

ESTIMATING THE CONCENTRATION OF SECONDARY QUINOLINE INSOLUBLES†

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(Received 17 July 1985; in revised form 8 August 1985)

Abstract—The concentration of secondary quinoline insolubles (SQI) in coal tar pitches corresponds to the increase of quinoline insolubles (QI) due to the heat treatment. A series of experimental pitches was used for the analytical estimate of SQI by several methods sensitive to heat treatment.

The determination of the size of QI by small angle, forward-scattering light from a laser beam projected through a stream of isolated QI dispersed in toluene yielded results most suitable for the quantitative estimate of SQI concentration in heat treated coal tar pitches.

Key Words—Coal tar pitch, quinoline insoluble, light scattering, toluene, laser.

1. INTRODUCTION

Primary quinoline insolubles (PQI) is formed by vapor phase cracking of tar vapors during carbonization and is concentrated in pitch after the distillation of tar is completed.

When the concentration of quinoline insolubles does not reach the specified level of QI in industrial pitches additional QI may be formed by exposing tar or pitch to elevated temperatures (380–450°C) for an extended period of time (1–5 hours).

Since heat treated and non-heat-treated industrial pitches perform differently when industrial carbons are fabricated the users of pitch need a reliable analytical tool for estimating the degree of heat treatment. SQI seems to be the most suitable indicator for assessing this property of pitch.

A method for the quantitative determination of PQI by absorption of microwaves was published[2]. This procedure yields unreliable data when the microwaves are absorbed by the isotropic matrix of pitch.

The objective of this paper is to evaluate the merits of other procedures suitable for estimating the concentration of SQI.

Because there is no method known for an effective separation of PQI from SQI, the change in properties of the total amount of isolated QI due to the presence of SQI has to be used for analytical determination.

SQI differs from PQI in three properties:

1. It may be detected in polished pitch samples by optical microscope in reflected light as mesophase spheroids.
2. The concentration of hydrogen is higher in SQI because the dehydrogenation in the liquid phase is not as intensive as in the vapor phase.
3. The size of SQI is usually larger than the size of PQI (around 1 μm).

2. EXPERIMENTAL

All pitches were prepared by vacuum distillation of tar to pitch softening point of 110°C. Pitches containing SQI were prepared from tars heat-treated under nitrogen atmosphere in agitated autoclave for 1 to 2 hours and at temperatures of 420–450°C.

The increase of QI by heat treatment (=SQI) was calculated so that the concentration of PQI was subtracted from the total QI (PQI + SQI) found in heat treated pitches. This concentration of PQI was determined from the concentration of QI in control pitches (no heat treatment) corrected for the difference in pitch yields in control and heat treated samples.

QI were isolated from pitches by the procedure previously published[3]. The principle of the procedure is dissolving pitch in hot quinoline and separating QI by filtration of this solution through a heated pressure filter. The filter cake of QI was washed with acetone and dried at 110°C.

The determination of mesophase in heat-treated samples was performed by Dr. David Ball, Union Carbide Corporation, according to the published procedure[4]. The principle of the procedure is the determination of the area occupied by mesophase spheroids in a micrograph of the pitch sample encapsulated in resin and polished to a flat surface for examination in reflected light by optical microscope.

The determination of carbon and hydrogen of isolated QI was performed by Koppers Analytical Department using the common method of ultimate analysis.

The determination of particle size of isolated QI was performed by Dr. Plantz at Leeds & Northrup Microtrac Laboratory using the Microtrac 7991-2 Small Particle Analyzer. This instrument utilizes the phenomenon of Fraunhofer diffraction[5].

Light from a He-Ne laser beam is projected through a stream of particles dispersed in a suitable liquid. Small particles cause light to be scattered at larger angles than large particles, but at a lower intensity. Appropriate optical treatment and digital technology permit collection of the scattered light and final presentation of the particle

†Presented at the 114th AIME Meeting in New York City, 1985[1].

Table I. Properties of QI and mesophase content in experimental pitches, S.Pt. = 110°C

Pitch No.	Pitch from Tar No.	QI %	PQI (a) %	SQI (b) %	SQI in QI %	QI Size, 50% Mean, (c) μm	C/H of QI	H of QI %	MPh (d) %	Heat Treatment
128-230	1	9	9	0	0	1.2	3.8	2.0	0	No
128-239	1	10	8.3	1.7	17	3.3	3.5	2.2	1.6	Yes
4493-28	1	10	7.8	2.2	22	3.2	2.6	2.2	1.6	Yes
128-257	1	12	8	4	33	5.3	3.2	2.4	6.0	Yes
128-235	2	6	6	0	0	2.7	4.2	1.9	0	No
128-236	2	9	5.2	3.8	42	6.0	2.9	2.7	2.1	Yes
128-149	3	8	8	0	0	1.2	4.0	1.9	0	No
128-151	3	9	7.6	1.4	16	3.7	3.3	2.4	0	Yes
128-152	3	11	7.3	3.7	34	4.0	3.1	2.6	0	Yes

Notes:

- (a) PQI = Primary QI
 (b) SQI = Secondary QI
 (c) Determined by Microtrac Small Particle Size Analyzer
 (d) MPh = Mesophase (Since the specific gravity of mesophase is about the same as the specific gravity of pitch, volume % mesophase determined by optical microscopy may be taken as equal to weight %).

