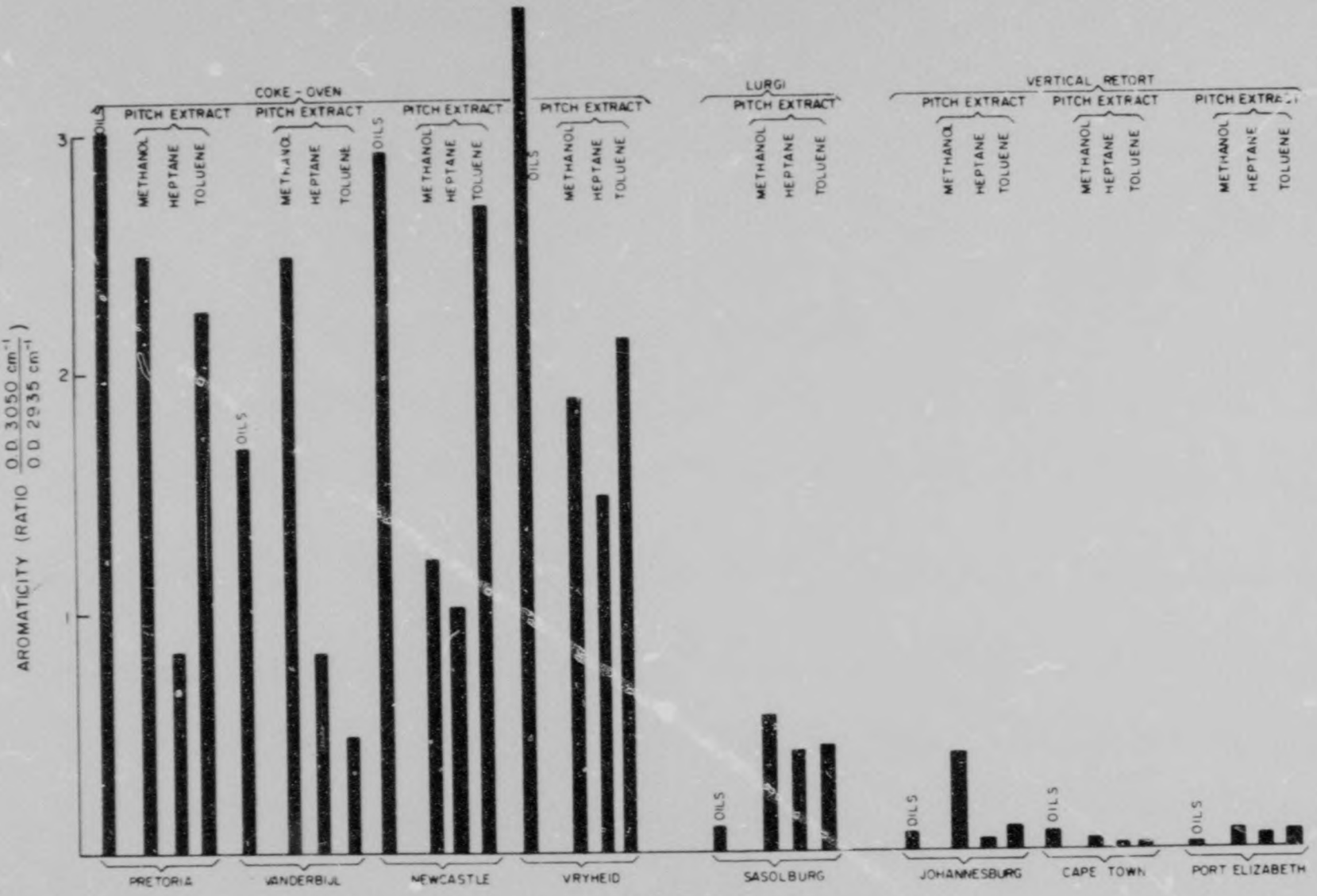


FIGURE 2-15

THE AROMATICITY OF OILS AND PITCH FRACTIONS DETERMINED FROM INFRA-RED DATA (RATIO $\frac{O.D.\ 3050\ cm^{-1}}{O.D.\ 2935\ cm^{-1}}$)

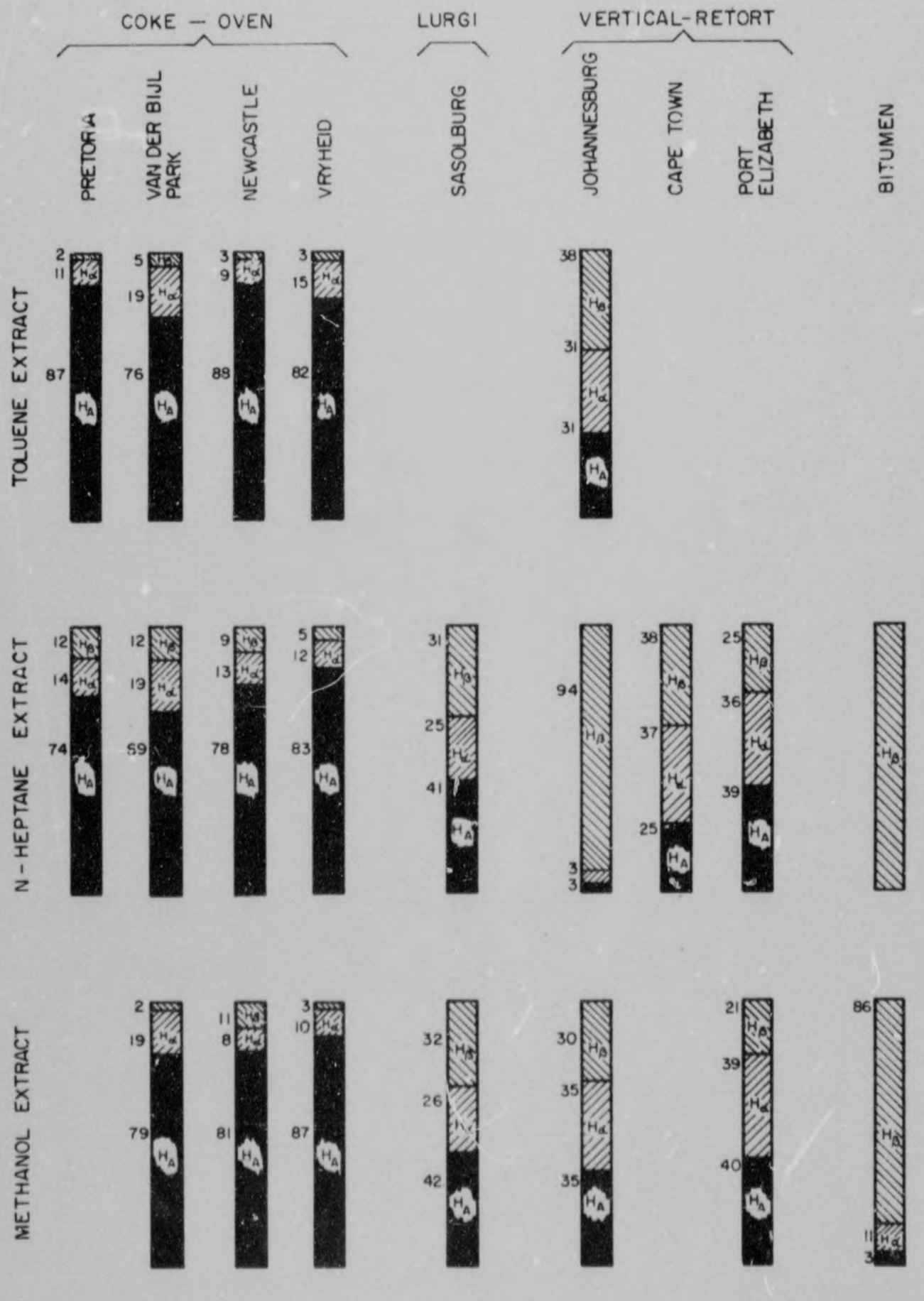


FIGURE 2-16

HYDROGEN DISTRIBUTION (H_A/H_α/H_β) IN SOLVENT EXTRACTS OF SOUTH AFRICAN PITCHES, AND BITUMEN.

For each pitch extract the values of the following parameters are illustrated in Figure 2 - 17: the ratios of aromatic to total carbon, the number of aromatic rings per average molecule, the percentage alkyl substituents on non-bridging aromatic carbons, and the average number of alkyl substituents per average molecule. Despite similar molecular masses the number of aromatic rings was less in the vertical-retort type than the coke-oven type because of the high proportion of saturate carbon in the former. The percentage alkyl substitution on peripheral carbons in the pitch extracts is similar to that in the oils (Figure 2 - 13) but because the molecules in the pitch are larger than those present in the oils the number of alkyl substituents per average molecule in the former is correspondingly greater. The number of alkyl substituents per average molecule for the oils and pitch extracts of the coke-oven and vertical-retort types is shown in Table 2 - 11

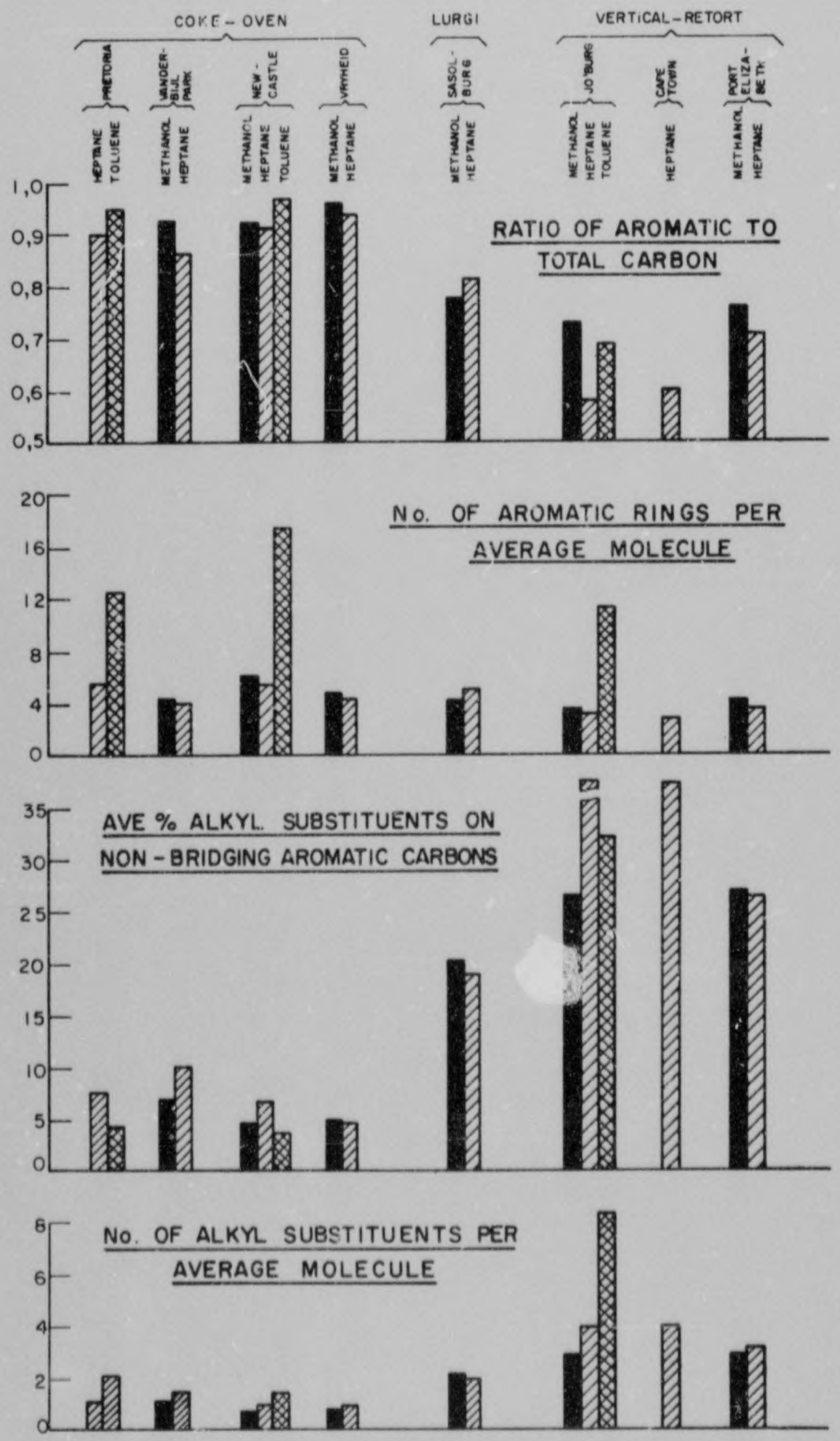
TABLE 2 - 11

DEGREE OF ALKYL SUBSTITUTION IN THE OIL AND PITCH EXTRACTS OF COKE-OVEN AND VERTICAL-RETORT FRACTIONS

Fraction	Coke-oven type	Vertical-retort type
Oils	0,5 - 0,6	1,7 - 2,1
methanol	0,5 - 0,9	2,2 - 2,9
n-heptane	0,7 - 1,4	2,0 - 4,1
toluene	1,4 - 2,1	8,4

These results are in good agreement with results reported by Wilman(1966) who found that coke-oven tars contain 0,5 substituents per average molecule in the low molecular mass fraction and 2,0 substituents per average molecule in the higher fraction whereas in vertical-retort tars the range was 2,5 - 6,0 .

From the structural parameter values (Appendix C, Tables IV - VI) it is possible to suggest average molecular structures that would indicate the degree of ring condensation and alkyl substitution. Average structures for the methanol, heptane and toluene extracts of one coke-oven pitch (ex Iscor, Newcastle) and one vertical-retort pitch (ex Johannesburg gas works) are shown in Figure 2 - 18 .



940-01-4-1620/2

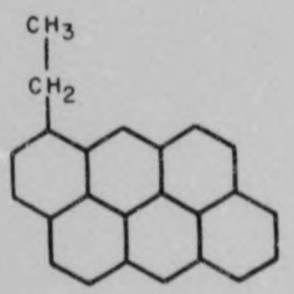
FIGURE 2-17

STRUCTURAL PARAMETER VALUES FOR EXTRACTS OF LOCALLY DERIVED PITCHES.

