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Influence of processed carbon black in the filler composition on the characteristics of baked carbon mixes

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Several carbon products such as carbon brushes, special nuclear carbons, seal rings, etc. require carbon black in the filler composition. In the present study, the raw carbon black was mixed with a coal tar pitch and the resulting carbon mix was shaped, calcined and finally crushed into a fine powder for its subsequent use. The influence of this modified (processed) carbon black in the filler composition on the characteristics of the final calcined petroleum coke, processed carbon black and coal tar pitch-based carbon mixes has been investigated.

1. Introduction

Carbon black is used as one of the filler components in the manufacture of special grades of electrical brushes, nuclear carbons, seal rings and for other special applications [1–4]. The purpose of its incorporation in the carbon mix is to increase the density, strength and hence wear-life of the final product. Search of the literature revealed only one paper, by Fialkov [5], which describes the dependence of the physical properties of carbon mixtures on their composition. According to his work, the introduction of lamp black into the binder increases the viscosity, binding properties and mechanical strength of the latter and, in consequence, the strength of the composition. Girolami [6] studied the effect of petroleum coke additions in different coal tar and petroleum pitches and observed an enhancement in coking yields of the pitches in the pitch-aggregate mixtures after being subjected to pre-heating. Further, this enhancement was found to be dependent on the quantity and fineness of the petroleum coke powders. Later, Bradford *et al.* [7] observed that the addition of a carbon black to a coal tar pitch modified its thermal degradation by the extent of the surface area of the carbon black in contact with it: the greater the surface area, the lesser the material lost as volatiles. In another study, Williams and Imprescia [8] found a marked increase in the coking yield when a fine channel black was dispersed in a coal tar pitch. However, this increase in coking yield was reduced when the channel black was heated to 1800° C before being dispersed in the coal tar pitch. The latter effect was attributed to a decrease in the acidity of the channel black upon the heat treatment. In other studies, the addition of lamp black [9] or furnace black [10] to quinoline insolubles (QI)-free petroleum pitches resulted in substantial gains in the compressive strength of the baked carbons. In a recent publication, Ball [11] reported that addition of QI-concentrate, carbon black or mesophase (through heat treatment) to a QI-lean coal tar pitch did not up-grade it. However, Romovacek [12] has attributed this finding (no improvement in the QI-lean pitch) to the unsatisfactory dispersion of carbon black in the pitch. In another recent publication, Morelli and Rakszawski [13] have shown that a lower-cost thermal black could replace the lamp black in the lamp black grade graphite brushes.

It may be noted here that all the above studies describe, in different ways, the interaction of carbon black with coal tar or petroleum pitch. However, no systematic study of the effect of carbon black in the filler composition on the physical characteristics of the resulting carbons seems to have so far been reported in the literature. Further-

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more, it has been found that the binder requirement for carbon black-rich filler compositions is very high because of the extremely fine particle size of carbon blacks. This, in turn, leads to the formation of severe cracks in the final product due to the evolution of a large quantity of volatiles during baking. The severity of this crack formation is enhanced by the generation of occluded gases resulting from the presence of certain surface groups on most of the carbon blacks. This difficulty has been overcome in the present study by mixing the raw carbon black with a suitable amount of binder pitch and then shaping the resulting carbon mix into small blocks which are then baked, crushed, ground and finally sieved to pass through a fine mesh. The material so obtained will be referred to as the "processed carbon black" and the effect of its incorporation in the filler composition upon the characteristics of resulting baked carbon mixes has been investigated in the work reported in this paper.

2. Experimental procedure

The raw carbon black, a furnace black manufactured by Philips India Ltd, having the specifications given in Table I, was hot-mixed with a coal tar pitch, having the characteristics given in Table II, in proportions varying from 80 to 140 % of the weight of the black. Each of the different carbon mixes were passed over steam rollers, heated to a temperature of 120° C, for about 20 min and subsequently cooled and crushed to pass through a 60 BS-mesh. Ten 12 g portions were taken from each of these powdered mixes and each was moulded into a 20 mm diameter cylindrical block at a temperature of 120° C in an oil-heated die at a pressure of 183 kg cm^{-2}. The green densities of these blocks were determined from measurements of their masses and dimensions. The blocks were then baked at a temperature of 950° C in an electrical muffle furnace for a five-day baking cycle. Finally, the baked blocks were cleaned for any packing material adhering to them and subjected to baked density, electrical resistivity and crushing strength measurements performed using methods described elsewhere [14].

