Effect of Petroleum Coke on Certain Paraffinic-Waxy Asphalt Cement Characteristics

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ABSTRACT

The findings of a laboratory investigation are reported. The investigation was performed to evaluate the effect of using petroleum coke (with different percentages and degrees of fineness) as an additive to paraffinic-waxy asphalt cement (AC 60/70) produced in Alexandria, Egypt, refineries. Also reported are its physical properties and the engineering properties of its asphalt concrete mixtures. One aggregate type and gradation and one asphalt cement type and grade were used in the study. Marshall and Hveem tests were used to evaluate the properties of the asphalt concrete mixture. The evaluation resulted in a number of significant results. The use of petroleum coke as an additive to Alexandria asphalt cement (AC 60/70) proved to be beneficial in improving its properties. The experiments also indicated that the degree of fineness of the petroleum coke plays a significant role in affecting the degree of improvement.

The production of asphalt cement in Egypt takes place in Suez and Alexandria. In Suez refineries asphalt cements are produced by a straight-run distillation process that uses crude oils recovered from the eastern region. These asphalt cements were successfully used in hot asphaltic mixtures and provided roads with satisfactory service records. In Alexandria refineries asphalt cements are produced by means of propane deasphalting and phenol extraction processes that use a mixture of crudes recovered from the western desert region. These asphalt cements caused serious performance and construction problems and were classified according to the base of its crude oil as paraffinic-waxy asphalts (1-3).

Previous work conducted in the area of improving asphalt cement or its mix characteristics indicated that one of the most successful methods followed is the use of additives. The most commonly used additives are resins, rubber, sulfur, and carbon black. The results of several studies on carbon black and sulfur (4) directed this study to the use of petroleum coke (which contains about 90 percent carbon and sulfur) as an additive to the western desert paraffinic-waxy asphalt cement.

Petroleum coke, which is a by-product of the coking process performed on heavy petroleum products to produce light fractions, has a crystal structure similar to carbon black but differs in the size of crystallites (5). Sachanen (6) defined petroleum coke as an ultimate condensation product of petroleum residues. He stated that petroleum coke has an intermediate structure between that of asphalt and metallurgical coke. Therefore, petroleum coke, when added to asphalts, may act as a bodying agent similar to asphaltenes and also as a reinforcing agent similar to carbon black (4).

Reported in this paper are the findings of a laboratory investigation to evaluate the effect of using petroleum coke with different percentages and degrees of fineness as an additive to paraffinic-waxy asphalt cement (AC 60/70) produced in Alexandria refineries. Also reported are its physical properties and the engineering properties of its asphalt concrete mixtures.

One aggregate type and gradation and one asphalt cement type and grade were used in the study. Marshall and Hveem tests were used to evaluate the properties of the asphalt concrete mixture.

EXPERIMENTAL DESIGN

A complete laboratory testing program that used two factors--the petroleum coke content and its degree of fineness--was conducted on Alexandria 60/70 asphalt cement (see Table 1) to evaluate the following items:

1. Effect of petroleum coke content and degree of fineness on the physical properties of asphalt cement (i.e., penetration, kinematic viscosity, absolute viscosity, and softening point), and
2. Effect of petroleum coke content and degree of fineness on engineering properties of the asphalt concrete mixture of the treated asphalt cement (i.e., Marshall stability and Hveem cohesion).

In addition, the same testing program was conducted on a Suez asphalt cement sample without additive for comparative study (Table 1).

TABLE 1 Experimental Program

Sample No.	Asphalt Cement Source		Petroleum Coke Content[a]				Degree of Fineness[b]		
	Alexandria	Suez	0%	7%	10%	15%	1	2	3
1		X	X						
2	X		X						
3	X			X			X		
4	X			X				X	
5	X			X					X
6	X				X		X		
7	X				X			X	
8	X				X				X
9	X					X	X		
10	X					X		X	
11	X					X			X

[a]Percent by weight of asphalt cement.
[b]See Table 4.

MATERIALS

Asphalt Cement

Two samples of asphalt cement (AC) 60/70 were secured--one from the production of an Alexandria refinery and the other from the production of a Suez refinery. The physical properties and the chemical constituents of these two samples are given in Table 2.