COKE - OVEN PITCH TRACTS

(EX NEWCASTLE PITCH)

METHANOL EXTRACT



No. RINGS = 6 (6,07)

C_A = 22 (21, 27)

C_I = 12 (11, 12)

C_I / # C_A = 0,545 (0,523)

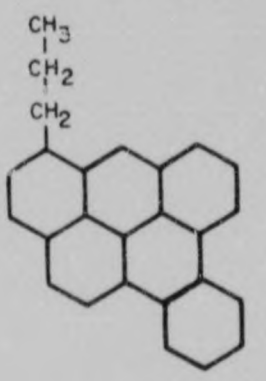
Rs_A = 1 (0,51)

n = 2 (2,30)

MASS = 304 (286)

(WITHOUT N, Se O)

HEPTANE EXTRACT



No RINGS = 6 (6,03)

C_A = 23 (22,51)

C_I = 13 (12,45)

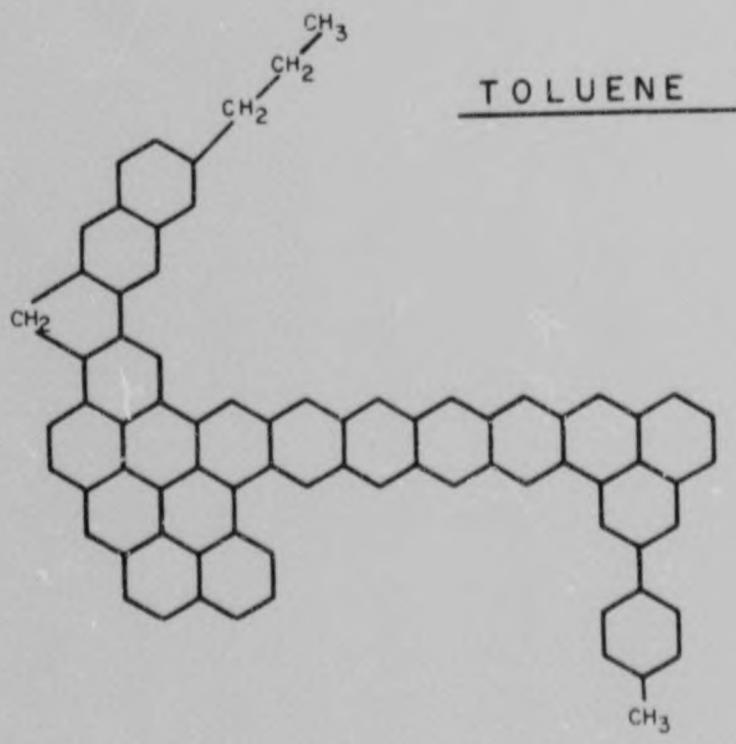
C_I / # C_A = 0,565 (0,553)

n = 3 (2,31)

MASS = 331 (306)

(WITHOUT N, Se O)

TOLUENE EXTRACT



No. RINGS = 18 (17,44)

C_A = 70 (70, 5)

C_I = 37 (37,6)

C_I / # C_A = 0,529 (0,533)

Rs_A = 2 (1,41)

Rs_F = 1 (0, 33)

Rs_{AC} = 0 (0,33)

n = 1,7 (2, 46)

f = 5,00 (4,88)

MASS = 945 (906)

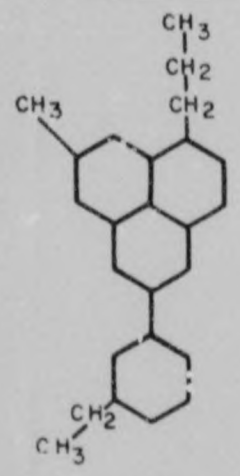
(WITHOUT N, S e O)

FIGU

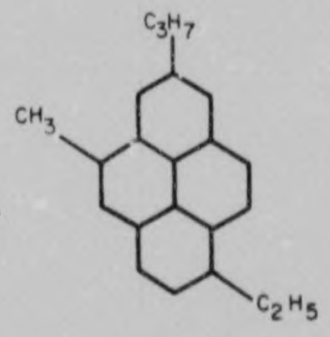
DEGREE OF RING CONDENSATION AND ALKYL SUBST
OF EXTRACTS OF LOCAL COKE OVEN AND VERTICAL
FOR OH GROUPS AND OXYGEN AN

VERTICAL-RETORT PITCH EXTRACTS
(EX JOHANNESBURG GAS WORKS PITCH)

METHANOL EXTRACT



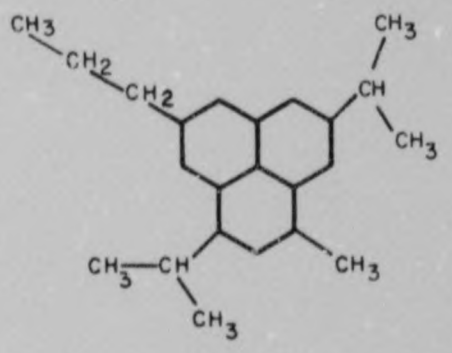
OR



No. RINGS	= 4 (3,5)
$\#C_A$	= 19 (15,87)
$\#C_1$	= 13 (10,88)
$\#C_1/\#C_A$	=0,684(0,686)
Rs_A	= 3 (2,86)
n	= 2 (2,42)
f	=4,8 (4,96)
MASS	=325 (274)
(WITHOUT N, S e O)	

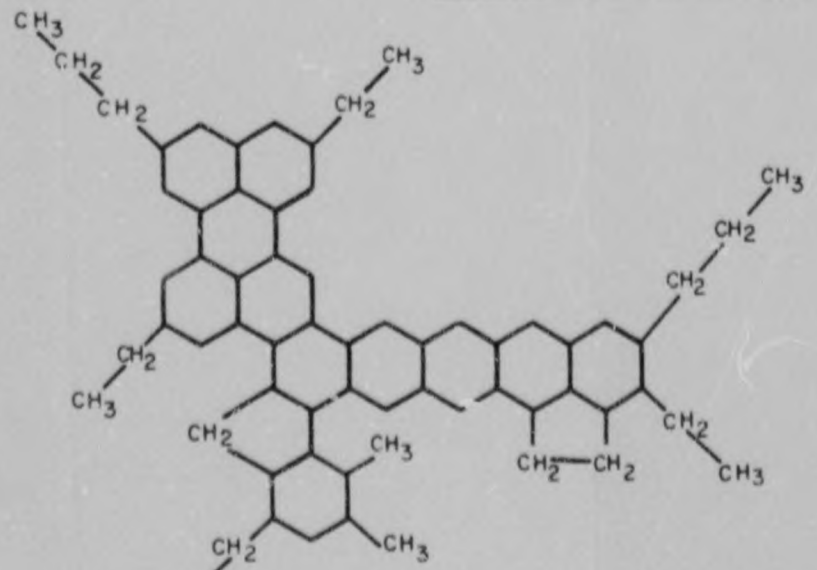
No. RINGS	= 4 (3,5)
$\#C_A$	=16 (15,37)
$\#C_1$	=10 (10,87)
$\#C_1/\#C_A$	=0,625(0,686)
Rs_A	= 3 (2,86)
n	= 2 (2,42)
f	= 4,8 (4,96)
MASS	= 286 (274)
(WITHOUT N, S e O)	

HEPTANE EXTRACT



No. RINGS	= 3 (3,12)
$\#C_A$	= 13 (12,92)
$\#C_1$	= 9 (8,69)
$\#C_1/\#C_A$	=0,692 (0,673)
Rs_A	= 4 (4,06)
n	= 2,5 (2,36)
f	= 5,00 (5,08)
MASS	= 305 (290)
(WITHOUT N, S e O)	

TOLUENE EXTRACT



No. RINGS	= 11 (10, 93)
$\#C_A$	= 46 (45, 86)
$\#C_1$	= 26 (26,00)
$\#C_1/\#C_A$	=0,565(0,567)
Rs_A	=8 (8, 38)
Rs_F	= 1 (1, 28)
Rs_{AC}	= 1 (0,71)
n	= 1,58 (2,28)
f	=4,96 (5,26)
MASS	= 840 (824)
(WITHOUT N, S e O)	

FIGURE 2-18

ALKYL SUBSTITUTION IN AVERAGE STRUCTURES REPRESENTATIVE AND VERTICAL-RETORT PITCHES. (NO ALLOWANCE HAS BEEN MADE D OXYGEN AND NITROGEN IN RING SYSTEMS)

In these structures no provision has been made for attached OH groups or cyclic groups containing oxygen and nitrogen. The aromatic structures of the coke-oven extracts are mainly linear, which is in agreement with the findings of Wilman (1966) and Karr et al. (1967). There is some variation in the degree of ring condensation and the structures ranged from linear chains or acene type structures to ortho- and peri-fused structures. In some cases the H/C atom ratios could only be satisfied by assuming the existence of one and in some cases more than one, diphenyl-type linkage. In future work the existence of diphenyl linkages in the average molecule may be substantiated by carbon-13 magnetic resonance spectroscopy. However, these variations are within limited confines and as a group the structures of coke-oven pitch extracts are substantially different from those of the Lurgi and vertical-retort pitch extracts.

2.2.3.6 Discussion of results; pyridine, quinoline and nitrobenzene extracts and nitrobenzene insolubles

These investigations were possible only in the case of the coke-oven pitches, as the Lurgi and vertical retort pitches were virtually completely removed at the conclusion of the toluene extraction (see Figure 2 - 14).

These extracts were harder than the methanol, heptane and toluene extracts and were difficult to redissolve, even in the solvent used for their extraction. They had a slightly lower carbon content than the more soluble extracts and contained an appreciable amount of fine mineral matter.

The nature of the less soluble portions of pitch is relevant to its utilisation in industry and the macromolecular constituents are said to contribute to their binding properties (Greenhow and Sugowdz , 1961). Jannik (1965) found that the toluene insolubles of pitches contained some dust though Kekin et al. (1968) showed that high molecular mass materials in pitches had a planar structure and he associated greater order and aromaticity with decreasing solubility.

The formation of crystalline structures takes place when the pitch is in a molten condition, and the alignment of large plate-like aromatic molecules begins with the formation of spherical shapes, probably due to the surface tension at the interface of the liquid crystal and the bulk of the isotropic phase in which they are suspended. Because of the high density of the spheres or "spherules" they gradually

settle out, and on contact coalesce to form a bulk mesophase which turns to graphite on prolonged heating.

Photomicrographs of polished specimens of coke-oven pitch extracts are shown in Figures 2 - 19 to 2 - 21. Some polarised light reflectance was apparent, in varying degrees, in all cases but only the quinoline extracts revealed any sign of angular material or crystalline order. The light reflectance was somewhat less than that given by the graphite specimens shown in Figure 2 - 22. The only evidence of spherule formation and mesophase alignment was found in the quinoline-soluble extract of the Vanderbijlpark pitch, Figure 2 - 20, (This was noted in a less highly abraded area of the specimen.)

X-ray spectroscopy of the nitrobenzene insoluble portion showed some d-spacings characteristic of graphite, as shown in Figure 2 - 23.

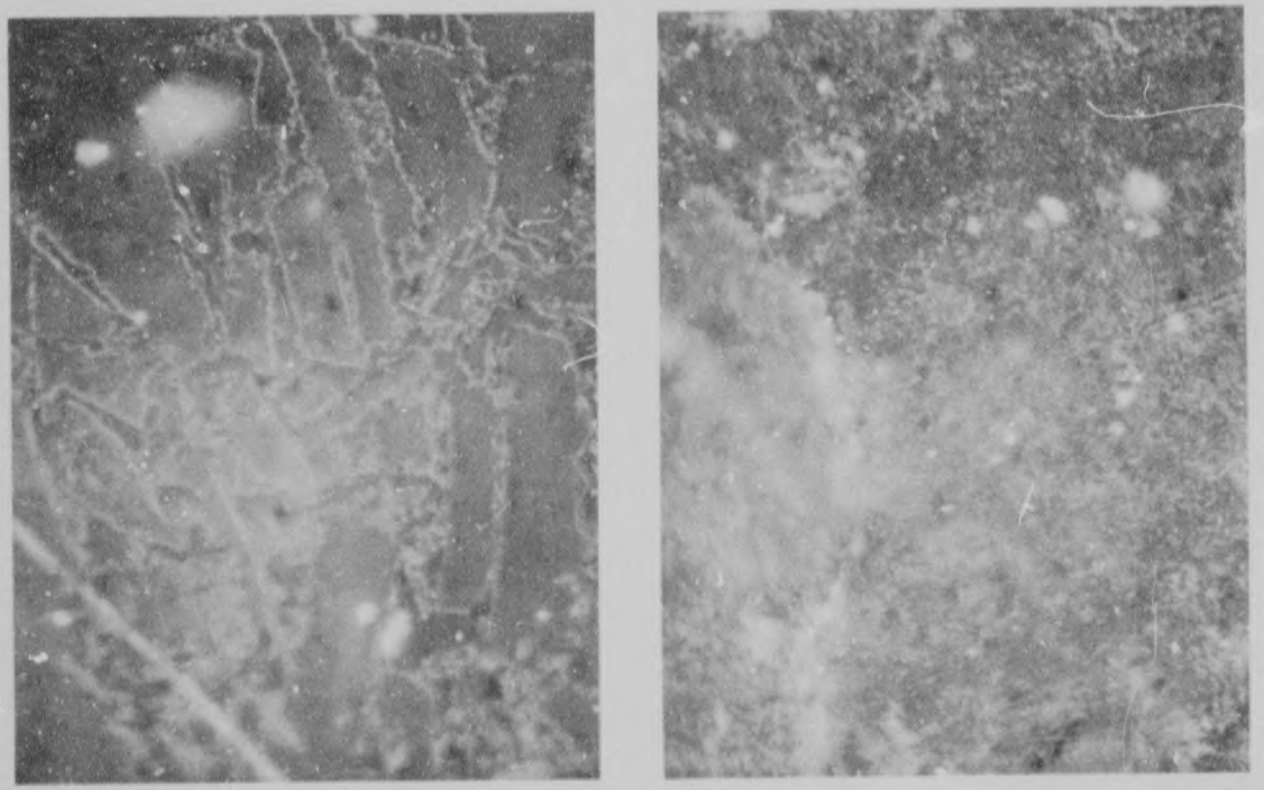
2.2.4 Particular chemical characteristics of Lurgi gasification tars

An important objective of the chemical work was a comparison between Lurgi tar, a comparatively unknown type of tar, and vertical-retort and coke-oven tars in order to assess the potential of the former as a road binder.

In section 2.2.1. it was shown that Lurgi tar is similar to gasification tars as regards density (Figure 2 - 2) and in the proportions of the oil and pitch components (Figure 2 - 3).

Terres and Hahn (1959) identified the constituents of the tar oils by chromatographic methods. They found considerable paraffinic character and that the aromatic portion was alkyl-substituted to a large extent and was also highly phenolic. In the present study it was shown (Table 2 - 11) that the number of alkyl substituents per average molecule was slightly more than is normal in coke-oven tar-oils, whereas the phenol content was very high, 26 per cent of the oils. In terms of the number of alkyl substituents per average molecule and in terms of the phenol contents, Lurgi tar-oils are more closely related to vertical-retort tar-oils than to the oils of coke-oven tars.