TABLE I Characteristics of different filler components

Characteristic	Raw carbon black	Processed carbon black	Calcined petroleum coke
Particle size (BS-mesh)	(– 325)	(– 200)	(– 100 + 200) : 30 wt% (– 200 + 300) : 30 wt% (– 300) : 40 wt%
Volatile matter (wt%)	2.46		
Surface area ($m^2 g^{-1}$)	83		
pH value (pH)	7.8		
Ash content (wt%)	0.21	0.74	0.41
Bulk density (g cm^{-3})	0.42	0.66	0.77
Kerosene density (g cm^{-3})	1.82	1.82	2.10
Electrical resistivity at a pressure of 183 kg cm^{-2} (mΩ cm)	171	81	39

TABLE II Characteristics of coal tar pitch binder

Characteristic	Value
Softening point (Ring & Ball)	70° C
Density	1.30 g cm^{-3}
Coking value	55 wt%
Ash content	0.27 wt%
Benzene insolubles	30.9 wt%
Quinoline insolubles	12.5 wt%
β-resins	18.4 wt%

In the next part of this work, 2 kg of the raw carbon black was mixed within a ratio of 5 : 6 w/w with the above coal tar pitch (CTP) to obtain baked carbon blocks, using the same method as that above. These blocks were subsequently crushed, ground and finally sieved through a 200 BS-mesh to obtain the processed carbon black (PCB). This was then blended with a calcined petroleum coke (CPC), having the characteristics given in Table I, in varying proportions of 0 to 100 wt % in five steps of 20 wt % to obtain different fillers each of which was hot-mixed with 30 and 35 wt% pitch to obtain 12 different carbon mixes in all, as shown in Table III. Subsequently, these mixes were moulded and baked in the manner described above. Finally, the baked blocks were investigated to determine their apparent density, electrical resistivity, crushing strength and shore hardness.

3. Results and discussion

Fig. 1 shows the variation of green density, baked density, crushing strength, electrical resistivity and volume shrinkage of raw carbon black and coal tar pitch-based carbons with varying binder pitch contents, ranging from 80 to 140 wt%. It is seen

TABLE III Composition of different fillers and carbon mixes

Filler Number	Proportions of filler components		Binder content by weight of filler (%)	Carbon mix number
	Calcined petroleum coke (wt%)	Processed carbon black (wt%)		
1	100	0	30	1A
			35	1B
2	80	20	30	2A
			35	2B
3	60	40	30	3A
			35	3B
4	40	60	30	4A
			35	4B
5	20	80	30	5A
			35	5B
6	0	100	30	6A
			35	6B

that the green density of the carbons goes on increasing with the increasing binder content up to 120 wt%, beyond which it starts decreasing very slowly. This increase in the green density may be attributed to a filling-up of the vacant voids by the pitch and to the decrease to the replacement of the carbon black by the pitch. The baked density, on the other hand, goes on increasing right upto the highest binder content. Compared to the green density, the lowering of the baked density for samples with between 80 and 130 wt% binder content may be due to the escape of volatiles from the binder without much volume shrinkage, whereas, the increase of the baked density over the green density for binder contents greater than 130 wt% may result from the dominance of volume shrinkage (approximately 24 vol%) over the weight loss due to volatiles.

The crushing strength increases to a maximum at a binder content of 110 wt% after which it decreases. The above increase in the strength is due to the increasing availability of the pitch necessary for bonding and the decrease may be because of microcrack formation resulting from excessive shrinkage of the binder.

The electrical resistivity is seen to decrease to a minimum value at a binder proportion of 120 wt%, beyond which it increases. The reasons proposed to explain the variation of crushing strength with binder content could also be applied to explain the electrical resistivity behaviour.

It may thus be concluded from Fig. 1 that a weight ratio of coal tar pitch to carbon black of 6:5 would seem to be the optimum composition producing the best overall characteristics.