TABLE 2 Physical Properties and Chemical Constituents of AC 60/70

Asphalt Source	Physical Properties						Chemical Constituents			
	Pen. 0.1 mm.	Duct. cm	Soft. point °C	Kin. visc. c.st. 135°C	Abs. visc. poises. 60°C	Sp.Gr. 60°C	Wax(3) %	Oils %	Resins %	Asphaltene. %
Alex.	66	100+	47	230	986	1.018	7.5	33	51	16
Suez	62	100+	52	358	2122	1.020	5.5	26	49	25
Spec. Limits(1)	60/70	90+	45/55	320(2)	-	-	-	-	-	-

(1) Egyptian Standard Specifications.

(2) Proposed.

(3) Determined by modified Hold's method (7).

Mineral Aggregate

Based on previous field experience, the severity of the performance problems of waxy asphalt appears to depend on two main factors related to mix components: the coarse aggregate type and the gradation of the aggregate mix.

The research work of the Cairo University/Massachusetts Institute of Technology (CU/MIT) Technological Planning Program (4) performed on the Alexandria asphalt cement hot mixtures indicated that the Asphalt Institute dense gradation (4-C) and crushed limestone are the best gradation and type of coarse aggregate to be used with the Alexandria waxy asphalt cement. Consequently, the experimental program in this study was designed to use crushed limestone as the coarse aggregate material in the asphalt cement hot mixtures. Silicious sand and limestone dust were used as the fine aggregate and mineral filler, respectively.

The data in Table 3 present test properties of the aggregate components used together with the percentages of each component to meet the midpoint gradation of the Asphalt Institute dense gradation 4-C.

TABLE 3 Physical Properties of the Mineral Aggregate

Properties	Aggregate Components			Standard Specifications
	Crushed Limestone	Silicious Sand	Limestone Dust	
Bulk specific gravity	2.45	2.68	2.80	
Bulk specific gravity (SSD)	2.583			
Apparent specific gravity	2.663			
Percent absorption	1.88			5[a]
Percent wear (Los Angeles test)	31.8			40[a]
Percent in aggregate combination[b]	57.5	37	5.5	

[a]Maximum.
[b]Percentages of different components to meet the midpoint gradation of the AI gradation (4-C).

Petroleum Coke

Petroleum coke samples were secured from the production of the Suez Oil Processing Company. The analysis and constituents of the petroleum coke samples are given in the following table:

Constituents	Percent by Weight
Moisture content	0.40
Ash content	0.49
Volatile matter	9.8
Total carbon	83.4
Sulfur content	5.6
Total hydrogen	0.39

The existing price of Alexandria asphalt cement is about 20 £E per ton and the price of petroleum coke is about 100 £E per ton. Based on cost analyses and economic considerations, petroleum coke can be added to a content not more than 15 percent, thus making the price of the treated asphalt cement less than 32.5 £E per ton, which is approximately the price of the Suez asphalt cement.

Petroleum coke was ground to three different degrees of fineness (Table 4) and then mixed with Alexandria AC 60/70 at a temperature of 150°C and a mixing time of 30 min by using manganese stearate as a dispersing agent with a content of 0.1 percent by weight of asphalt.

ANALYSIS OF RESULTS

Physical Properties

Figures 1-3 illustrate the concentration effects of the three different degrees of fineness of petroleum

TABLE 4 Degrees of Fineness of Petroleum Coke

Degree of Fineness	Petroleum Coke (%)			Surface Area (ft^2/lb)
	Passing #100	Passing #140	Passing #200	
1	100	90	74	535
2	100	100	87	570
3	100	100	100	600

