THE EFFECT OF PITCH QUINOLINE INSOLUBLES ON GRAPHITE PROPERTIES

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INTRODUCTION

For several years Airco Speer has been working with raw materials suppliers in order to characterize or better define these raw materials, in terms of their effects on final graphite properties. In particular, Airco Speer's work with Allied Chemical Company, a major pitch supplier, was directed toward the development of a better electrode binder, through a clearer definition of their process parameters (such as column atmospheres, distillation temperatures, tar sources and other feed stream variables), as they affect pitch characteristics, hence, graphite properties.

Of the many pitch characteristics specified by the graphite electrode industry,[1,2,3] the Q.I. content was chosen the subject of this investigation. The Q.I.'s consist primarily of solid particles[4,5,6] ranging in size from colloidal to coarse[7]. The colloidal particles are mostly complex hydrocarbons of high molecular weight. They are derived from the decomposition of coal directly or may be derived indirectly from the condensation and dehydrogenation of small aromatic molecules coming from the coal. The coarse particles can be any insoluble "dirt", such as coal or coke dust. The function of the Q.I. is to provide sites for crystallite growth (nucleation) during carbonization or graphitization.[8]

Many investigators feel that the Q.I. of coal tar pitch is important in determining graphite quality.[9,10] It is known, for example, that the higher the Q.I., the higher will be the graphite strength, density and conductivity. However, Q.I. levels of over 16 to 18% generally have no beneficial effect and, in fact, may be detrimental. Not as well known, but perhaps more important, is the type of Q.I., vis., the process parameters by which certain levels are attained, affect not only those levels, but also the nature of the Q.I., and, consequently, may affect the nature of the graphite.

EXPERIMENTAL

After managerial approval of both Companies, the basic plan was formulated. A 3 x 4 factorial-type experiment was proposed in which Allied would process one low (~5%) Q.I. tar by filtration, distillation, two heat treatments, addition of Thermax (a thermatomically decomposed "black") and blending. Four different pitches would initially be made. Each would be modified by the processes described, to contain three levels of Q.I. --about 7, 14 and 21%. Twelve (12) pitches in all would result.

In the preparation of the raw materials and the blend components (Figure 1), the starting material was feed Tar "A", with a low (5%) Q.I. This tar was filtered to yield low (4%) Q.I. Pitch "Z". This, in turn, was used as the blending pitch for Processes I through IV. The residue from feed Tar "A" was used to make the high (12%) Q.I. Tar "B", which was used as the raw material in Processes I and II.

In the preparation of natural Q.I. pitches (Process I), the high Q.I. Tar "B" was distilled (Figure 2) to yield a high Q.I. Pitch "Y", raising the Q.I. from 12 to about 21%. This pitch was blended with low Q.I. Pitch "Z" to give Pitches "X" and "W", thus lowering the Q.I. to about 7 and 14%, respectively.

The pitches in Process II were produced from the high Q.I. Tar "B" in Process I (Figure 3). This pitch was distilled to yield Pitch "U", with a Q.I. of 21%. As in Process I, this pitch was blended with low Q.I. Pitch "Z" to give Pitches "T" and "S", again, lowering the Q.I. to 7 and 14%, respectively.

The high Q.I. tar from Experimental Process II was used in preparing the pitches in Process III (Figure 4). This tar was distilled to yield Pitch "P", with a Q.I. of about 21%. Pitch "P" was blended with Pitch "Z" to give Pitches "Q" and "N", with Q.I.'s of 7 and 14%, respectively.

Process IV pitches were prepared by starting with one of the original raw materials, low Q.I. Tar "C", which was feed Tar "A" with the insolubles removed by filtration. The low Q.I. Tar "C" then had Thermax dispersed in it, thus raising the Q.I. from 2 to about 12% (Figure 5), resulting in high Q.I. Tar "E". By distillation, the Q.I. was increased to about 21% and was now called Pitch "M". The Q.I. content of Pitch "M" was lowered to 7 and 14%, by blending with Pitch "Z" to yield Pitches "L" and "K", respectively.

