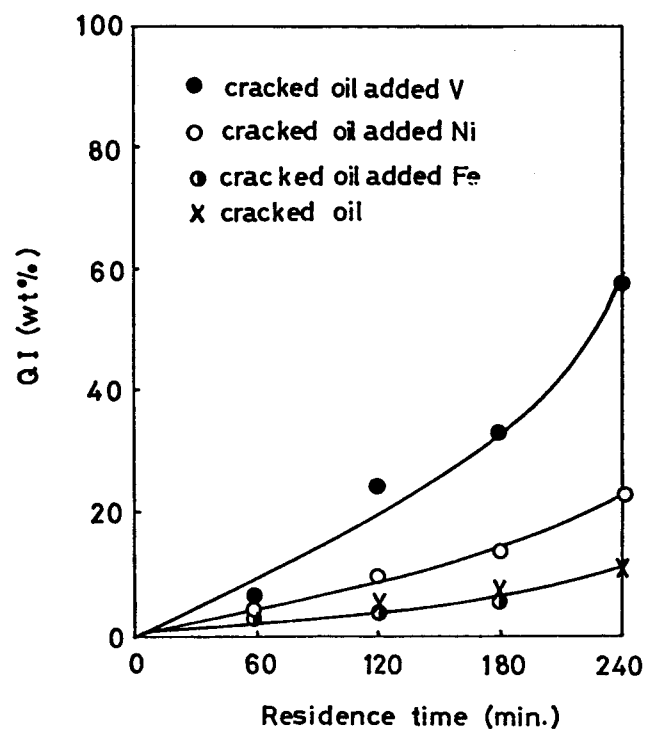


Fig. 2 Relation between amounts of quinoline insolubles and residence time

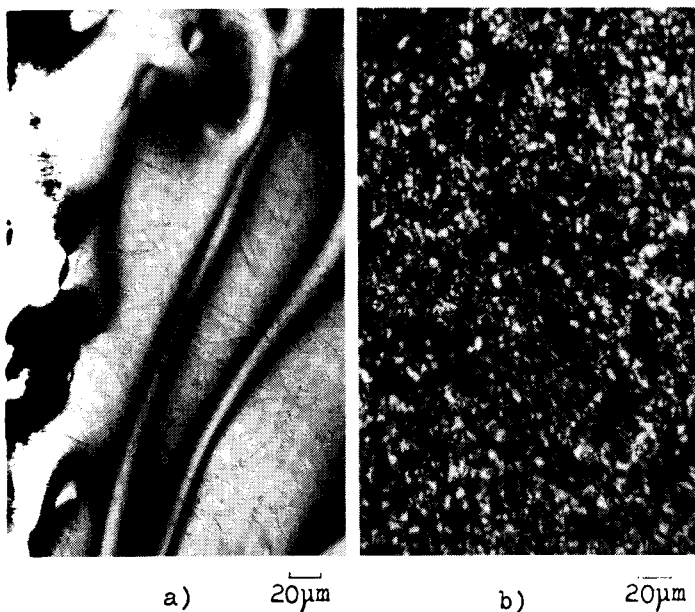


Fig. 1 Mesophase formed in cracked oil heat-treated at 430°C for 180 min.

a) cracked oil b) cracked oil added V