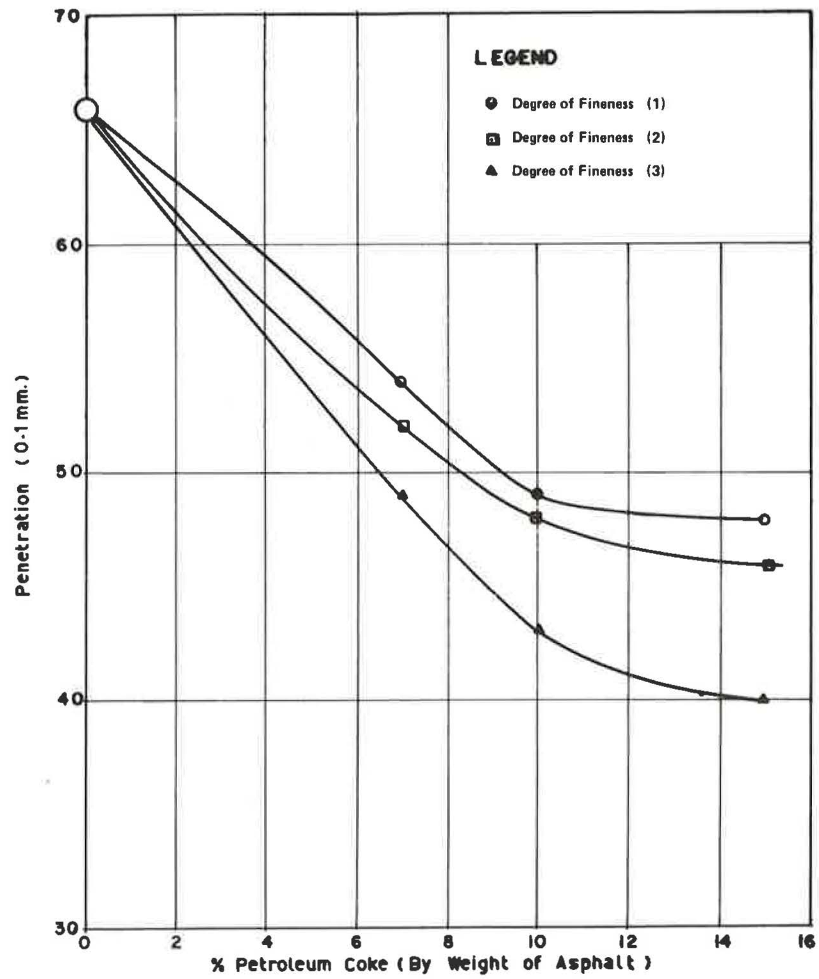

FIGURE 1 Effect of coke content and degree of fineness on penetration of coke-asphalt cement blends.

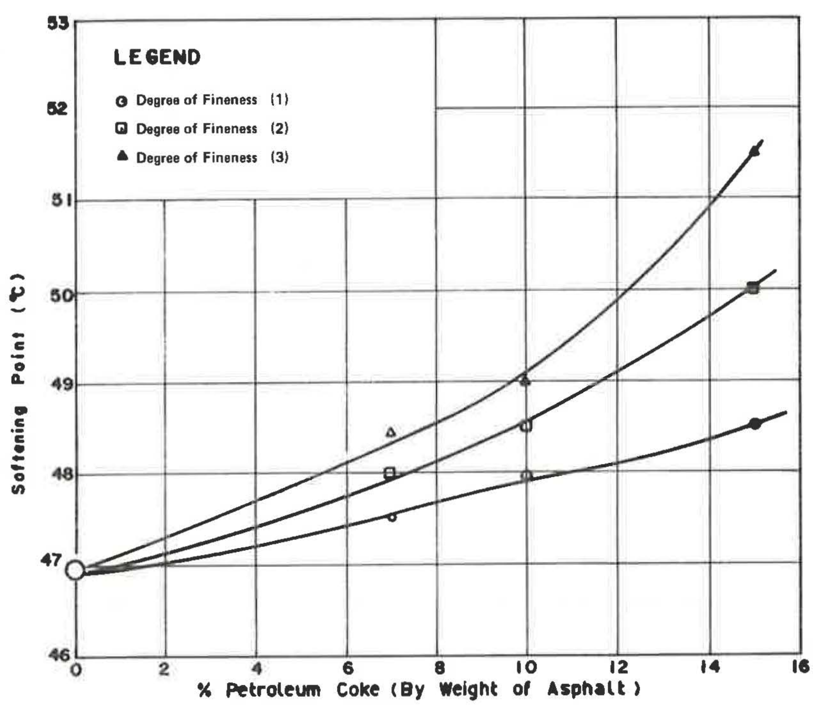

FIGURE 2 Effect of coke content and degree of fineness on softening point of coke-asphalt cement blends.