The characteristics of all these pitches, as received by Airco Speer, is shown in Table 1. Since Allied used new or modified polymerization techniques, it proved difficult to make some of the pitches with specific Q.I. values. In particular, Pitch "P" was considerably lower in Q.I. than predicted. To be consistent with their process scheme, it would have been economically impractical or technically impossible for them to change their processing to raise the Q.I.

When Airco Speer received the pitches, they were extruded in an electrode formulation in the Pilot Plant, in five inch diameter rods. Concurrently, a control lot, using a standard binder pitch, was also extruded.

It was the intention to extrude all pitches at three binder levels, according to standard Pilot Plant operating procedures. However, Pitches "K", "M" and "P" were non-extrudable at the lower binder level. The as-formed rods were then baked to about 800 C in the Pilot Plant furnace, then graphitized to about 2800 C. All stock was tested by the Chemical and Physical Measurements Group of the Research Department.

RESULTS AND DISCUSSION

Table 2 summarizes all of the pertinent graphite data and also gives the relative

Table 1

CHARACTERISTICS OF 12 ALLIED EXPERIMENTAL PITCHES

Pitch Type	Softening Point C	Q.I. (Predicted) %	Q.I. (Airco Speer) %	Q.I. (Allied) %	Carbon Disulfide Insoluble %
Y	102	21.0	20.5	20.0	34.1
W	104	14.0	14.6	14.5	32.9
X	103	7.0	9.9	8.6	29.2
M	103	21.0	20.8	21.7	38.4
K	104	14.0	15.6	15.0	34.2
L	102	7.0	9.4	8.9	28.1
U	105	21.0	17.4	18.9	37.1
S	105	14.0	13.8	12.0	33.8
T	105	7.0	9.4	7.3	29.8
P	105	21.0	12.3	10.9	35.5
N	105	14.0	10.7	9.7	32.6
Q	105	7.0	7.7	7.2	28.5

binder levels at which the formulations were extruded. Since these were electrode formulations, it is reasonable to assume that the spread in binder levels, 2 pph, can result in significant differences in graphite properties. The actual binder levels and formulations are proprietary. It should also be noted that the graphite properties are coded. Though the actual values are not represented, they do show the true, relative differences in values, which correctly shows the change in effects due to the different pitches.

A portion of the data is graphically represented in Figures 6, 7 and 8. Only the optimum values for some of the most important properties were plotted. These values are: transverse coefficient of thermal expansion (T-CTE), flexural strength and apparent density. Thus, for the T-CTE's (Figure 6), only the binder levels that resulted in the lowest CTE, were considered. Those binder levels are not necessarily the same ones that resulted in optimum flexural strengths (Figure 7) or apparent densities (Figure 8), and vice versa. In determining the suitability of a particular pitch for further evaluation, a compromise is sometimes necessary in considering which binder levels merit most attention.

On this basis, the most important process, in terms of T-CTE, is Process III. In particular, Pitch "P", at its optimum value (Figure 6), had a T-CTE of about 0.54×10^{-6}/C, which was substantially lower than the standard. However, the flexural strengths (Figure 7) were also lower, but could be increased, if required, through impregnation. It is of further interest to note that all of the T-CTE's were either lower or equivalent to the standard, with no apparent degradation of structural integrity.

Pitch "Y", from Process I, is also important, not only because of its low graphite T-CTE, but also because the flexural strengths and apparent densities (Figure 8) were at least equivalent to the standard. From the same standpoint, but to a somewhat lesser degree, Pitches Q, N and W were also important because of their low T-CTE's. Graphite strengths were equivalent to the standard.

From the longitudinal electrical resistivity data (Table 2) it can be seen that all the values were higher than the standard, with the exception of graphites from Pitches "T", "U" and possibly "L" and "N", which were about equivalent. However, even those with equivalent resistivities were no better than the standard, in terms of apparent density, flexural strength or transverse CTE.