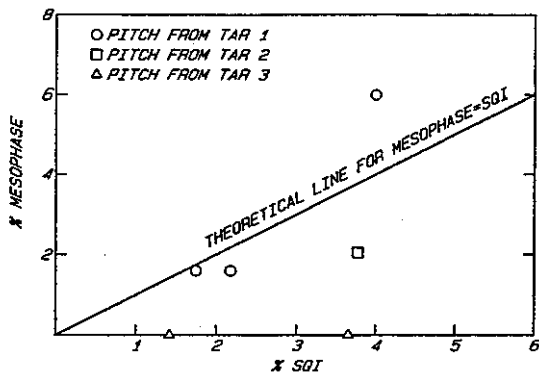


Fig. 1. The correlation % mesophase versus % SQI.

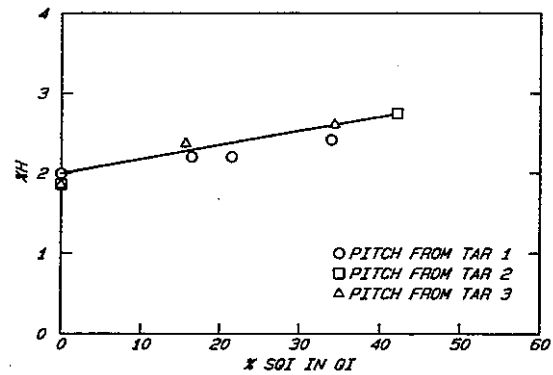


Fig. 3. The correlation of % H in isolated QI versus % SQI in the total of isolated QI.

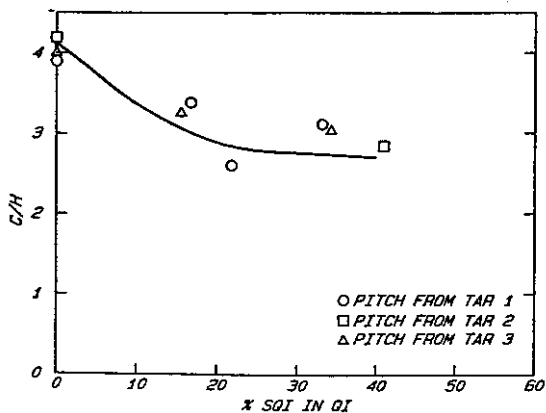
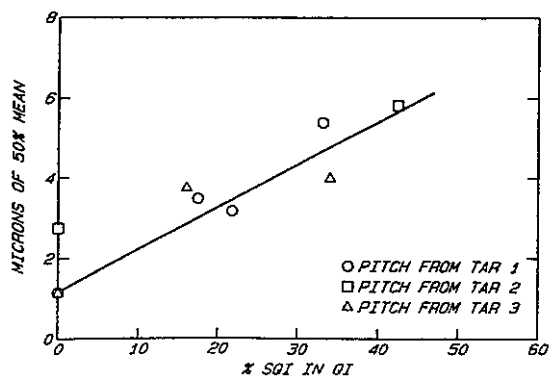


Fig. 2. The correlation of C/H in isolated QI versus % SQI in the total of isolated QI.

Fig. 4. The correlation of QI size in μm versus % SQI in the total of isolated QI.

size as a volume size distribution in a variety of selectable formats.

A small amount (40–80 mg) of isolated QI was dispersed in 80 ml toluene for about 3 minutes in an ultrasonic probe at 300 watts and was evaluated by light microscopy for confirmation of complete dispersion. As long as the concentration stays within 0.05–0.1% the measurement of the particle size distribution is not affected. A portion of the prepared sample was transferred to a small volume recirculator pump containing toluene for transport through the laser beam and subsequent particle size measurement. The median size (50th percentile) was used as the size characteristic of the sample. The repeatability of the measurement is about $\pm 3\%$ and the results are not affected by the roughness of the particles which is similar in the case of coal tar pitches which always contain aggregates of SQI with PQI.

3. RESULTS (summary given in Table 1)

3.1 *Mesophase* (Fig. 1) determined by optical microscopy is unsuitable for the estimate of SQI.