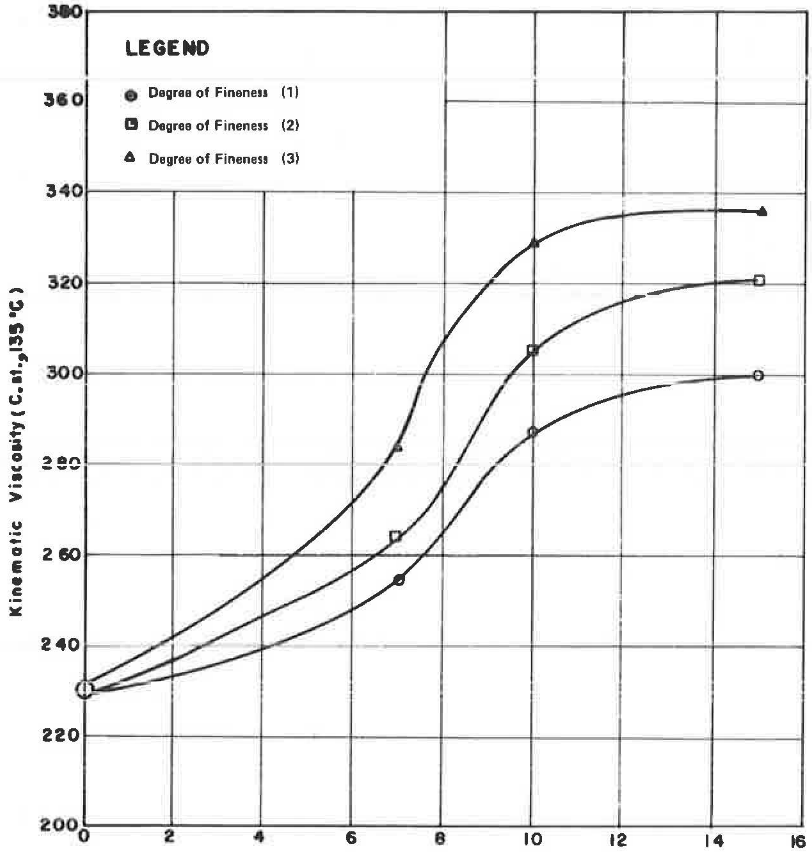

FIGURE 3 Effect of coke content and degree of fineness on kinematic viscosity of coke-asphalt cement blends.

coke on the penetration, softening point, and kinematic viscosity of coke-asphalt cement mixtures. The test results performed on coke-asphalt blends are as follows.

1. The increase of coke content consistently reduces the penetration of the mixture. In addition, the increase in the degree of fineness (i.e., increase in surface area) of the petroleum coke reduces the penetration of the coke-asphalt cement mixture. The effect of the degree of fineness is more pronounced at high concentrations of coke.
2. Softening point versus coke concentration trends indicate a slight increase in the softening point of the mixture with the increase of coke concentration. The effect of coke concentration is more pronounced when increasing the surface area of coke.
3. The increase of coke content consistently increases the kinematic viscosity of the mixture at 135°C. In addition, the increase in the degree of fineness of the petroleum coke increases the kinematic viscosity of the coke-asphalt cement mixtures. Again, the effect of the degree of fineness on kinematic viscosity is more pronounced at higher concentrations of coke.
4. The percentage increase in absolute viscosity values at 60°C were similar to viscosity changes at 135°C for the different concentrations and surface areas.
5. At the concentrations used, petroleum coke tends to harden the asphalt to a great extent. In addition, when the surface area of petroleum coke is higher there is an increase in the viscosity and the softening point and a decrease in the penetration. This could be attributed to the fact that the smaller the particle size of coke, the easier it is dispersed in asphalt and, hence, it strongly affects its physical properties.
6. The addition of coke to asphalt increases its kinematic viscosity to a limit that meets the proposed minimum value in the Egyptian standard specifications for this grade of asphalt (320 C.St. min). The addition of coke also reduces the gap between Alexandria and Suez asphalt cements. This result is obtained when using a coke content of 10 to 15 percent that has a surface area more than 570 ft²/lb.
7. The results also indicate that the use of petroleum coke as an additive to Alexandria asphalt cement (AC 60/70) provides a product that is close in its characteristics to Alexandria asphalt cement (AC 40/50 grade). This suggests that the use of AC 40/50 grade could be a promising alternative for overcoming the reported problems that are associated with the use of Alexandria asphalt cement (AC 60/70 grade).