CONCLUSION

The most significant fact to arise out of our research is that graphite physical properties, such as CTE, flexural strength, apparent density and electrical resistivity, are apparently unrelated to pitch Q.I. levels, alone, but to the nature or type of Q.I. This, in turn, is directly related to the method of preparation, i.e., process route, by which specific Q.I. levels are attained.

GRAPHITE PROPERTIES OF 12 ALLIED EXPERIMENTAL PITCHES

Pitch Type	Pitch Process	AD g/cc	Long. Resist. x 10^{-5} ohm-in	Trans. Resist. x 10^{-5} ohm-in	Long. CTE x 10^{-6}/C	Trans. CTE x 10^{-6}/C	FS psi	Binder Level
K	IV	1.23	7.8	18.1	0.59	1.32	499	M
K	IV	1.15	9.5	10.9	0.57	1.14	211	H
L	IV	1.17	4.9	6.2	0.57	0.99	311	L
L	IV	1.15	7.6	10.9	0.61	1.18	344	M
L	IV	1.15	8.9	13.3	0.61	1.18	309	H
M	IV	1.21	10.3	29.2	0.68	1.04	307	M
M	IV	1.19	10.5	32.2	0.61	1.04	291	H
N	III	1.12	5.0	20.6	0.49	0.83	235	L
N	III	1.10	8.5	31.8	0.58	1.13	292	M
N	III	1.12	5.4	23.2	0.53	0.94	269	H
Q	III	1.13	10.1	31.2	0.49	0.99	189	L
Q	III	1.14	9.3	22.6	0.55	1.04	202	M
Q	III	1.13	7.7	29.6	0.55	0.91	222	H
P	III	1.01	14.8	32.2	0.65	0.67	28	M
P	III	1.08	9.0	31.9	0.61	1.11	201	H
S	II	1.18	8.4	11.6	0.58	1.18	232	L
S	II	1.19	6.8	13.8	0.57	1.52	430	M
S	II	1.12	8.8	14.5	0.54	1.33	227	H
T	II	1.17	2.9	16.3	0.48	0.96	306	L
T	II	1.15	4.2	18.9	0.51	0.99	281	M
T	II	1.13	6.8	25.0	0.49	1.00	239	H
U	II	1.14	8.8	24.7	0.58	0.99	295	L
U	II	1.17	4.0	26.1	0.69	1.13	332	M
U	II	1.12	7.4	29.9	0.65	1.00	263	H
W	I	1.18	7.9	9.6	0.60	0.90	323	M
W	I	1.15	9.2	9.8	0.59	0.92	334	H
X	I	1.18	9.4	11.9	0.56	1.20	290	L
X	I	1.16	9.2	30.9	0.57	1.17	366	M
X	I	1.17	8.6	15.8	0.45	1.13	412	H
Y	I	1.19	7.1	28.5	0.66	1.11	280	L
Y	I	1.19	7.6	24.4	0.57	0.91	347	M
Y	I	1.17	7.9	24.4	0.59	1.00	245	H
Standard		1.21	2.4	16.4	0.68	1.21	375	M

Note: Binder Level--H - high, M - medium, L - low. There is a difference of 2 pph of binder (based on the weight of filler) between each binder level; thus, there is a spread of 4 pph between the highest (H) and lowest (L) level.