Examination of the capillary chromatograms in Figure 2 - 8 suggests, however, that the major constituents of the oils are the same hydrocarbons that form the major constituents of coke-oven tar-oils. When the GLC profiles given in Figure 2 - 8 are compared, peaks 14, 20 and 21, in the Lurgi-tar chromatogram appear to be naphthalene, 2-methyl naphthalene, and 1-methylnaphthalene respectively and the two largest peaks may be fluorene (46) and phenanthrene + anthracene (66).



Quinoline soluble extract *Pyridine soluble extract*

Figure 2 - 19: Photomicrographs of Pretoria (coke-oven) pitch extracts.
(Magnification x360)

(Magnification x 145)

(Magnification x 360)

Figure 2 - 20: Photomicrographs of the Quinoline soluble extract of Vanderbijlpark (Coke-oven) pitch

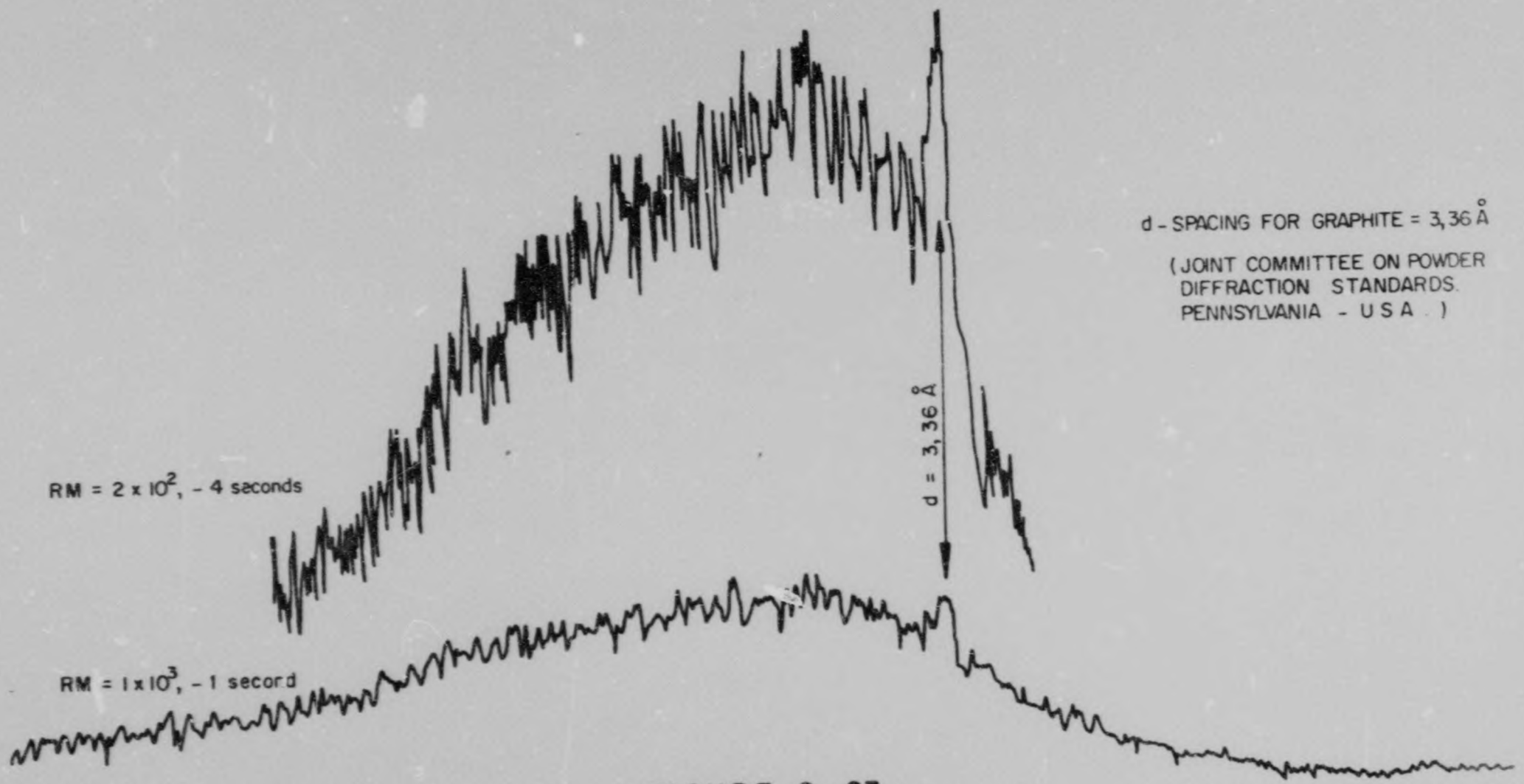
Pyridine soluble extract

Nitrobezene insolubles

Quincline soluble extract

Figure 2 - 21: Photomicrographs of extracts of Newcastle (Coke-oven) pitch.
(Magnification x 360)

Figure 2 - 22: Photomicrograph of a graphite specimen.
(Magnification x 360)



d - SPACING FOR GRAPHITE = 3,36 Å

(JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS. PENNSYLVANIA - U S A .)

FIGURE 2-23

X-RAY SPECTRA OF NITROBENZENE-INSOLUBLE FRACTION OF COKE-OVEN PITCH.

The identities of the major peaks in the chromatogram of Lurgi tar oils were determined by a combination of vacuum distillation, preparative gas-liquid chromatography (to separate and trap individual constituents)and infra-red spectroscopy(for identification of the constituents). (Details of the preparative chromatography and infra-red spectroscopic techniques used are given in Appendices A 1.4 and B. 2 respectively.) Finally the identity of the constituents was confirmed by gas chromatography of solutions "spiked" with additions of the pure " suspected " hydrocarbons.

The GLC-IR method proved satisfactory for the identification of the volatile constituents, but the trapping of the heavier constituents, which emerged in aerosol form, was less successful. The concentration of constituent peaks under study was effectively increased by fractionating the oils by vacuum distillation. This was necessary to trap sufficient amounts for the infra-red examinations. Fractions having the following equivalent cut-point temperatures at 100 kPa pressure were isolated:

1	0 - 200 °C
2	200 - 270 °C
3	270 - 300 °C
4	300 - 370 °C
5	370 - 400 °C

A preparative chromatogram of the unfractionated oils is given in Figure 2 - 24 and chromatograms of fractions 1 - 3 are given in Figure 2 - 25. The constituents that were identified are given in Table 2 - 12. This work showed that the initial assumptions as to the identity of the particular peaks in the capillary chromatogram (Figure 2 - 8) were probably correct.

The properties of the pitch confirm the similarity with the vertical-retort products although certain properties are intermediate between those of vertical-retort and coke-oven pitches. The pitch had a higher softening point than the three vertical-retort pitches (Figure 2 - 6)and the solubility in methanol was intermediate between that given by the vertical-retort and coke-oven pitches. The proton magnetic resonance data showed the Lurgi pitch to be slightly more aromatic than the vertical-retort pitches as denoted by a higher H_A content in the n-heptane extract.

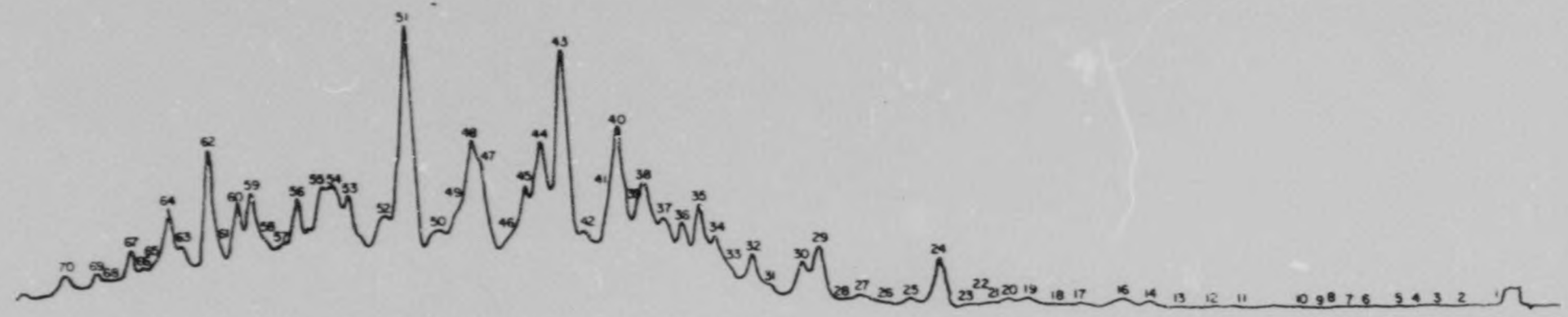


FIGURE 2-24

PREPARATIVE CHROMATOGRAM OF LURGI TAR OILS
(1,1 m Columns 9mm bore. Flow 40 ml/min. Programme 100°C for 10 mins, 100-350°C at 3°/min, Sample 25 µl of 25 % in CS_2)

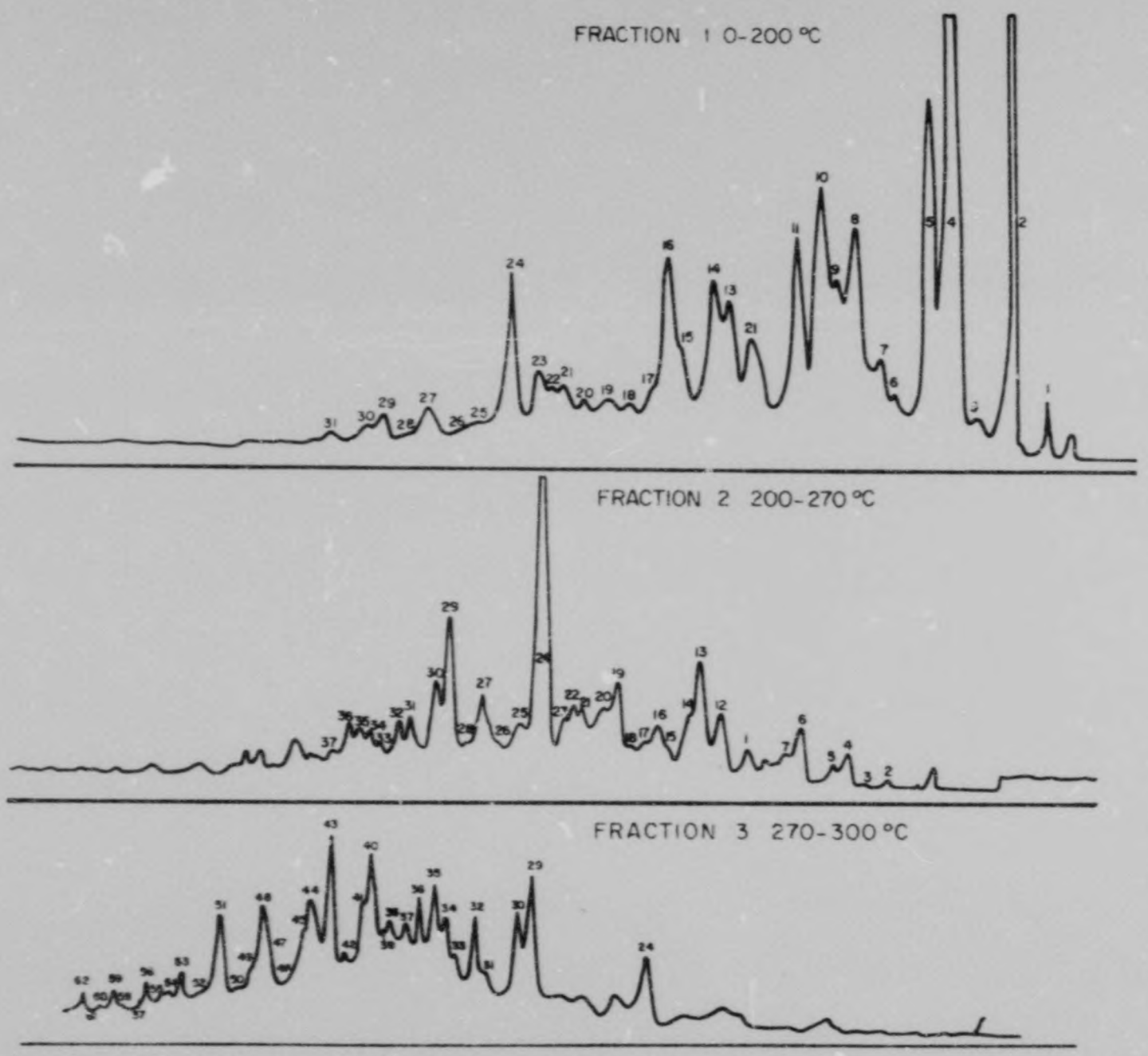


FIGURE 2-25 : *PREPARATIVE CHROMATOGRAMS OF FRACTIONS OF LURGI TAR-OILS (10 µl of 25% sample in CS_2. Atten 5×10^2 Programme 100°C (10 mins) 100-350 °C @ 4°/min)*

TABLE 2 - 12

THE IDENTITY OF PEAKS IN CHROMATOGRAMS OF

LURGI TAR-OILS (FIGURE 2 - 24 AND FIGURE 2 - 25)

Peak No.	Constituent		Boiling point °C at 760 mm Hg pressure
	Suggested	Confirmed	
1	Benzene		80
2		Toluene	110
3	Pyridine		183
4		m-and p-xylenes	138 and 139
5		o-xylene	144
7	Phenol		182
12		o-cresol	191
13		m-cresol	202
14	Indene and p-cresol	p-cresol	202
17		2,6-xylenol	201
21		3,5-xylenol	221
24		Naphthalene	217
29		2-methylnaphthalene	241
30		1-methylnaphthalene	244
39		Acenaphthene	277
40		Diphenyleneoxide	285
43		Fluorene	298
47	2-methylfluorene		318
51	Phenanthrene and Anthracene		340
52	Carbazole		355
56	3-methylphenanthrene		352
62	Pyrene		393

In view of these results it may be concluded that Lurgi tar is similar in properties to vertical-retort tar and that it can be expected to behave similarly when used as a road binder. This is a finding of some considerable importance to the South African road industry for, as mentioned previously, prior to the decline in the European gas-producing industry, considerable quantities of vertical-retort tar were used in road construction and maintenance. These tars were used in surface treatments and wearing and basecourses. They are particularly suitable for use in tar/bitumen and pitch/bitumen blends (McNeil, 1970).

As the binder is more"reactive " and less thermally stable than coke-oven tar it may be less suitable for use in surface courses in South Africa because of the more severe weathering conditions. In Part 3, Chapter 2 the weathering properties and general physical properties of blends of this tar with bitumen are described and in Part 3, Chapter 3 the results of an initial road experiment are given in which the tar was used in the lower layer and in both upper and lower layers of double-surface treatments.