In the case of pitch from Tar 1, the mesophase concentration was in two instances fairly close to the concentration of SQI. Nevertheless, the concentration of mesophase was too high at higher concentration of SQI in this pitch. In the case of pitch from Tar 2, the concentration of mesophase was too low.

In the case of pitch from Tar 3, no mesophase was detected, although a considerable concentration of SQI was present.

3.2 *C/H Ratio and H concentration of isolated QI*

C/H ratio and H concentration of isolated QI have been used for many years as a qualitative indicator for heat-treated pitches. The correlation in Fig. 2 indicates that C/H ratio is not a consistent indicator for the concentration of SQI. Although it is fairly sensitive to heat treatment, i.e. it drops when SQI is present, it does not show any good trend with the increasing concentration of SQI. The main reason for this is inadequate accuracy in the determination of high concentration of C in the sample of QI.

Percent H (Fig. 3) is a much better indicator—it shows a steadily increasing trend with the increasing concen-

Table 2. Estimated concentration of SQI in isolated QI from the size determined by Microtrac

Sec. QI in QI, %	QI Size, μm 50% mean
0	1-2
10	2-3
20	3-4
30	4-5
40	5-6
50	6-7

tration of SQI. The disadvantage is very low sensitivity (small slope of the correlation) to the change of SQI concentration.

3.3 *Particle size of QI* (Fig. 4)

Particle size of QI measured by Microtrac is sensitive enough to the concentration of SQI and, therefore, seems to be the best method for estimating the degree of heat treatment.

Table 2 is based on the linear correlation in Fig. 4 and may be used for estimating the concentration of secondary QI when the particle size distribution of isolated QI is known.

The estimated concentration of SQI corresponds to the percentage of SQI (given in Table 2) from the total amount of QI determined by filtration. The comparison between the actual and estimated concentration of SQI for pitches listed in Table 1 is given in Table 3. The agreement between the actual and estimated values is fair considering an indirect method used for estimating the SQI concentration.

4. DISCUSSION

Mesophase determination cannot be used for estimating SQI concentration. One reason is the solubility of mesophase in quinoline[6]. Secondly, the presence of PQI influences the formation of mesophase—higher concentration of PQI delaying the development of mesophase[7].

During the heat treatment of tars and pitches a stage is reached when the products of polymerization and polycondensation separate as a second phase. In the absence of PQI this second phase has initially a form of tiny

Table 3. Comparison between actual and estimated (from size) concentration of SQI

Pitch No.	QI, %	Sec. QI, %	Estimated		QI Size, μm 50% mean
			Sec. QI, %	QI, %	
128-230	9	0	0.0		1.2
128-235	6	0	0.6		2.7
128-149	8	0	0.0		1.2
128-151	9	1.4	1.8		3.7
128-239	10	1.7	2.0		3.3
4493-28	10	2.2	2.0		3.2
128-257	12	4.0	4.8		5.3
128-152	11	3.7	3.3		4.0
128-236	9	3.8	4.5		6.0

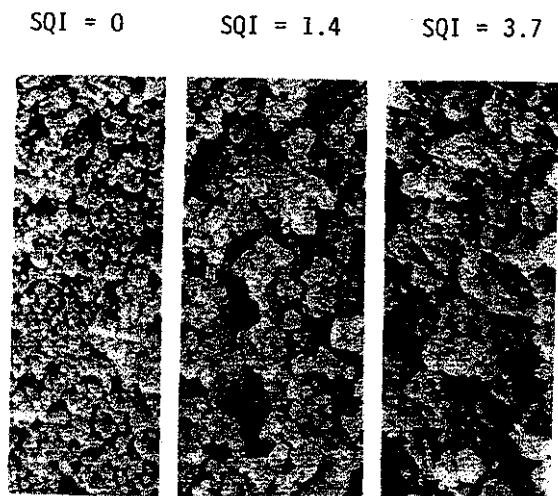


Fig. 5. Comparison of isolated QI from untreated and heat treated pitches (SEM, 2000 \times) after dispersion by ultrasound for 70 seconds in toluene.

spheres (1 μm or less). These spheres grow with progressive degree of heat treatment and become detectable by optical microscopy when they reach a definite minimum size (about 4 μm for magnification 400 \times –500 \times).

In the presence of PQI the growth of spheres by coalescence is suppressed due to the formation of aggregates of PQI with SQI.

Although the formation of these aggregates contributes to the size increase of insoluble particles and also to higher value of total QI, the detectability of mesophase by optical microscopy is not possible as long as the individual anisotropic spheroid within the aggregate remains small, i.e. below the detection limit of the optical microscope.