Figs 2 to 6 show the variation of green density,

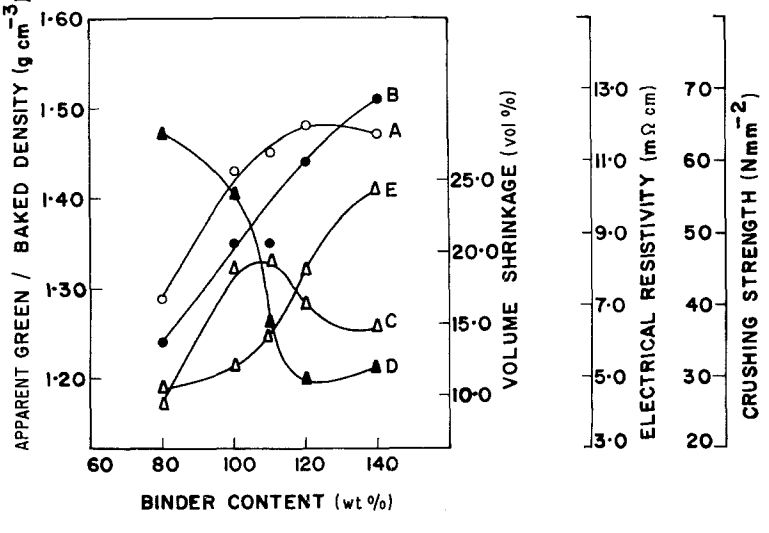

Figure 1 Variation of the green density (A), baked density (B), crushing strength (C), electrical resistivity (D), and volume shrinkage (E), of raw carbon black–coal tar pitch-based carbon mixes with different binder pitch contents.

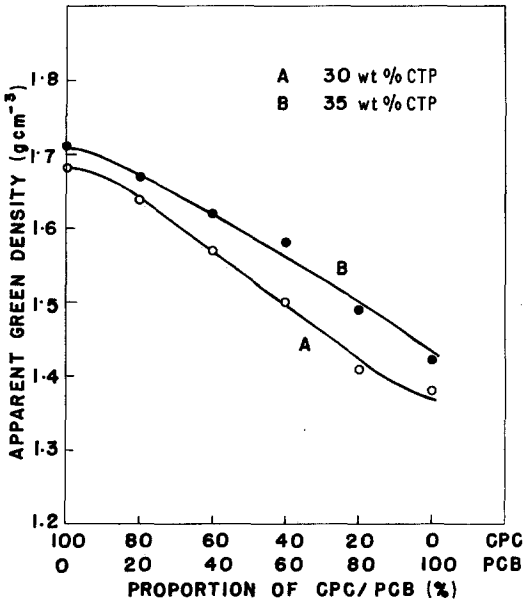

Figure 2 Variation of apparent green density of calcined petroleum coke (CPC)–processed carbon black (PCB)–coal tar pitch (CTP)-based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% CTP contents.

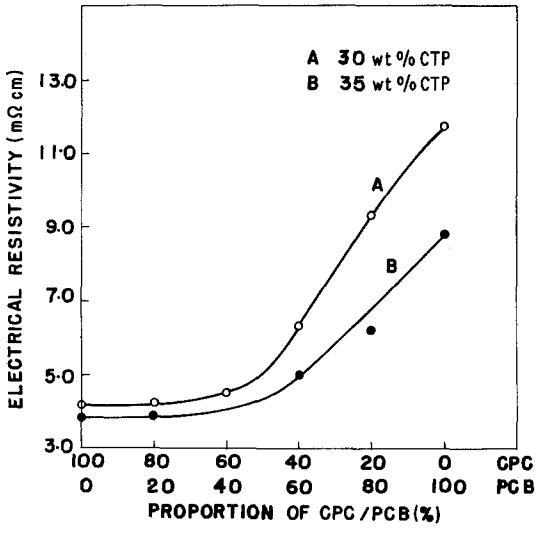

Figure 4 Variation of electrical resistivity of calcined petroleum coke (CPC)–processed carbon black (PCB)–coal tar pitch (CTP)-based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% CTP contents.

baked density, electrical resistivity, crushing strength and shore hardness, respectively, of the calcined petroleum coke, processed carbon black and the coal tar pitch based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% pitch contents. It is seen in Fig. 2 that the densities of green carbons go on decreasing with increasing proportion of PCB in the fillers for both the binder contents. This gradual fall in the green density may be due to the replacement of denser filler components CPC (bulk