2.2.5 Summary of findings from the chemical work

The main conclusions from the chemical investigations are as follows:

(1) For the first time ever a combination of sophisticated analytical techniques were used to study the chemical characteristics of all major sources of tar available in South Africa. This included the by-product tar derived from the Lurgi gasification process and as a result the potential value of this material to the South African road industry has been established.

(11) In general the results concur with data obtained by other workers overseas. Local tars may be classified into two types; the highly aromatic coke-oven type and the vertical-retort type. The latter is less aromatic than coke-oven tar and the aromatic hydrocarbon constituents contain appreciable numbers of alkyl substituents and a high content of phenolic matter. In terms of aromaticity, alkyl substitution and phenolic content, Lurgi tar conforms to the vertical-retort type.

(111) The crude tars were examined as such and further examinations were carried out on the separate oil and pitch fractions. Subsequently, each pitch was fractionated by solvent extraction and the solvent extracts were examined.

(iv) The unrefined crude vertical-retort tars comply with specifications for primes made from these tars except for water content and the viscosity, which is slightly low.

(v) Chromatographic and infra-red and proton magnetic resonance spectroscopic methods were used to characterise the oils and pitch extracts.

(vi) Methods for the determination of average molecular structures have been tested using coke-oven tar oil whose constitution is well known. A method based on fundamental principles gave results which conformed most closely to the known constitution.

(vii) Using this method the number of alkyl substituents per average molecule of the pitch extracts and the degree of condensation in aromatic structures were estimated.

(viii) In the coke-oven pitches the average number of substituents per average molecule ranged from 0,5 - 2,1 while the oils gave a value of 0,5. Vertical-retort pitches had from 2,9 - 8,4 substituents per average molecule, while in the oils the range was 1,7 - 2,1.

(ix) There was some variation in the degree of ring condensation in the extracts of coke-oven pitches, and this ranged from linear acene arrangements with some diphenyl character to partly condensed ring systems of the aphene type.

(x) Constituents of Lurgi tar oils were identified and they were shown to be the same hydrocarbons which predominate in the oils of coke-oven tars.

(xi) The existence of graphitic or semi-graphitic matter in the less soluble pitch extracts was identified by polarised light microscopy and there was slight evidence of the presence of carbonaceous mesophase.

The variability in the structures of molecules which constitute pitch has implications as regards the thermal stability, oxidation-susceptibility and compatibility with polymers of road tars. Paraffinic linkages, which are predominant in bitumen, will be more stable and render molecules less reactive than the aromatic systems which comprise tars. In turn, tars (vertical-retort) in which molecules contain alkyl-substituted aromatic ring systems will be less stable and more reactive than tars (coke-oven) in which unsubstituted aromatic rings predominate, due to the electron-withdrawing effect of the alkyl substituents which lowers

aromatic ring stability and increases reactivity. In a similar way the presence of nucleophilic hydroxyl groups will increase the reactivity due to its effect on the electrons in the ring and its own inherent reactivity.

It will be apparent that the knowledge of the chemical constitution of petroleum bitumens and tars, from various sources, affords an explanation for the behaviour of these materials, and particularly their weathering behaviour when they are employed as road binders. The paraffinic character of bitumen explains its thermal stability and low oxidation-susceptibility, while of the two types of tar the high phenolic content and the number of alkyl substituents in the vertical-retort type accounts for its high oxidation-susceptibility and thermal instability at high temperature.

2.3 THE PREPARATION OF ROAD TARS

Resumé

Methods for the distillation of crude tar are briefly mentioned and the formulation of road tars from distillation products is described. The concept of volatile and plasticising oils is introduced and it is shown that low-volatile road tars may be most conveniently prepared by using heavy oils and high-softening point pitches. The significance of this in terms of the composition of various types of crude is mentioned.

The volatile matter evolved from coal during the carbonisation process is condensed and collected as described by McNeil (1966a) and others (Smith et al. 1966). This crude tar is then distilled to yield a number of oil fractions and a pitch residue. The pitch is then combined with selected oil fractions to yield road tars of prescribed viscosity grades.

2.3.1 Distillation of crude tars

Tingle and Green (1964) have reviewed the development of tars for use in road construction from the time when crude tars were first used in Europe. These were variable in performance and had several disadvantages due to the presence of water and light oils. As a result a prolonged "boiling" of the tar to remove the light "ends" was recommended (Wynne-Roberts, 1910). While numerous types of distillation plants exist, in South Africa the Wilton type of plant has been used exclusively in recent times for the distillation of coke-oven, Lurgi and vertical-retort crudes. In future most of this country's crude coke-oven tar will be distilled in the Koppers distillation unit which has recently been installed by Iskop at Vanderbijlpark. Flow diagrams of Wilton and Koppers distillation plants are shown in Appendix D.

It has been shown that the proportions of the crude tar may vary according to type (Figure 2 - 3), and in addition the amount of oils in each boiling range and the hardness of the pitch can be controlled by varying the plant operating conditions and particularly temperatures.

It may be thought that these may also affect the chemical characteristics of tars which may influence their properties and behaviour as road binders. However, McNeil, and Vaughan (1953) showed that chemical changes occur only in the case of thermally unstable tars and that continuous distillation processes such as the Wilton and Koppers type were less severe on these tars than a batch distillation process which was used, extensively in Europe (and in places in South Africa) at one time. Thus one would not expect the coke-oven tar, which is the predominant type available locally for road tar production, to be affected significantly during distillation in the plants used in South Africa. Binders derived from Lurgi and vertical-retort tar may be affected to a greater extent because of their relative thermal instability.

2.3.2 Blending of road tars

Road tar binders can be prepared by blending the pitch with selected oil fractions obtained from the Wilton process to achieve the desired viscosity. Road tars are graded in terms of the temperature at which they have a particular viscosity, and in South Africa, as in several European countries, the equiviscous temperature (Evt) scale is used. This is the temperature at which the tar has an efflux time of 50 seconds from the standard tar viscometer (Watkins, 1967) and is equivalent to a viscosity of 25 Ns/m^2 (250 poises). Grades used in South Africa vary from 35 - 40°C to 50 - 55°C for surface treatments and from 45 - 50°C to 60 - 65°C for tar-aggregate mixtures.

Theoretically these grades can be prepared by combining any pitch softening point and oil type but as will be described in section 2.5 and Part 3, the composition of the binder has a marked effect upon its performance. At this stage it may be pointed out that the oils with low boiling points will have a high vapour pressure at normal road temperatures experienced in South Africa, and it is convenient to define the volatile oils as those boiling below 340°C in the standard distillation test; SABS specification 1971 (Jamieson, 1974a). In the earlier study of the evaporation of tar oils from surface treatments, the author (Jamieson, 1974a) showed that eventually all oils boiling below 300°C were lost and that a substantial proportion of oils boiling below 340°C were lost. Oils boiling above 340°C are relatively non-volatile and may be termed "plasticising oils".

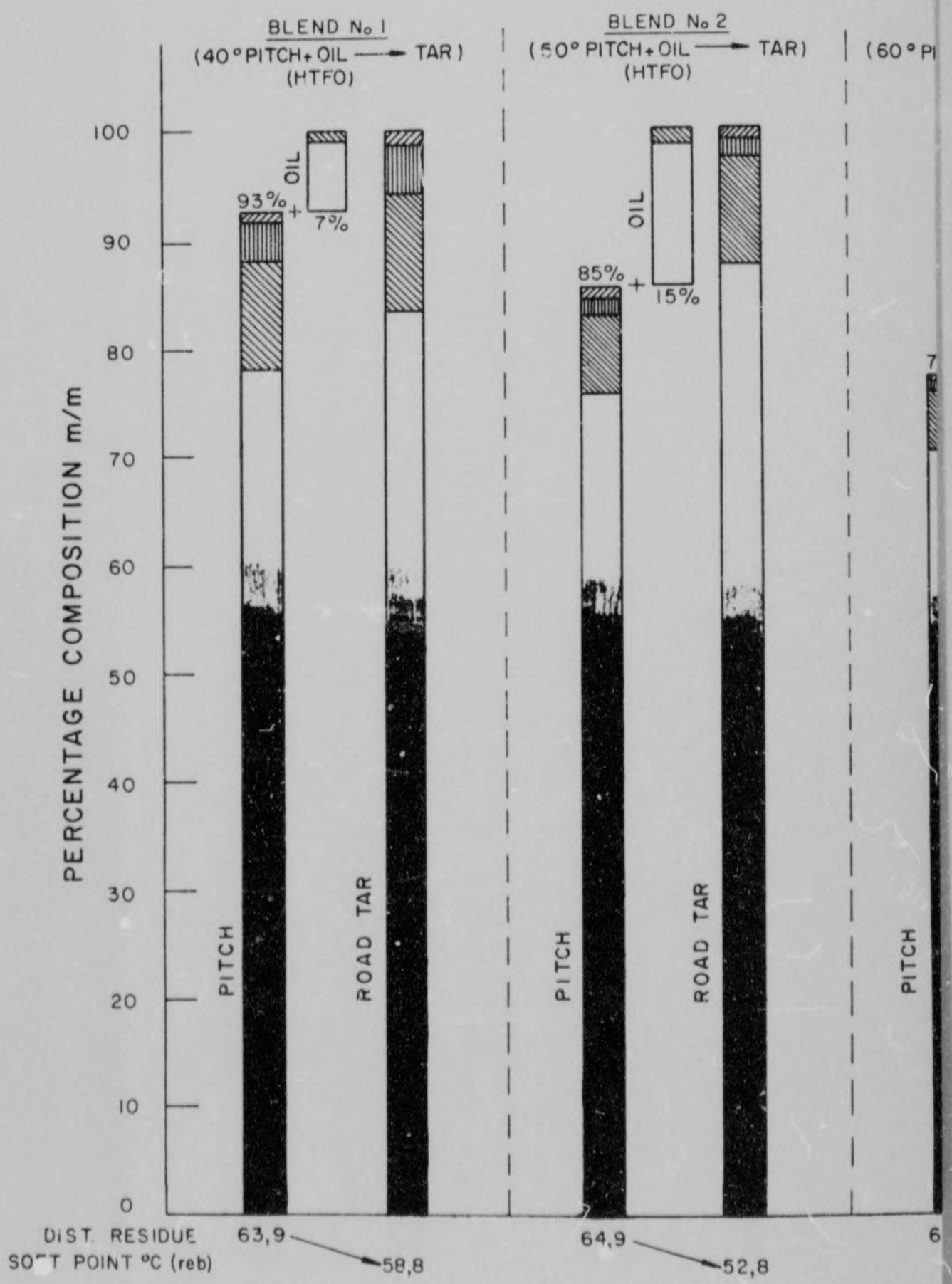
It will be shown Section 2.5 and Part 3, Chapter 1, that in order to improve the durability of tar and modified tars used in surfacings, it is

essential to use heavy oils in the preparation of the binder. The availability of these oils can be increased by operating distillation plants at temperatures which produce pitches with softening points of about 70 - 80°C (ring and ball). Figure 2 - 26 shows that the amount of heavy plasticising oil in the road tar binder increases with increasing hardness of the pitch due to the additional oils necessary to "flux" the pitch to the required viscosity (Evt). Although the exact proportions of plasticising oil in these tar blends was not measurable, the variation in the proportion of this component in the road tar is reflected in the hardness of the distillation test residue .

The blends in Figure 2 - 26 have pitch/heavy-oil ratios ranging from 1,9/1 to 14/1; all of these blends have Evts of approximately 53°C (52,5 - 54,5°C) and all conform to the current SABS road tar specification (SABS 748:1971). As a direct result of the work described in this thesis this specification is under revision and it is proposed to reduce the volatile content of local tars. This will result in smaller pitch to oil ratios than were formerly necessary. As a consequence there may be a tendency for an imbalance to occur in the utilisation of crude tar components (i.e. there may be insufficient heavy oil to flux all the pitch produced)* . Unless manufacturers have an alternative outlet for the excess pitch, the loss in production must be regarded as a price that may have to be paid to ensure that road tars are of good quality.

* As shown in Figure 2 - 3, Lurgi crude tar contains a smaller amount of pitch and an amount of heavy oils similar to that of the coke-oven crudes. Thus there may be less of a problem in making low-volatile road tars from Lurgi crudes.

COMPOSITION OF BL



COMPOSITION AND DISTILLATION CHARACT
(HTFO) AND PITCHES OF HARD

ON OF BLENDS OF SIMILAR EVT (52,5°-54,5°)

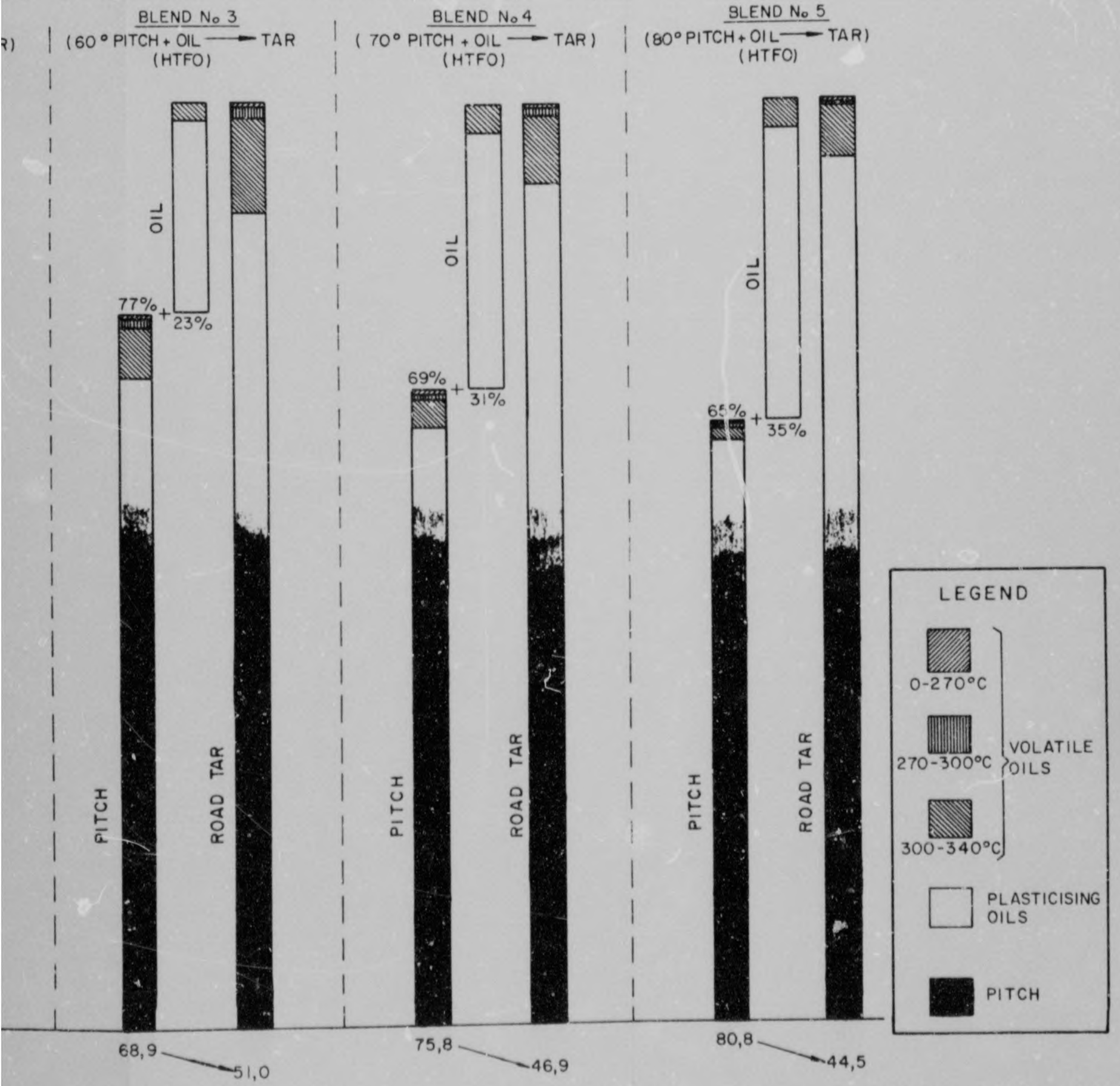


FIGURE 2-26

CHARACTERISTICS OF TAR BLENDS MADE FROM A HEAVY OIL OF HARDNESSES VARYING FROM 40-80°C (reb)