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FIGURE 1
PREPARATION OF RAW MATERIAL
AND BLEND COMPONENTS

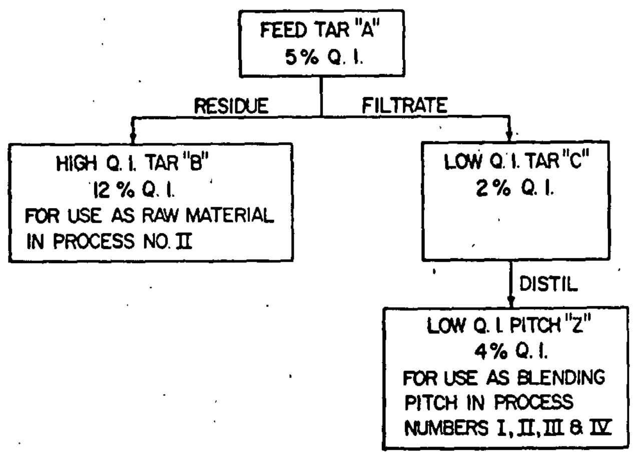


FIGURE 2
PROCESS NO. I
PREPARATION OF NATURAL Q. I. PITCH

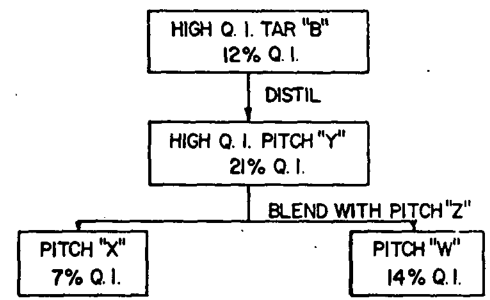


FIGURE 3
PROCESS NO. II
PREPARATION OF PITCH USING
EXPERIMENTAL PROCESS TYPE I

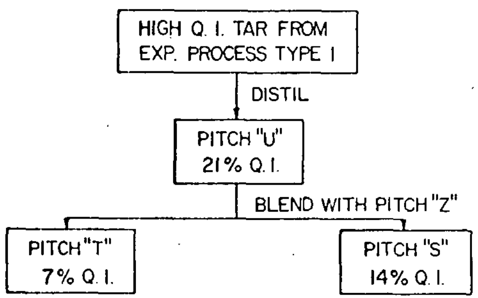


FIGURE 4
PREPARATION OF PITCH USING
EXPERIMENTAL PROCESS TYPE II

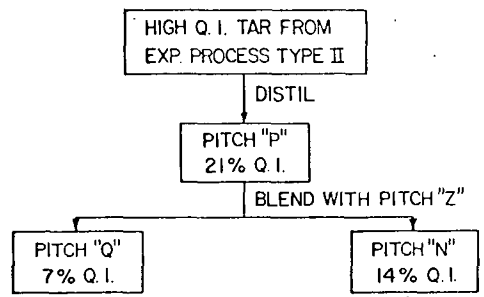
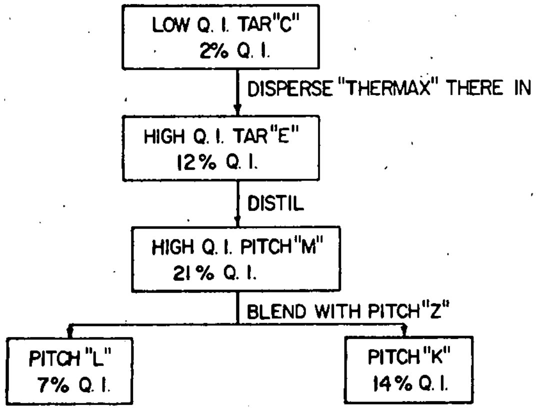