Temperature Sensitivity

Three asphalt cement samples were selected for the temperature sensitivity analysis. The first represented Alexandria asphalt cement (AC 60/70), the second was prepared by blending the original Alexandria asphalt cement (AC 60/70) with 10 percent coke that has a surface area of 600 ft²/lb, and the third sample represented Suez asphalt cement (AC 60/70). The second sample was selected because the kinematic viscosity value (330 C.St.) of this sample

exceeds the minimum value proposed in the Egyptian standard specifications for AC 60/70 (320 C.St. min.), and because the sample complies with the economic requirements for the price of local asphalt cement produced in Egypt.

Figure 4 shows the bitumen test data chart suggested by Heukelom (8) to relate the consistency of asphalt with temperature. Results of the penetration tests conducted at 10°, 15°, and 25°C are plotted on the upper left part of the chart, and results of viscosity tests (in poises) at 60° and 135°C are plotted on the lower part of the chart.

It is clear from the chart that the penetration lines did not coincide with the viscosity lines. The observed shift for the Suez asphalt sample was the smallest shift reported for the three samples. This indicated that the paraffinic-waxy nature was more pronounced for Alexandria asphalt cement (refer also to Table 2). Furthermore, the observed shift for Alexandria asphalt cement was almost equal to that observed for the Alexandria asphalt blended with 10 percent coke. This also reflects that coke concentration does not affect the paraffinic-waxy nature of Alexandria asphalt cement, although it improves its viscosity.

Also, it is apparent from the data in Figure 4 that the slopes of the three viscosity-temperature lines are almost the same, which indicates that they have about the same temperature sensitivity. However, the slopes of lines 2 and 3 tend to be more flat than that of line 1. This indicates that the use of coke as an additive slightly affected the temperature sensitivity of Alexandria asphalt cement to a limit that is equal to that of Suez asphalt cement.

Engineering Properties of AC 60/70 Paving Mixtures

It was anticipated that the surface area and amount of petroleum coke would influence the behavior of the pavement during all phases of construction and service life. Consequently, the influence of coke on asphalt concrete mixture properties such as density, stability, and cohesion were evaluated by using Marshall tests together with the Hveem cohesion test.

The data in Table 5 present the engineering properties of coke-Alexandria asphalt concrete mixtures at optimum asphalt contents together with the properties of the original untreated Alexandria and Suez asphalt concrete mixtures. The aggregate type and gradation in all mixtures were the same, as previously discussed.

Study of test results presented in Table 5 and Figures 5 and 6 indicate that all measured properties were affected quite pronouncedly by the amount and surface area of petroleum coke. In addition, optimum asphalt contents for samples that had various coke concentrations were greater than those of the original samples without coke by about 0.5 percent. This increase could be attributed to the fact that the coke acted only as a filler in the asphaltic mix (it should also be noted that the concentration of coke in asphalt represented approximately 0.5 percent of the mix).

The density and Marshall flow of the asphalt concrete mix are not significantly affected by the amount of coke used. However, the addition of coke significantly increased the stability and cohesion of the asphalt concrete mix. At the three surface areas (535, 570, and 600 ft^2/lb), the coke concentration of 10 percent provided the optimum increase