2.4 THE PHYSICAL AND RHEOLOGICAL PROPERTIES OF ROAD TARS AS COMPARED WITH THOSE OF PETROLEUM BITUMEN

Resumé

Tar and bitumen are multi-component solid solutions; although bitumen unlike tar, is a colloidal system. The effect of adding bitumen to tar is explained. Tar exhibits Newtonian flow while the viscosity of bitumen is less temperature-susceptible. A review of the behaviour of binders under load applications that occur under light traffic conditions shows the value of the Fraass method for determining the brittleness of binders, and that low volumes of light, fast traffic are the most severe test of a surface treatment. Rheologically bitumen is superior to tar.

Comprehensive data on the physical properties of tars are given in the Coal Tar Data Book (Coal Tar Research Association, 1965).

While the wetting and adhesion properties are very important, the most important single property of a road binder is its viscosity and the degree to which viscosity is affected by temperature.

To understand the rheological properties of road tars, an explanation of their actual physical structure is necessary.

2.4.1 Physical characteristics

Coal tar and petroleum bitumen are multi-component solid solutions. The freezing points of tar-oils at atmospheric pressures are well above the ambient temperature. Franck (1953) and Jamieson, (1974a) found that mixtures of constituents of tar-oils lower each other's freezing points i.e. the liquid state of tar is due to the formation of a multi-component eutectic.

Reerink (1971) proved conclusively that bitumens are actually colloidal systems with the heavier molecular mass constituents (asphaltenes) suspended in a continuous phase , which is the solid solution of the lower molecular mass constituents. The rheological behaviour of bitumen is consistent with such a hypothesis (Lamb, 1967). In the case of tar, the heaviest constituents have a much lower molecular mass and size than the asphaltene component of bitumens and the labile swarm theory suggested by Raich (1952) has been considered to be a more acceptable hypothesis (McNeil, 1966a). This incorporates the multi-component solid solution

concept but suggests that there are strong associative forces between certain of the heavier molecules leading to the formation of aggregations or swarms. These may be due to the steric intertanglement of the molecules or to inductive forces between the polar and the polarisable hydrocarbons structures. The molecules are thought to interchange between swarms or with unassociated portions of the system.

This theory can be used to explain the effects of different types of solvent (McNeil, 1966a), and the phenomena resulting when bitumen and tar are mixed (see Part,3, Chapter 2). The behaviour of the solvents would be expected to depend upon their polarity. A highly polar solvent would tend to weaken intermolecular forces, reducing the number and size of the swarms and reducing the viscosity. The addition of a non-polar solvent would reduce the attraction between the polar molecules and the unassociated part of the tar, would increase the size of the swarms and lead to their precipitation as they became too heavy to remain in solution by the weakened solven-solute bonds. Bitumen may be considered as a relatively non-polar solvent and its addition to tar, in almost equal quantities, causes a precipitation of a sludge of hydrocarbons. This is often a problem when the two substances are inadvertantly mixed in distributors.

2.4.2 Rheological properties

Although it may be said that tar and bitumen are used as road binders mainly because of their flow properties, the difference in physical structure causes them to exhibit slightly differing rheological behaviour. In particular the viscosity of bitumen is less affected by temperature changes than is the case with tar binders. Tars are Newtonian (the rate of flow or deformation is proportional to the applied stress) whereas bitumens are non-Newtonian.

The use of the equiviscous temperature (Evt) test for grading road tars has been mentioned and ideally the grade used should be such that at prevailing road temperatures the viscosity would be high enough to ensure retention of the chippings (in surface treatment work) or resist deformation (in surfacing mixes or basecourses) but not so high as to result in poor adhesion, or cause brittle failure or fracture of the binder film. The critical wetting viscosity has been determined as 10^4 Ns/m^2 (Briggs, 1970), and the brittle viscosity is in the region of 10^{10} Ns/m^2

The most widely used method of measuring the brittle viscosity is the Fraass brittle-point determination at which temperature the

viscosity is 4 x 10^8 Ns/m^2 (Rigden and Lee, 1953). This is actually a tensile failure test and this means that for road binders there is a characteristic temperature below which they fail in tension as brittle materials. In the Fraass test, a film of uniform thickness is coated onto a plaque. This is flexed, 1 cycle/minute, in a temperature-controlled environment. The temperature is lowered at 1°C/minute and the brittle point is taken as the temperature at which the first sign of a crack appears in the binder film. An automated version of the Fraass test as described by Briggs and Croft (1969) has been constructed for this work. In this version the cooling rate is controlled automatically and the plaque is constructed from a transparent polyester film. The detection of the appearance of a crack is facilitated by a light shining on the back of the film. However, because of the different material used for the plaque, a slight difference in plaque area and different procedures used for the coating, the results may differ slightly from those obtained by the original Fraass procedure. As shown by Krom (1968) these discrepencies only occur in the case of very hard materials (softening points (ring and ball) greater than 80°C). Details of the apparatus constructed for this work are given in Appendix G.

VIscosity-temperature plots for road binders derived from coke-oven and Lurgi tars and petroleum bitumens are shown in Figure 2 - 27. These measurements were taken using the sliding plate microviscometer (Labout and Van Oort, 1956) and readings were taken at a shear rate of 5 x 10^{-2} s^{-1} and over a temperature range of 10 - 40°C. The greater temperature-susceptibility of viscosity of the tars means that the temperature range between the Evt and the Fraass brittle point is smaller for a tar than for a bitumen, (bitumens will be able to experience a bigger temperature drop before becoming brittle). The concept of the Evt/brittle-temperature range has been frequently employed (Walker and Karius, 1962; Kuhnel and Wilman, 1969). Values for local types of road binder have been determined and these results are given in Table 2 - 13.

The real significance of the data can be seen against the background of the annual road surface temperature cycles experienced in South Africa. It has been shown (Jamieson, 1974b) that in Pretoria (Highveld region) the difference between the hottest and coldest road surface temperature is 51,5°C as compared with 29,0°C in Durban and 38,0°C in London. This evidence indicates that tar is less suitable for application in the

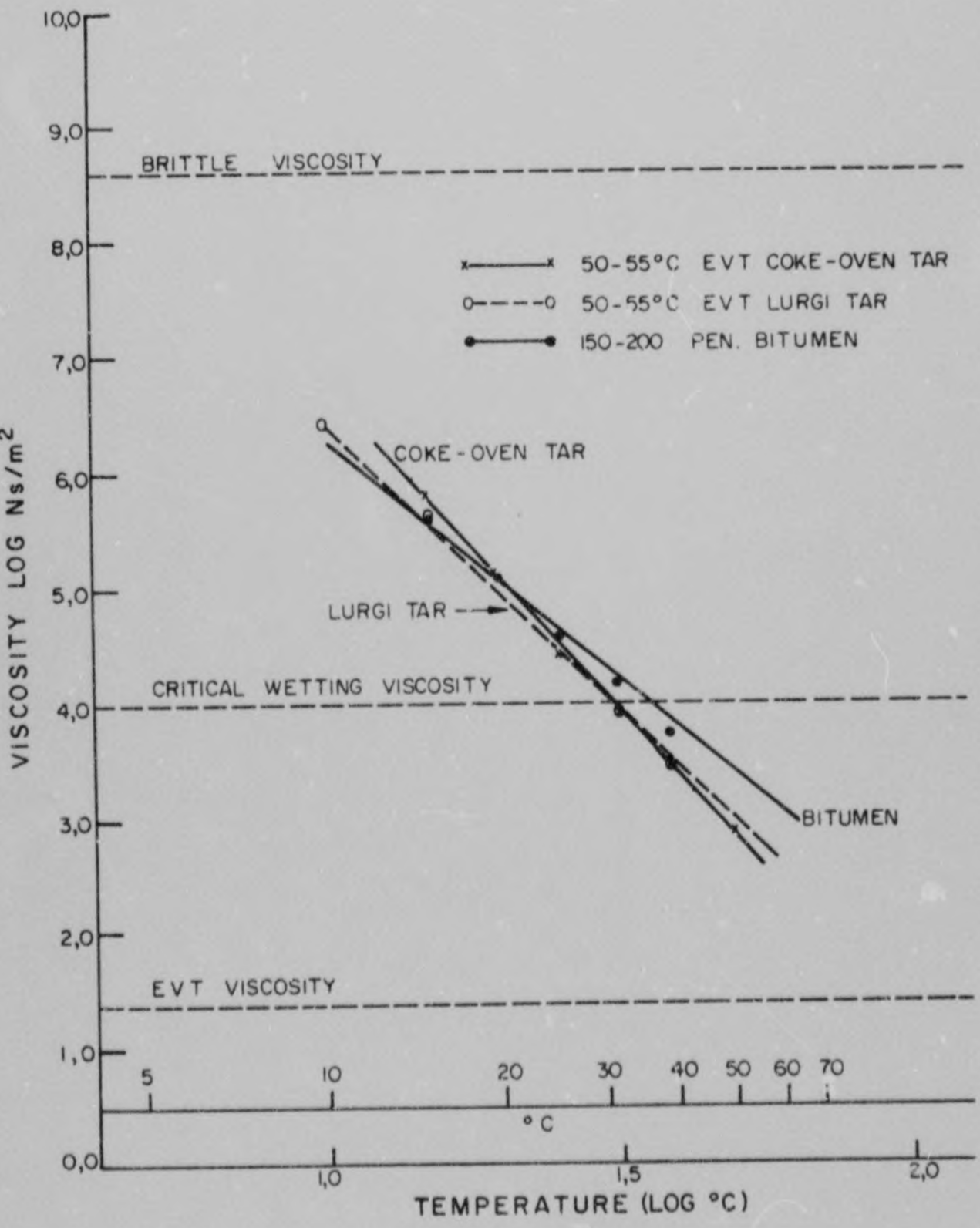


FIGURE 2-27

TYPICAL VISCOSITY - TEMPERATURE PLOTS FOR LOCALLY PREPARED ROAD TARS AND PETROLEUM BITUMEN.

Highveld (i.e where the cost advantage of tar is greatest) than at the coast where bitumen is actually cheaper.

TABLE 2 - 13

TYPICAL EVT-BRITTLE TEMPERATURE RANGES;

VARIOUS TYPES OF ROAD BINDER

Binder type	Evt (°C)	Brittle temperature (°C)	Evt-brittle temp. range (°C)
150/200 Pen. bitumens			
Ex Refinery X	67,7	-18,0	85,7
Ex Refinery Y	68,0	-16,7	84,7
Ex Refinery Z	67,5	-21,7	89,2
Coke-oven tars			
Ex Pretoria	52,3	- 7,0	59,3
Ex Vryheid	55,2	- 5,0	60,2
Ex Wankie	50,9	-11,0	61,9
Lurgi tars			
High-volatile type	42,9	-19,0	61,9
Low-volatile types	45,0	-12,5	57,5

Studies of the rheology of binders by tests which employ static or long times of application of loading are inadequate for assessing their behaviour in roads where rapid load applications occur. Their behaviour and that relative to the behaviour of other binders may be quite different under dynamic conditions. Van der Poel (1954) introduced the stiffness concept to express the resistance of binders to flow at specific loading times and temperatures. In such methods a sinusoidal stress or strain may be imposed and the resulting strain or stress which is also sinusoidal, but displaced in phase is measured. Stiffness moduli are usually plotted against time of loading on a log-log basis and the stiffness modulus is for all practical purposes independent of stress for a wide range of bituminous binders. (This is not the case in static tests.). The stiffness/rate-of-loading curve is referred to as the stiffness function.

Typical stiffness functions for tar and bitumen have been determined by Daines (1972) and it is apparent that tar has a higher stiffness than bitumen at low temperatures and rapid rates of loading.

Laboratory studies of the behaviour of binders under dynamic loading conditions are particularly relevant to their behaviour in surface treatments. At high road surface temperatures it has been shown that stiffness is approximately proportional to the frequency of loading or vehicle speed (Dorman and Jarman, 1958). The loading time varies from about 10^{-1} to 10^{-4} seconds. Because of the low stiffness of binders on newly laid surface treatments, the stones offer less resistance to displacement and this permits the formation of a tightly-knit mosaic of stones and embedment into the substrate. As the binder weathers, its viscosity and stiffness increase and this will be greater in cold weather. If this reaches 10^{9} Ns/m^{2} the result may be brittle failure. The stiffness will also be greatest on surfaces carrying the fastest traffic.

Briggs (1969) developed a simple impact test for measuring the energy absorbed in rupturing a film of road binder from which he was able to show that at moderate vehicle speeds the maximum temperatures at which binders behave as elastic solids (i.e. in which the failure mode is brittle fracture) was in good agreement with the Fraass brittle temperature (Briggs, 1973). The energy absorbed was calculated from the overswing of a pendulum whose purpose was to provide impact to separate two pieces of stone, of standard dimensions and type, cemented together by the binder under test. Typical impact-energy versus temperature curves for a tar and bitumen of similar Evt are shown in Figure 2 - 28.