FIGURE 5
PREPARATION OF "THERMAX"-
MODIFIED Q. I. PITCH



ACTUAL Q.I. LEVELS vs T-C.T.E. LEVELS

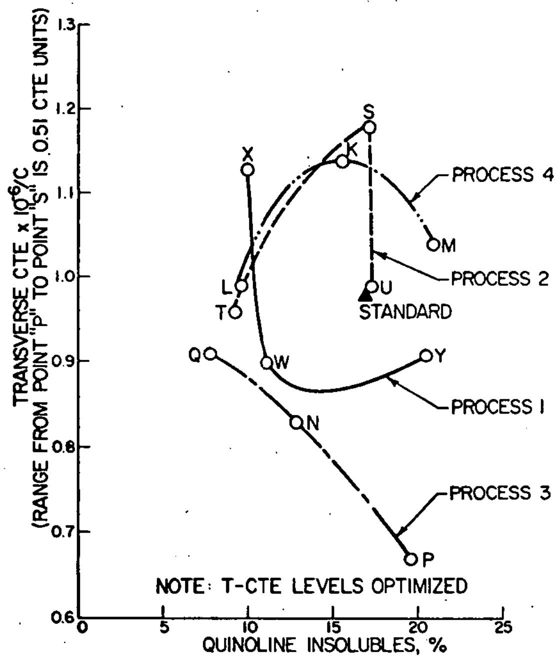


FIGURE 6

ACTUAL Q. I. LEVELS vs FLEXURAL STRENGTH LEVELS

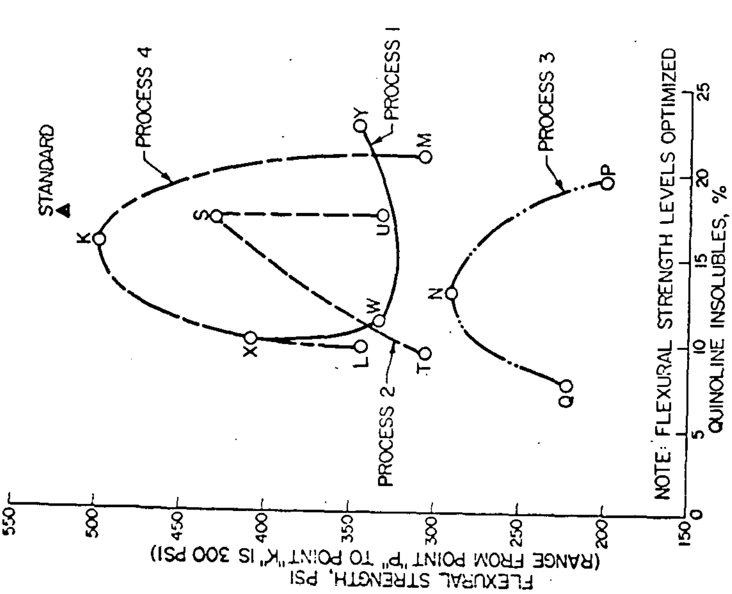


FIGURE 7

ACTUAL Q. I. LEVELS vs APPARENT DENSITY LEVELS

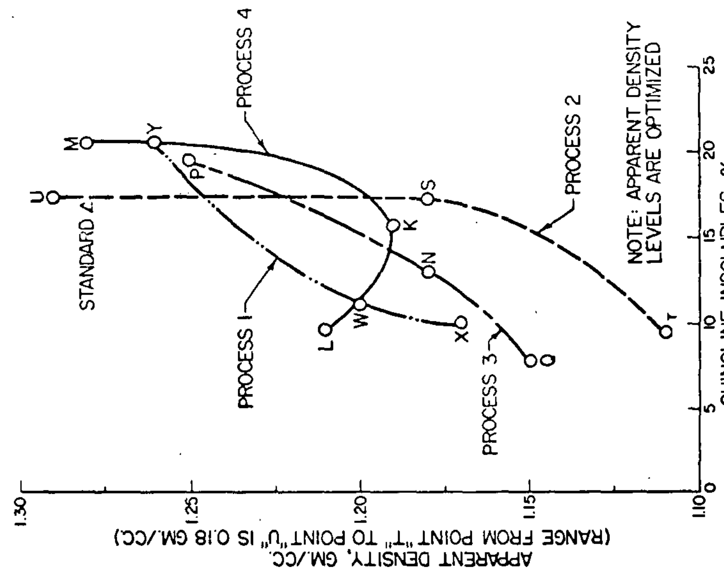


FIGURE 8