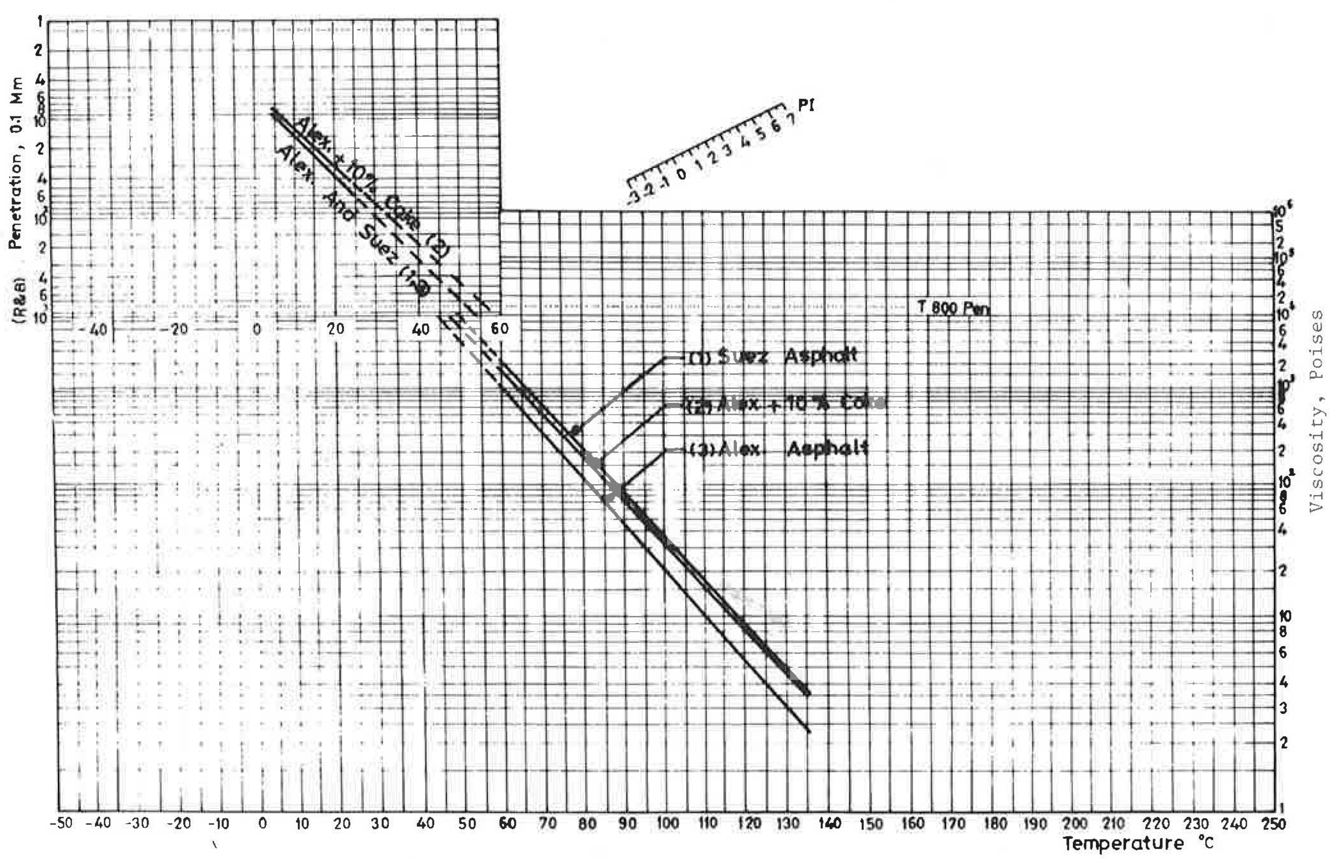

FIGURE 4 Heukelom bitumen test data chart.

TABLE 5 Investigation of Effects of Petroleum Coke on Mixture Properties at Optimum Asphalt Contents

Mix No.	Asphalt Source	Petroleum Coke(%*)	Coke Surface Area (ft^2/lb)	Optimum Asphalt Content (%**)	Marshall Stability (Lbs).	Unit Weight (pcf)	Air Voids (%)	Marshall Flow (0.01 in.)	Voids in Mineral Aggr.	Hveem cohesion (gm/in) at Optimum Asphalt cont.
1	Alex.	-	-	5.62	1420	147.2	3.1	10.5	15.5	193
2	Alex.	7	535	6.10	1620	146.8	3.8	11.3	15.5	245
3		10	"	6.15	1650	146.2	4.6	9.7	16.3	261
4		15	"	6.20	1630	146.6	3.9	9.6	16.2	250
5	Alex.	7	570	6.10	1910	145.3	4.7	9.5	15.5	255
6		10	"	6.20	2150	146.4	4.3	11.0	16.1	275
7		15	"	6.25	1960	146.0	3.8	10.8	15.6	265
8	Alex.	7	600	6.10	2200	146.4	3.8	9.7	15.5	290
9		10	"	6.25	2400	146.9	4.8	11.2	16.4	300
10		15	"	6.25	2280	147.0	4.4	11.5	16.2	290
11	Suez	-	-	5.60	2340	146.0	4.0	9.7	16.1	403