The temperature axis may be divided into three regions. At temperatures above Evt + 5°C the disruption of the bond is by viscous flow, and as the temperature drops below the Evt + 5°C, the impact energy increases until a maximum is reached at the ultimate strength of the binder. This is the visco-elastic region in which the binder may absorb energy by slight flow of the binder and small strains may be recovered, if the stress is not too great. At temperatures about 40°C below the Evt the energy decreases until a stage is reached when no flow occurs on stress application and failure in this elastic region is due to brittle fracture.

Briggs (1973) estimated a typical energy value transmitted by the

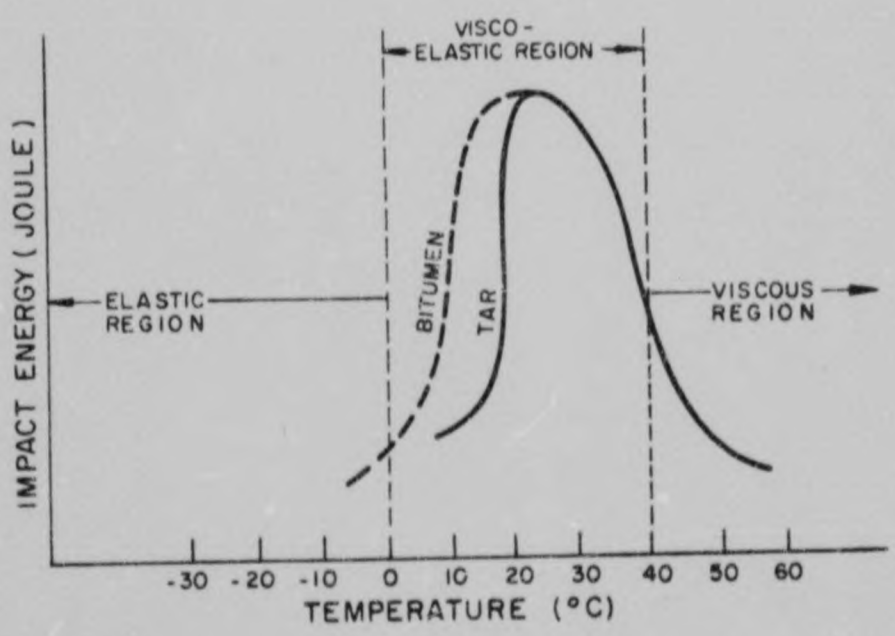


FIGURE 2-28

TYPICAL IMPACT ENERGY VS TEMPERATURE CURVES FOR COKE OVEN TAR AND BITUMEN OF THE SAME EVT (BRIGGS, 1973)

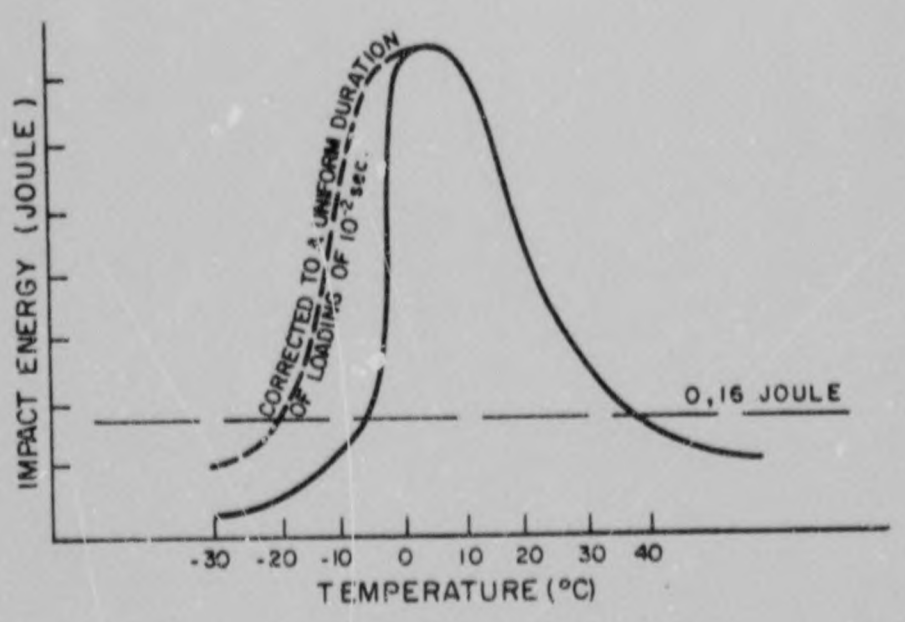


FIGURE 2-29

ENERGY TRANSMITTED TO A ROAD SURFACE BY A SALOON CAR TRAVELLING AT 50-60 km PER HOUR SUPERIMPOSED ON A TYPICAL ENERGY - TEMPERATURE CURVE FOR A COKE-OVEN TAR (BRIGGS, 1973)

wheels of a saloon car to the road surface. He obtained a value of 0,16 Joule which superimposed on an impact energy-temperature curve, Figure 2 - 29, cuts the high-temperature end of the curve near the Evt and at about 60°C below the Evt on the low-temperature end.* This is in agreement with the Evt-brittle point temperature interval determined for coke-oven tars (Table 2 - 13) and shows that the simple Fraass method measures a meaningful property of road binders. In practice the interlocking mosaic of the stones and their embedment into the substrate provide additional resistance to forces promoting rupture of the binder-stone bond. However, until this mechanical reinforcement builds up, the binder is the sole means by which the stone is retained on the road surface.

From the stiffness concept and Brigg's mechanical rupture studies it is apparent that increase in vehicle speed is equal to an effective increase in the temperature at which the brittle fracture may be expected to occur. Thus the most severe conditions for a surface treatment must be low volumes of light, rapidly moving traffic.

These studies also show that rheologically tar is an inferior product to bitumen particularly for use in surface treatments. This may be partly compensated for by superior adhesion characteristics of tar. Because of the polarisability of tar hydrocarbons, the interfacial bonding between tar and aggregate is superior to that between bitumen and aggregate. This property is demonstrated by the results of the detachment tests given in Part 3, Chapter 2, (Figure 3 - 28.).

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* Due to the shorter travel before rupture in the elastic region, the rate of loading in the test was much higher than in the viscous region and a correction had to be applied using frequency temperature superposition data.

2.5 A STUDY OF THE WEATHERING OF ROAD TARS IN THE HIGHVELD CLIMATE

Resumé

Road tars weather more rapidly on the South African Highveld than in Britain. A gas chromatographic method, previously developed by the author, was used to study changes in the composition of coke-oven tars in single-surface treatments over a period of four years. Correlation of this data with increase in viscosity suggests that evaporation of light oils is the major cause of weathering in the initial period of service but that other mechanisms may play an increasing role as the period in service increases. In non-coke-oven types other mechanisms may play a more important role.

The weathering of road binders is marked by an increase in viscosity and stiffness leading eventually to brittleness and loss in ductility. The rate at which these changes occur in a given binder is referred to as its durability.

It is well known that the durability of a binder may be decisive in determining the ultimate life of a road surfacing (Jamieson and Hattingh, 1970). Increase in stiffness may lead to eventual failure of surfacings due to loss of stone and cracking. These phenomena should not be confused with premature stone loss or bleeding in surface treatments, (due to incorrect selection of binder viscosity on application, to wet weather or dusty stone) or with premature distress in basecourses or surface courses mixes (which may be due to incorrect binder viscosity, excessive mixing temperature, insufficient compaction or inadequate supporting layers.).

The mechanisms by which road tars age have previously been discussed by the author (Jamieson, 1974a) and evaporation and oxidation both appeared to be of major importance. Both these processes were seen to be functions of the hydrocarbon type, the thickness of the binder film, viscosity and temperature.

South African road engineers have always maintained that the main reason for the poor performance of road tars in South Africa is the very strong oxidising conditions that exist in this country, particularly on the Highveld. Tar is more susceptible to oxidation than bitumen, as is

shown in Figure 2 - 30.* The author attempted a comparison between the weathering of road tars (of coke-oven origin) in British and South African climates using results obtained from an Accelerated Weathering Test known as the SEGAS test (Wood, 1971). The SEGAS test purports to simulate the hardening of tar after one year in a surface treatment in Britain and SEGAS test results were compared with the actual hardening of these binders after one year in a surface treatment laid near Pretoria. (The Evt of the tar after one year in the surface treatment was determine. by procedures previously described by the author (Jamieson, 1974a). A section of the surface treatment was removed by hand and the binder separated from the stone in a hot centrifuge. The Evt of the tar was then determined by means of a trough viscometer (Dewhurst and Deadman, 1956). The results of the comparison are shown in Table 2 - 14 and indicate that in South Africa the change in Evt of these coke-oven tars in the first twelve months of service is about 4 - 5 times greater than would have occurred if they had been used in Britain.

TABLE 2 - 14

INCREASE IN EVT OF TWO TARS AFTER ONE YEAR IN SURFACE TREATMENTS IN BRITAIN (SIMULATED CONDITIONS USING THE SEGAS TEST) AND IN SOUTH AFRICA (HIGHVELD)

Sample No.	Change in Evt °C	
	In SEGAS test	After 1 year's service in South Africa
1	10,1	44,8
2	6,6	33,3

* These tests were carried out using the Lee and Dickinson (1954) pressure oxidation bomb. The test temperature was modified so that all binders had the same viscosity under the actual test conditions so eliminating the effects of the viscosity variable. The oxidation-susceptibility was expressed as a ratio of the final to the initial viscosity measured by the sliding plate microviscometer. The 7 mm thick films were exposed to an oxygen pressure of 2070 kPa (300 psi) for 24, 72 and 96 hours.

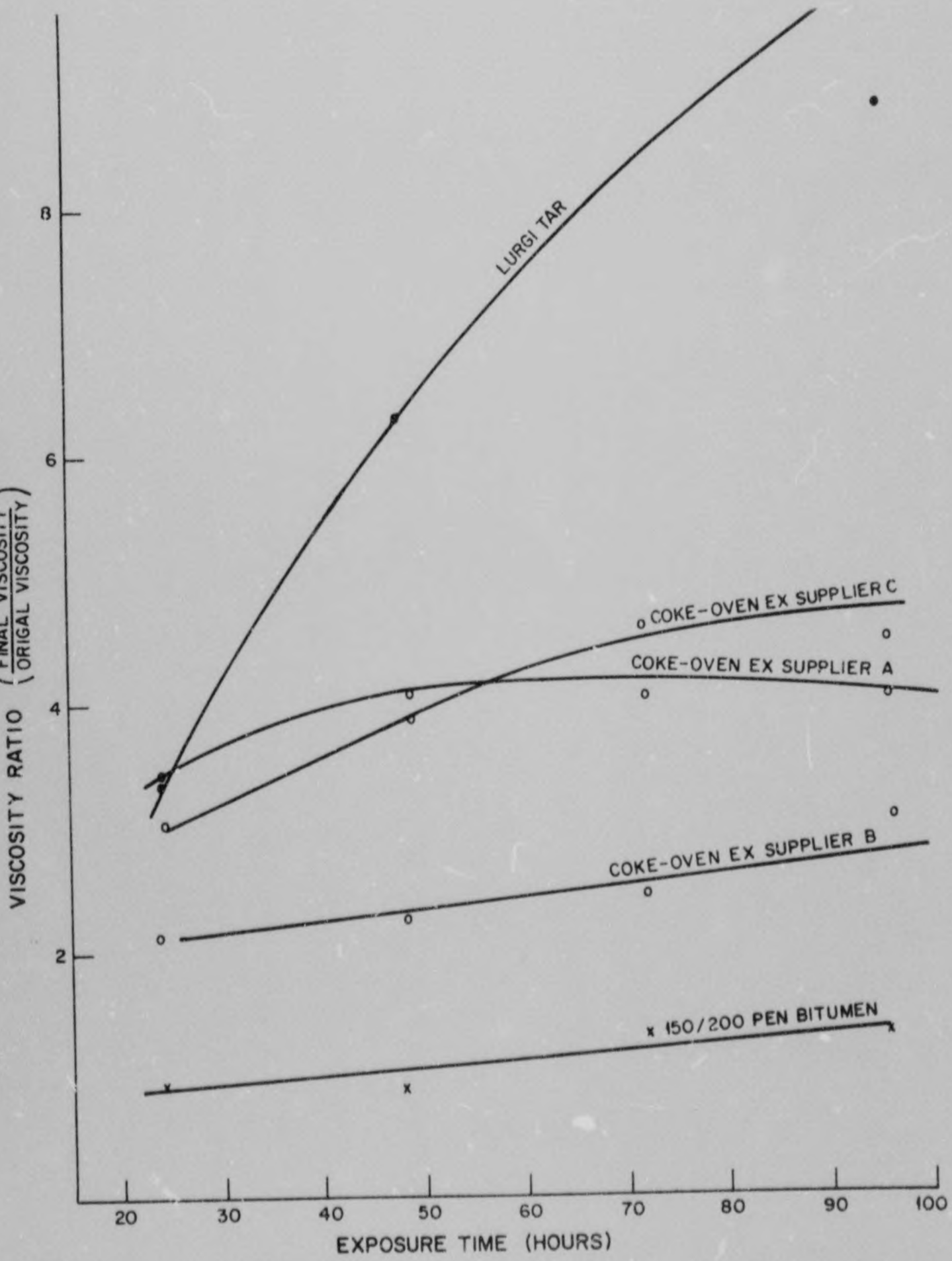

FIGURE 2-30

OXIDATION SUSCEPTIBILY OF VARIOUS LOCAL TARS AND A BITUMEN (FROM JAMIESON (1974a)

Previously Lee and Dickinson (1951), Dickinson et al. (1958) Krenkler (1962) and Swaminathan and Shukla (1967) have attempted to determine the predominant weathering mechanism. Green (1969) concluded that in the United Kingdom the predominant weathering mechanism in tars used in open-textured surfacings depended upon the source and type of tar. From Green's results it appeared (Jamieson 1974a) that evaporation was responsible for 60 - 80 per cent of the hardening of coke-oven tars. However, Bartle et al. (1969) who studied the weathering of these tars using sophisticated instrumental methods, found little evidence of any changes due to oxidation. Wilman (1966) had previously concluded that evaporation of the lower molecular mass constituents provided a satisfactory explanation for most of the changes detected and that oxidation played a relatively minor role.