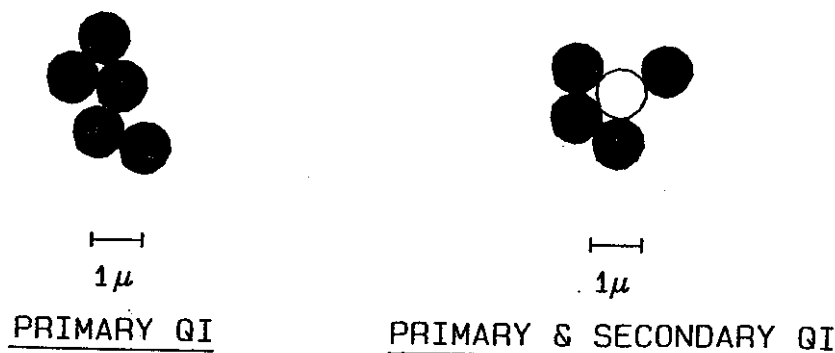
The isolated QI from the samples 128–149 (no heat treatment) and heat treated samples 128–151 and 128–152 with no detectable mesophase were observed by SEM. The increasing size of QI from these samples is apparent from the comparison given in Fig. 5 and showing scanning electron micrographs (2000 \times) of particles isolated from the above pitches.

What is likely to happen by heat treatment of pitches with sizable concentration of PQI is illustrated in the following Fig. 6.

In untreated pitches the PQI is present either in the form of individual particles or clusters of PQI easily dispersible in a solvent by means of ultrasound. The particle size of QI isolated from untreated pitches corresponds in this case to 1–2 μm .

The SQI formed by heat treatment is formed in preference at the surface of PQI as spheres of about the same or even smaller size than PQI (about 1–2 μm). Due to the formation of aggregates of SQI and PQI the average size of the isolated QI grows. Contrary to the case when PQI only are present, the aggregates from PQI and SQI cannot be dispersed by ultrasound in a solvent like toluene due to the residual plasticity of SQI and consequently more coherent aggregates.

Although at a magnification of 400–500 \times used for quantitative determination of mesophase (detection limit 4 μm) in pitch the mesophase spheres were not detected in samples 128–151 and 128–152, it was possible to trace



THE AGGREGATE CAN BE DISPERSED
IN SOLVENT BY ULTRASOUND

THE AGGREGATE CANNOT BE DISPERSED
IN SOLVENT BY ULTRASOUND

Fig. 6. Mechanisms of SQI formation in the presence of PQI (black circles represent PQI, white circles are SQI).

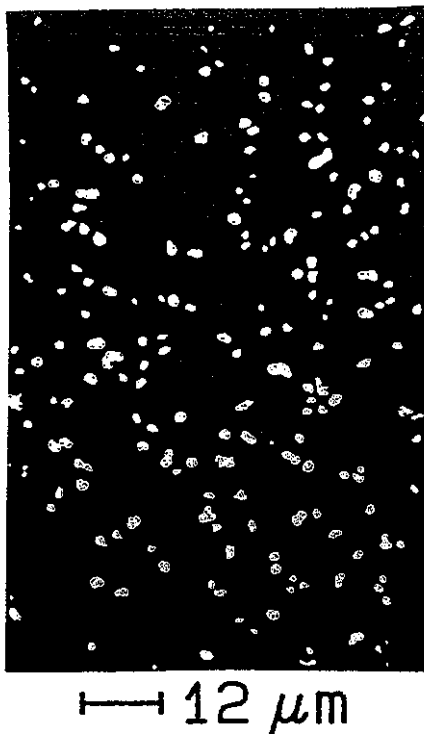


Fig. 7. SQI in isolated QI observed by optical microscope in polarized light with crossed nicols at $800\times$ magnification (negative picture of mesophase spheres traced with black ink on a transparent template).

by optical microscopy the onset of mesophase particles (about μm) within the aggregates with PQI when the quinoline insolubles were isolated, mounted in resin, polished and observed at a magnification of $800\times$ (Fig. 7). Due to the lack of contrast between mesophase spheroids and PQI in the original microphotograph the SQI

particles apparent as light dots in the micrograph were traced by the draftsman on the transparent template. Figure 7 is the negative picture of the template.

5. CONCLUSION

The size of isolated QI determined by Microtrac seems to be the best criterion for estimating the concentration of SQI. The results of this procedure are sensitive to the degree of heat treatment even in cases when mesophase cannot be detected by optical microscopy in heat treated pitches.

Acknowledgement—The author wishes to thank Dr. David R. Ball, Union Carbide Corporation, for analyzing the pitch samples on mesophase concentration and to Dr. P. E. Plantz, Microtrac Products, Leeds & Northrup for the determination of the particle size distribution of isolated QI.

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