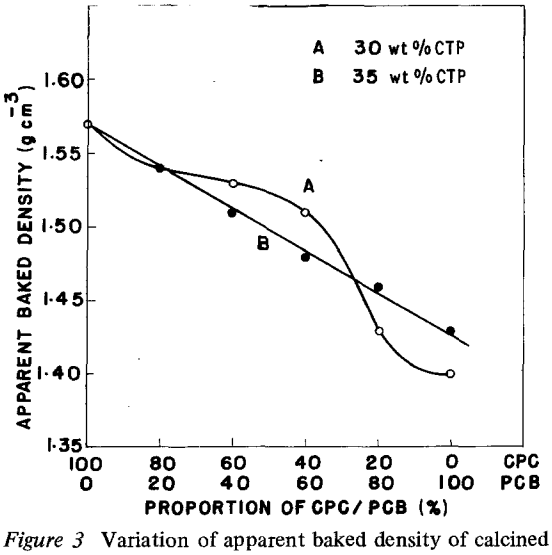

Figure 3 Variation of apparent baked density of calcined petroleum coke (CPC)–processed carbon black (PCB)–coal tar pitch (CTP)-based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% CTP contents.

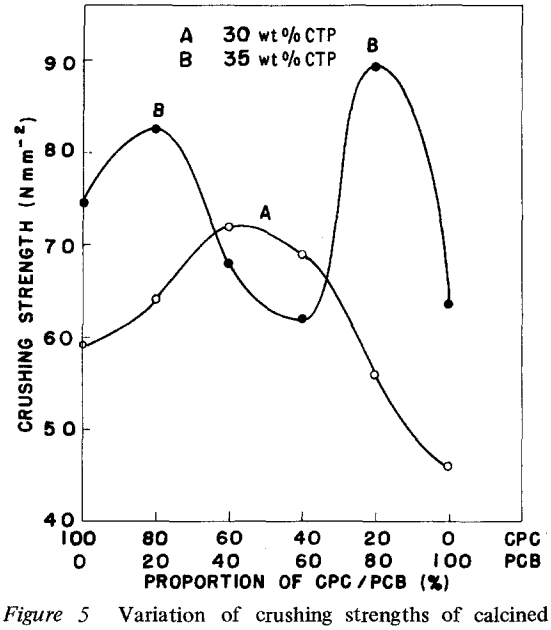

Figure 5 Variation of crushing strengths of calcined petroleum coke (CPC)–processed carbon black (PCB)–coal tar pitch (CTP)-based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% CTP contents.

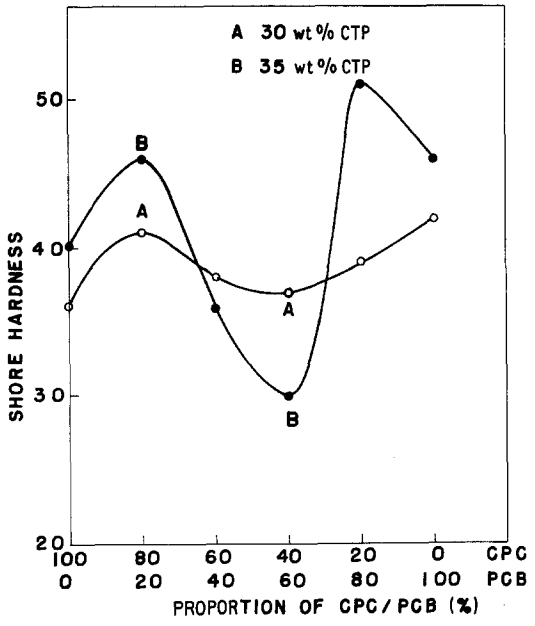

Figure 6 Variation of shore hardness of calcined petroleum coke (CPC)–processed carbon black (PCB)–coal tar pitch (CTP)-based carbon mixes with different relative proportions of CPC and PCB for 30 and 35 wt% CTP contents.

density = 0.77 g cm^{-3}) by the relatively lighter component PCB (bulk density = 0.66 g cm^{-3}). The shifting of the curve from Curve A to Curve B may be due to the filling up of vacant voids in the filler packing by the additional pitch.