Although environmental conditions on the South African Highveld are more favorable to oxidation than is the case in Europe, the extent of the actual oxidation taking place may depend upon the application, and in particular the thickness of the tar films may be critical. Williamson (1972) found that there was significantly more insolation on road surfaces in South Africa than in Europe and previously Dickinson (1949) and Dickinson et al. (1958) found that UV radiation promoted oxidation of hydrocarbons in organic binders. However, the latter authors showed that binders had strong light absorbing properties and that less than one per cent of light of wavelengths less than 5 000 Å was transmitted by tar films 10 µm thick. This has been given as an explanation (Nicholas and Boas-Traube, 1956) for the formation of a hard skin or oxidised layer on the surface of the binder films exposed to such radiations. In surface treatments film thicknesses are of the order of 1 mm (1 000 µm) and the presence of such a skin would be expected to have a lesser effect on the performance of the surfacing than in open-textured mixes where film thicknesses are of the order of 10 µm. In dense surface mixes (e.g. dense tar surfacings) the ultraviolet radiation would not penetrate to any significant extent.

The author previously developed a GLC simulated distillation method by which it was possible to monitor changes in the composition of the oil component of coke-oven road tars in service (Jamieson 1974a). A correlation between loss of oils from coke-oven tars and increase in Evt was obtained. In the present study further detailed

examinations of the tars used in these surfacings were made. A brief description of the method, together with the earlier and more recent results is given in Appendix A 1.1. and A 1.2.

The change in composition of tar-oil fractions over a period of one week in an experimental surfacing constructed on the route P43/2 between Orkney (Transvaal) and Bothaville (Orange Free State) is shown in Figure 2 - 31.* These results shown a definite trend towards a loss of oils, and although changes between successive samples are generally less than 2 x standard deviations of the method for each oil fraction, the total change over the week was significant for the lower boiling fractions (below 340°C). Similarly changes in compositions over a twelve month period following the application of a tar surface treatment on 5th Road, Greymont, Johannesburg are shown in Figure 2 - 32.

The results from the earlier study of tars weathered for one year and two years** show that correlations between oil losses and change in Evt (increase in viscosity) are most significant in the case of oils boiling below 340°C. These analyses are given in Tables 1 and 11 of Appendix A, and statistical comparisons are given in Table 2 - 15.

---

* As described in Appendix A in all cases the analyses of tar recovered from the road were corrected for the presence of detritus in the samples and for the oils lost from the tar so that the true loss of oils from each oil fraction could be determined.

** In this case the tars tested after one year were not the same as those tested after two years.

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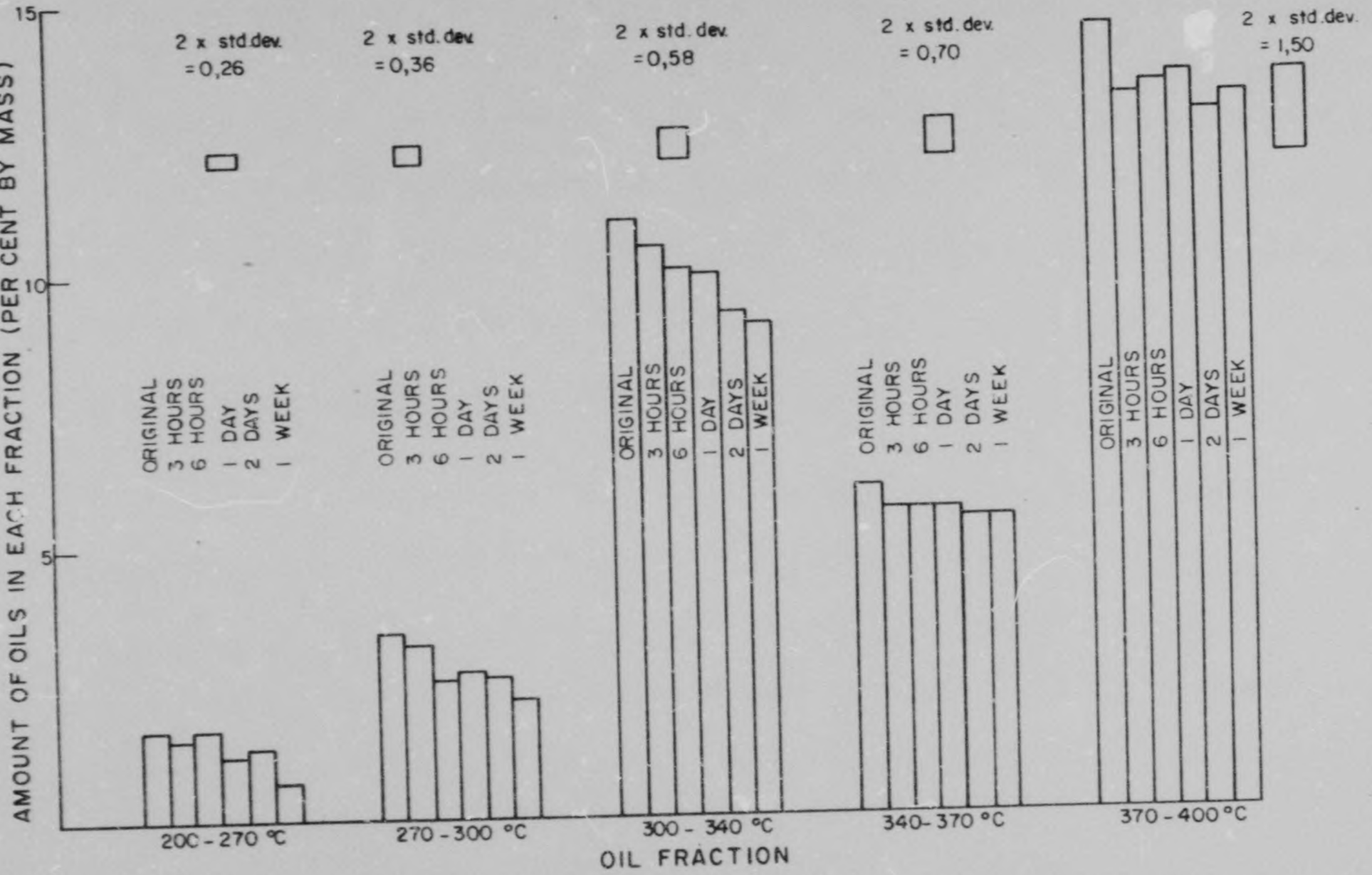

FIGURE 2-31

THE CHANGE IN COMPOSITION OF A ROAD TAR IN ONE WEEK IN A ROAD SURFACE (RESULTS EXPRESSED AS A PERCENTAGE OF ORIGINAL TAR)

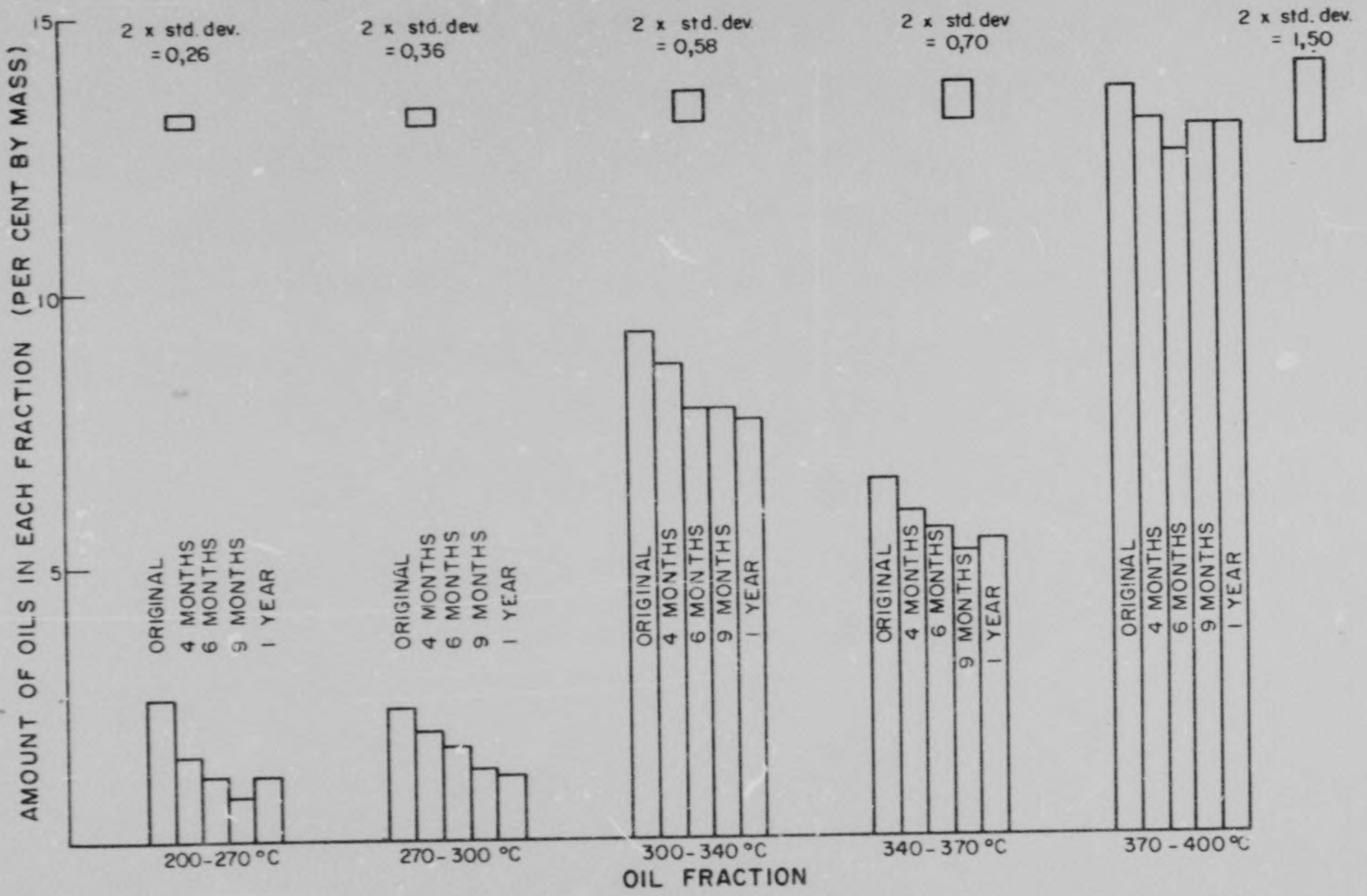

FIGURE 2-32

THE CHANGE IN COMPOSITION OF A ROAD TAR IN ONE YEAR IN A ROAD SURFACE (RESULTS EXPRESSED AS A PERCENTAGE OF ORIGINAL TAR)

TABLE 2 - 15.

CORRELATION BETWEEN THE PERCENTAGE OF OILS LOST IN THE VARIOUS CUMULATIVE OIL FRACTIONS AND THE INCREASE IN EVT

Oil fraction °C	Correlation coefficient	Significance level*
0 - 270	0,84	The probability that this correlation is spurious is less than 1 in 100
0 - 300	0,81	
0 - 340	0,83	
0 - 370	0,81	
0 - 400	0,73	The probability that this correlation is spurious is less than 5 in 100

*

NOTE

(i) The standard deviation in determining the amount of oils in each fraction is given in Appendix A.

(ii) The standard deviation involved in the weathering, the recovery and determination of the Evt of the weathered tars was 0,75°C

(iii) The confidence level was determined by the F test

$F = (N-2)\left(\frac{R^2}{1-R^2}\right)$ where N = number of samples and R = correlation coefficient

(Kenney and Keeping, 1961).

In extending this study the tars examined after one year in service were re-analysed after four years in service. Details of all the tars analysed after one year and again after four years in service are given in Table 111 of Appendix A 1.2. The correlation between loss of oils (boiling below 340°C) and change in Evt over the four year period was similar (correlation coefficient 0,77) and whereas R^2 can be taken as an indication of good fit in regression work, then it can be said that at least 59,3 per cent (R^2 x 100) or approximately 60 per cent of the change in Evt in the first four years of service is attributable to loss of oils boiling below 340°C.

Much stronger correlations were obtained from measurements taken on one tar over a shorter period - 38 days - in service (Appendix A Table V)

The regression lines for the various fractions were:

0 - 270 °C fraction: Change in Evt = 10 x oil loss + 0,1 (R = 0,93)
0 - 300 °C fraction: Change in Evt = 6 x oil loss + 6,0 (R = 0,96)
0 - 340 °C fraction: Change in Evt =3,25 x oil loss -1,4 (R = 0,98)
0 - 370 °C fraction: Change in Evt =2,54x oil loss + 0,2 (R = 0,98)
0 - 400 °C fraction: Change in Evt =2,21x oil loss + 1,8 (R = 0,98)

Plots of change in Evt versus total oil losses (0 - 400°C) recorded in the 38-day and one-and four-year investigations are shown in Figure 2 - 33. The strong correlation reaffirms that loss of oils is the major mechanism by which tars harden in surfacings of this type. These light hydrocarbons are not of the type found by Knotnerus (1971) to be most susceptible to oxidation and in view of the evidence given by Bartle et al. (1969) it seems, as pointed out by Wilman (1966), that evaporation is by far the most probable means by which these light oils are lost. As the correlations are strongest in the shorter period, it may be that evaporation accounts for virtually all the hardening initially and that hardening by oxidation and other mechanisms is minimal at this stage but becomes more important as the life of the surface increases. This is represented in Figure 2 - 34.

The main conclusion made from this study, that the hardening is closely associated with the oil losses, is substantiated by the fact that the change in Evt per per-cent of oils lost, is very similar to the fluxing power of tar-oils of similar constitution.

The fluxing power of the oils was established by subjecting a typical tar (blend No. 4 used in the four-year experiment) to vacuum distillation and determining the quantity of the oils removed and the Evt of the residual tar. The distillation was carried out to an equivalent final vapour temperature of 400 °C (at 100 kPa) and the process was interrupted at temperatures equivalent to the following at atmospheric pressure: 200 , 234 , 265 , 295 , 325 and 340°C at each of which the composition of the evaporated oils* and hardness of the tar left in the flask were determined. These results are given in Table 2 - 16

* Oil compositions were determined by GLC using the same operating conditions as before. In this case the amounts of the various fractions were calculated from the normalised peak areas.