* Asphalt Weight Bases ** By Weight of Aggregates

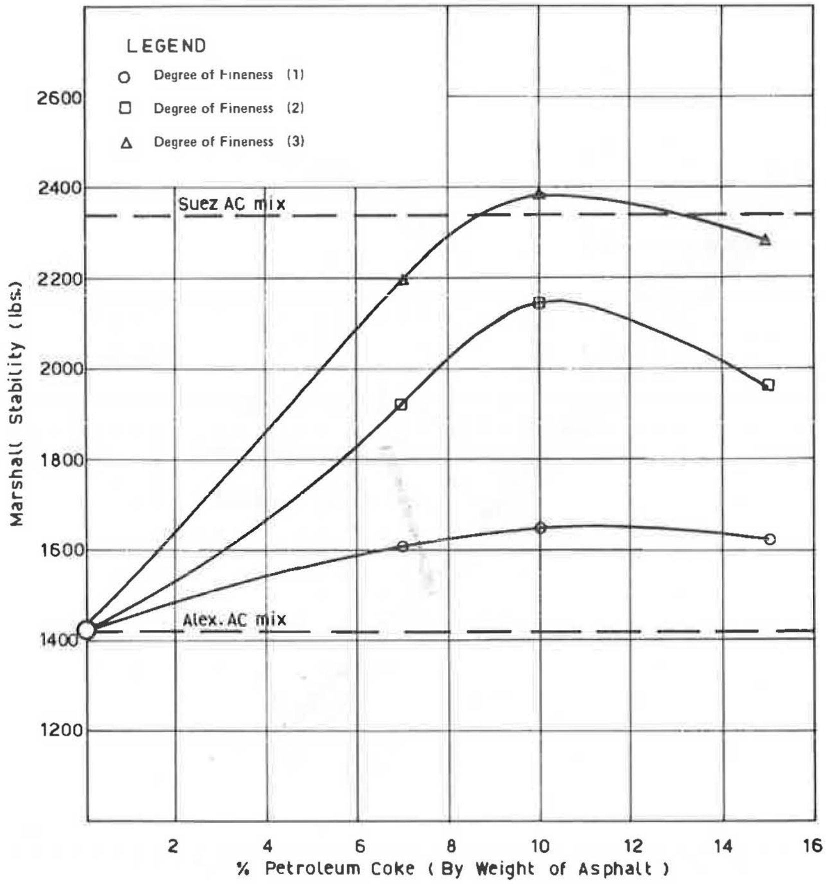

FIGURE 5 Effect of petroleum coke content and degree of fineness on Marshall stability.

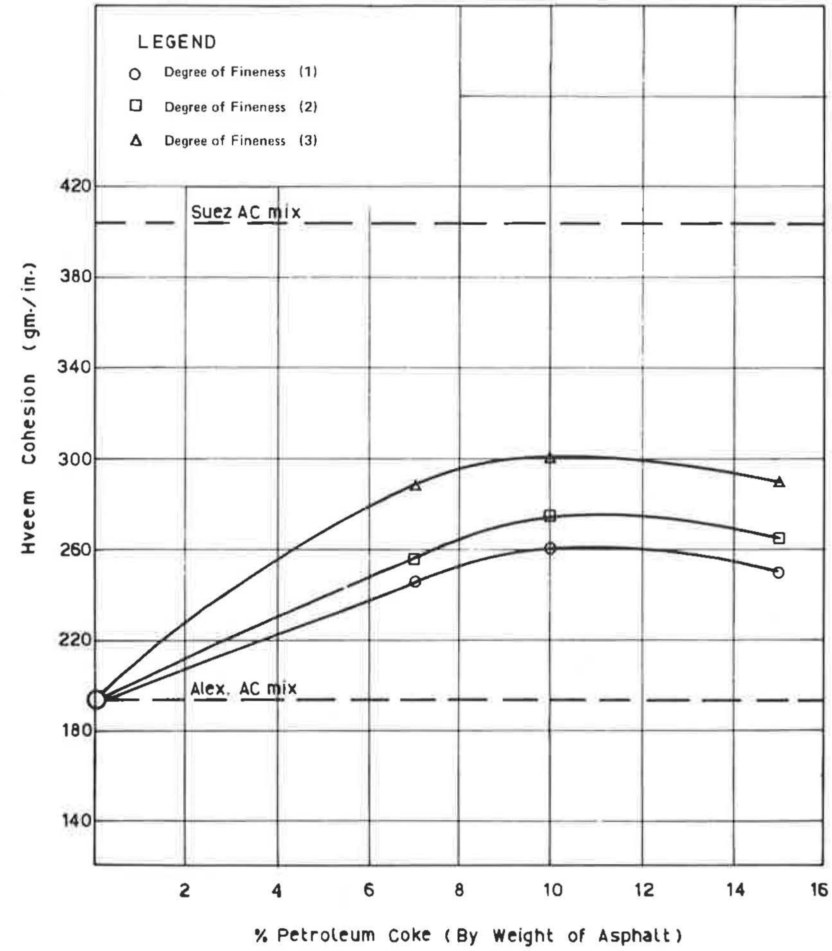

FIGURE 6 Effect of petroleum coke content and degree of fineness on Hveem cohesion.