As seen in Fig. 3, the baked densities of the carbons for both binder levels, are found to decrease continuously, though differently from each other, with the increasing PCB content. The same values of baked density were obtained for both 30 and 35 wt% binder contents for Fillers 1 and 2 and this suggests that these values lie around the optimum binder level. The decrease in the baked densities of carbons based on Fillers 3 and 4, as the binder level increases from 30 to 35 wt%, indicates that 35 wt% of the binder is higher than the optimum proposition; this is reasonable since the packing of finer PCB into the voids of relatively coarser CPC component would reduce the binder requirement. Finally, the baked densities of carbons based on Fillers 5 and 6 are higher for 35 wt% binder level because of the fineness of their major constituents. Fig. 4 indicates that the electrical resistivities of the carbons increase marginally upto a PCB content of 40 wt% in the filler for both binder levels, beyond which they rise substantially. Further, the resistivity of carbons, with any of the fillers is decreased as the binder content is increased to 35 wt% thereby indicating that in order to obtain the minimum electrical resistivity the binder content may need to be 35 wt% or more. These observations are in agreement with the results of our previous studies on baked carbon mixes [10, 14, 15].

Fig. 5 shows that the crushing strength of the carbons with 30 wt% binder content increases to a maximum with increasing PCB content (at 40 wt%), beyond which it decreases gradually. However, for 35 wt% binder content the crushing strength–PCB content plot shows a peculiar pattern with two maxima and a minimum. The increase in strength of the carbons using Fillers 1 and 2 shown with increase of the binder level from 30 to 35 wt% may be due to the attainment of the optimum quantity of binder which has been confirmed in a later study [16]. The decrease of strength in the case of the Fillers 3 and 4 as the binder level increases to 35 wt% indicates that the higher binder content is greater than the optimum value, which is in agreement with the baked density considerations also. Compared to the results for Fillers 3 and 4 with 35 wt% binder content, Filler 5 with 35 wt% binder content now shows a steep rise in strength over that obtained for the same filler with only 30 wt% binder, indicating that the higher binder content may be the optimum quantity for this comparatively finer filler. This conclusion has also been confirmed in a later study [16]. However, it appears that there is a possibility of obtaining a still higher strength in the case of Filler 6, the finest filler of all, if a binder content greater than 35 wt% is used. It may be noted here that the strengths of carbons based on fillers with PCB contents of 20 and 80 wt% are significantly higher than the strengths of carbons based on fillers with PCB contents of 40 and 60 wt%. This agrees with the findings of Failkov [5] that the strengths of carbons with intermediate lattice structures are lower than those of carbons with either the coke or black lattice structures. Further, as seen in Fig. 6, the relative variation of shore hardness of carbons, in case of 30 and 35 wt% binder contents, for all the fillers follows a similar trend to that seen in the investigation of crushing strength.

It is interesting to note that the raw carbon black-based carbons studied invariably developed cracks during baking, regardless of the binder content. Further, it was noticed that compositions

based on calcined petroleum coke and raw carbon black containing raw carbon black in amounts exceeding 20 wt% also produced cracks in the baked artefacts [16]. In the present study, no cracks were observed in the baked carbons based on any of the fillers employing CPC and PCB in a wide range of relative proportions.

4. Conclusions

(a) Unlike the raw carbon black, which leads to the formation of cracks when added in amounts exceeding 20% of the weight of the filler, the processing of raw carbon black results in the possibility of obtaining a crack-free carbon product, even from a filler composed purely of processed carbon black.

(b) The apparent density of green and baked carbons decreases continuously with increasing content of processed carbon black in the filler.

(c) The electrical resistivity of baked carbons increases slowly up to 40 wt% content of processed carbon black in the filler, above which it increases substantially.

(d) The crushing strength and hardness of the carbons vary in a similar manner and show an irregular behaviour with increasing proportions of the processed carbon black in the filler. Improved values of strength and hardness are obtained for processed carbon black contents in the filler either up to about 30 wt% or more than about 70 wt%, whereas inferior strength and hardness values are obtained for the intermediate proportions (between 30 and 70 wt%) compared to the properties of carbons based on pure calcined petroleum coke.

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