in stability and cohesion (Figures 5 and 6). Furthermore, at all coke concentrations (7, 10, and 15 percent), the stability and cohesion of the asphaltic mix increased with the increase of surface area. However, cohesion values and most of the stability values of all samples treated by coke were still less than those of the original untreated Suez asphalt cement (Figures 5 and 6).

SUMMARY OF RESULTS

The analysis and evaluation of the test data revealed a number of significant results that pertain to the effect of petroleum coke concentration and degree of fineness of the physical properties of the local paraffinic-waxy asphalt cement (AC 60/70) and the engineering properties of its mixtures. The main results are as follows.

1. Petroleum coke tends to harden the asphalt to a great extent. The increase of coke content increases the viscosity and softening point and decreases the penetration. This effect was apparent for the three degrees of fineness used.

2. When the surface area of coke is high, there is an increase in viscosity and softening point and a decrease in the penetration of the coke-asphalt cement blend. This could be attributed to the fact that the smaller the particle size of coke, the easier it is dispersed in the asphalt and hence strongly affects its physical properties.

3. The use of petroleum coke with a surface area of more than 570 ft^2/lb and a concentration of 10 percent as an additive to Alexandria asphalt cement (AC 60/70) will result in an increase in its kinematic viscosity at 135°C to a limit that meets the minimum proposed value in the Egyptian standard specifications.

4. The addition of 10 percent petroleum coke to Alexandria asphalt cement (AC 60/70) slightly reduced its temperature sensitivity without causing any change in its paraffinic-waxy nature.

5. Petroleum coke significantly increased the stability and cohesion of the paving mixture. The use of 10 percent coke by weight of asphalt could be considered optimum. In addition, at all coke concentrations the stability and cohesion of the paving mixture increased with the increase of the surface area.

6. The use of petroleum coke as an additive to Alexandria asphalt cement (AC 60/70) acts as a filler and plays a dual role in paving mixtures. First, it forms with asphalt a high consistency binder and cements the aggregates. Second, it acts as a part of the mineral aggregates, fills the interstices, and provides contact points between particles, thereby strengthening the paving mixture.

7. Suez asphalt concrete mixtures still have better cohesion than the improved Alexandria asphalt concrete mixtures.

8. The use of petroleum coke as an additive to Alexandria asphalt cement (AC 60/70) provides a product that is close in its characteristics to

Alexandria asphalt cement (AC 40/50). This result suggests that the use of AC 40/50 grade could be a promising alternative for overcoming the reported performance problems that are associated with the use of Alexandria AC 60/70 grade.

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Effect of Diatomite Filler on Performance of Asphalt Pavements

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ABSTRACT

Diatomite, a widely used industrial filler, has been evaluated in heavy-duty pavements in Houston, Calgary, and Los Angeles. These pavements typically have high density, extremely low permeability, and a low initial asphalt hardening rate, with or without an increase in asphalt content. After 2 and 3 years in Calgary and Houston, recovered asphalt shows penetration values of 88 and 90 percent of the original 164 and 104 asphalt penetration at 77°F, respectively. Resistance to rutting at low void contents and characteristic abrasion resistance of the mortar is attributed to microaggregate interlock of diatom particles within the mastic films. One percent diatomite appears capable of either stabilizing pavements or permitting a 15 percent increase in standard asphalt content. The primary value of diatomite appears to be that it allows the use of softer asphalt, which alone should greatly increase pavement life. The effect of increasing the cost per ton of mix (10 to 20 percent) on cost per square yard of pavement was eliminated recently in Los Angeles by reducing overlay thickness by 50 percent. Eight different grades, types, and sources of diatomite were also evaluated in small paving sheets under truck traffic at Denison, Texas, and Lompoc, California. Several types gave extremely unsatisfactory resistance to plastic flow. Tests are under way to correlate basic diatomite properties (shape, size, purity, and so forth) with pavement performance. The scope of the program to date has been limited to dense-graded city pavements. The results are reported here to generate interest in more trials needed to justify continuation of the program.