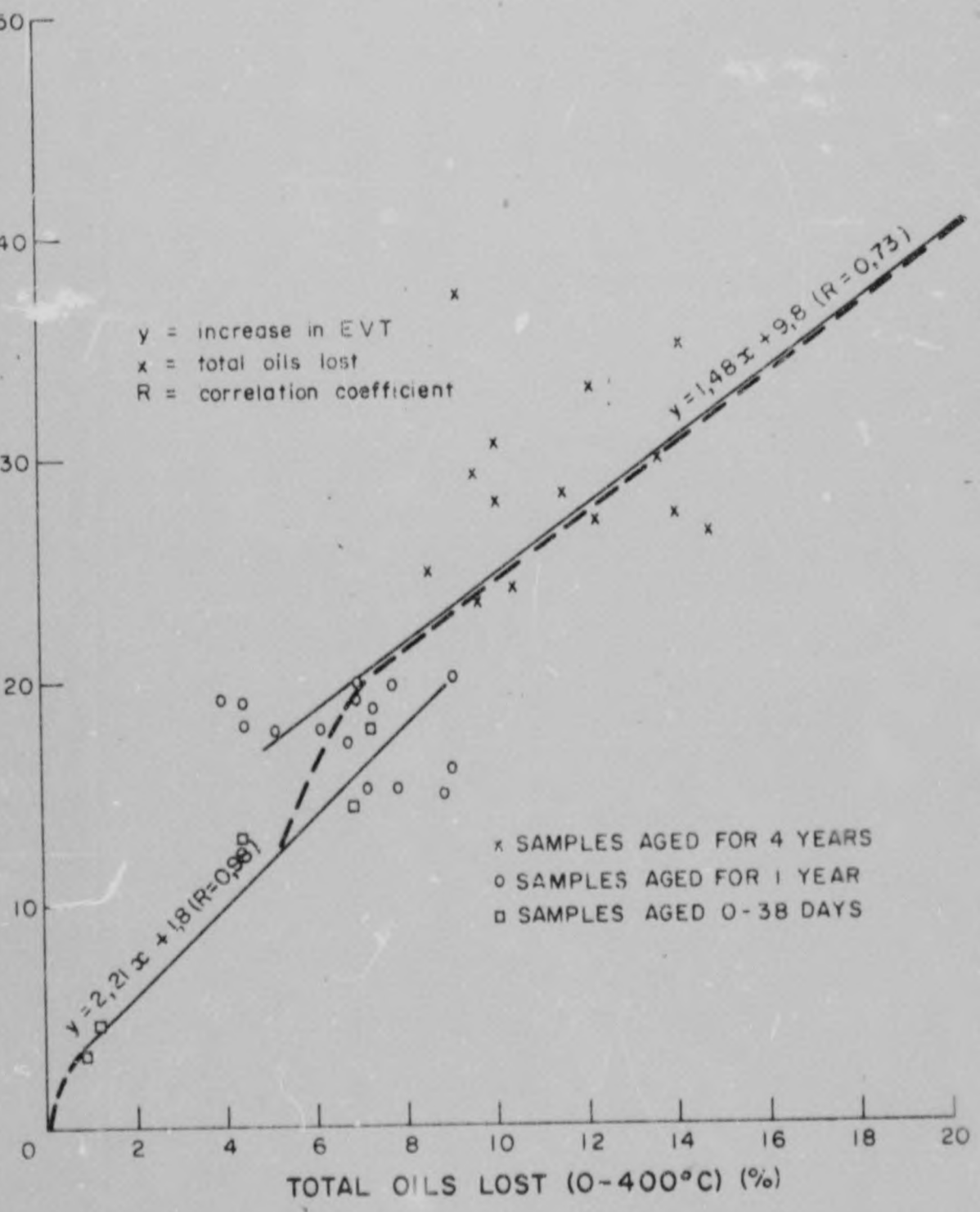

FIGURE 2-33

RELATIONSHIP BETWEEN LOSS OF OILS AND CHANGE OF EVT IN SERVICE

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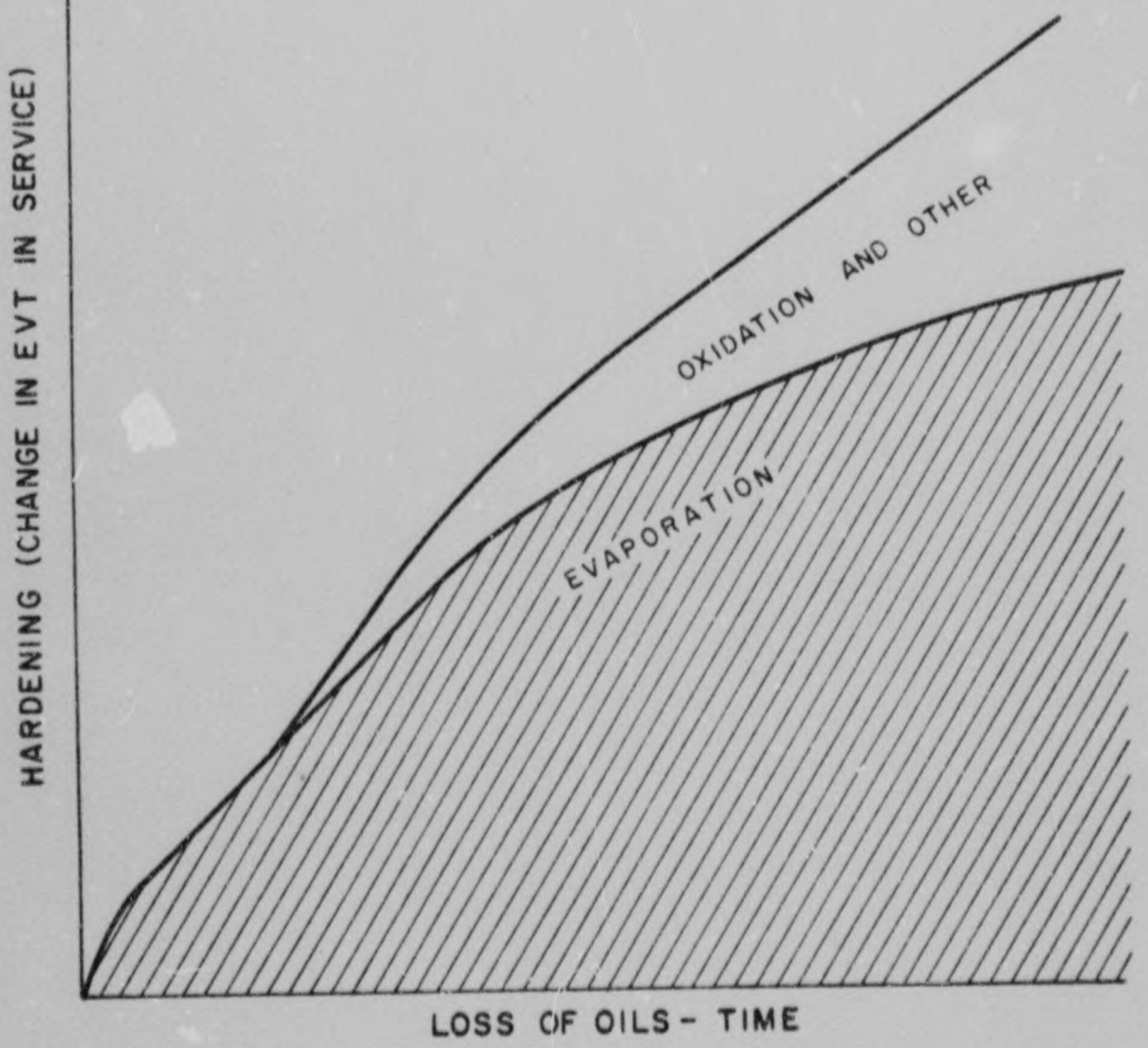

FIGURE 2-34

THE ROLE OF EVAPORATION AND OXIDATION IN THE HARDENING OF COKE-OVEN TARS IN SURFACE TREATMENTS

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TABLE 2 - 16

THE QUANTITY AND COMPOSITION OF OILS SEPARATED FROM ROAD TAR BY VACUUM DISTILLATION AND THE EFFECT OF THEIR REMOVAL ON THE EVT OF THE UNDISTILLED PORTION

Property	Fraction No.					Total oils removed
	1	2	3	4	5	
Nominal Boiling range of oils removed (°C)	0-234°C	234-265	265-295	295-325	325-340	0-340°C
Quantity of oils removed (% by mass)	0	0,5	1,5	2,8	4,2	9,0
Actual oil composition (% by mass).						
0 - 200 °C	0	1,4	0,0	0,0	0,0	0,3
200 - 234 °C	0	43,5	29,1	19,1	3,1	14,7
234 - 270 °C	0	14,4	10,0	11,4	2,2	7,0
270 - 300 °C	0	15,2	22,9	15,4	17,0	17,4
300 - 340 °C	0	17,8	21,4	27,5	40,5	32,0
340 - 370 °C	0	5,5	8,4	12,8	18,4	14,3
370 - 400 °C	0	2,5	6,8	13,4	18,8	14,3
Evt of undistilled tar portion	54,0	54,9	57,1	62,3	71,4	71,4
Δ Evt (°C) / % oil lost	-	1,8	1,5	1,9	2,2	1,8

The similarity between the fluxing power determined from the distillation procedure, and the change in Evt per per cent of oil lost from samples weathered on the road is shown in the boiling-point composition diagram, Figure 2 - 35. The range in compositions of oils lost in service is indicated by the shaded area (actual compositions of oils lost are shown in Table 1V Appendix A), and superimposed on this are the compositions of the oils evaporated off during the distillation procedure. Estimates of the fluxing power of fractions 1, 2, and 3 (Table

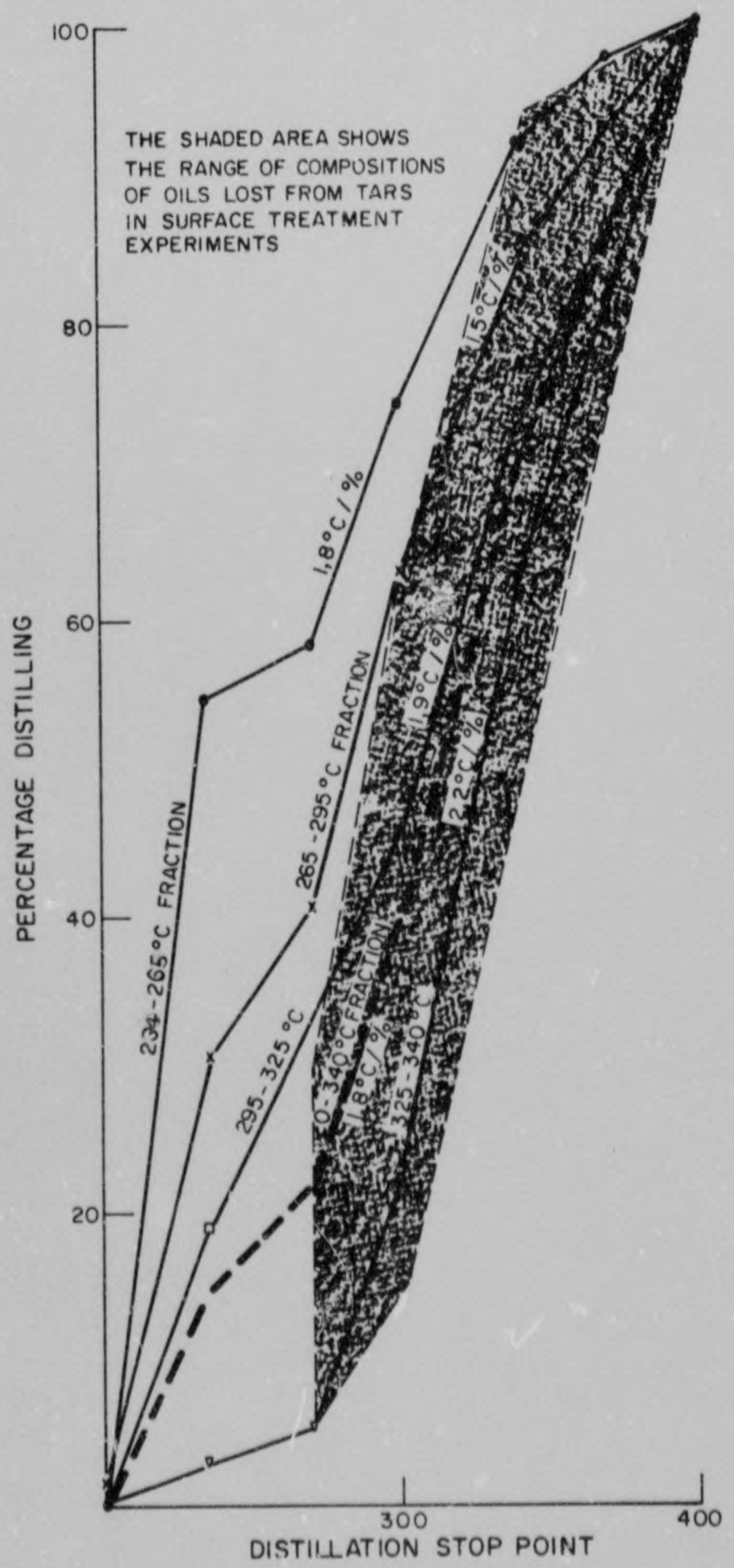

FIGURE 2-35

THE COMPOSITION OF OILS REMOVED FROM ROAD TAR BY VACUUM DISTILLATION AND THEIR FLUXING POWER.

2 - 16) can only be approximate because of the small loss of oil and the consequent small change in Evt of the residue. The compositions of fractions 4 and 5 and of the total oil fraction are within the range of compositions of the oils lost from tars in service and the fluxing powers of these oils (1,9°C, 2,2°C and 1,8°C/per cent respectively, as shown in Figure 2 - 35) correspond to the change in Evt per per cent of oil lost in service (2,2°C/per cent (0 - 38 days) and 1,5°C/per cent (1 - 4 years) as shown in Figure 2 - 33.

The estimated fluxing power of oils lost in service was similar to fluxing power-composition data obtained by addition of various tar-oils to an 80°C softening point (ring and ball) pitch (as supplied in a private communication from Wilman). (A softening point of 80°C (ring and ball) is approximately equivalent to an Evt of 100°C which is slightly higher than is normally obtained by weathered road tars even in the South African climate.). In Figure 2 - 36 this data has been compared with the composition of the oils lost in service in a manner similar to that given in Figure 2 - 35. In this case the shaded area spans boiling point-composition curves of oils which have fluxing powers in the range 2,1 - 2,6°C/per cent; this is in reasonable agreement with the data in Figure 2 - 35.

Thus it would appear from this estimate of the fluxing power of the oils lost by evaporation that if loss of oils is the major ageing mechanism, increases in Evt of the same order as those actually recorded would be expected.

It must be emphasised that these conclusions apply only to coke-oven tars used in surface treatments. In a laboratory Accelerated Weathering Test (the Accelerated Weathering Test described in Appendix - L.1.1) tars containing large amounts of naphtha oils (comprising mainly phenolic constituents) showed a greater increase in Evt per per cent of oils loss than other tars. Oil losses were determined by the GLC simulated distillation technique and these results plotted against the change in Evt are shown in Figure 2 - 37. The Accelerated Weathering Test was repeated under nitrogen and again the hardening of these tars was greater than that of the other blends. This may mean that inter-reactions between phenolic constituents of tar have a greater influence on the hardening of tars in service than oxidation. Although such constituents do not

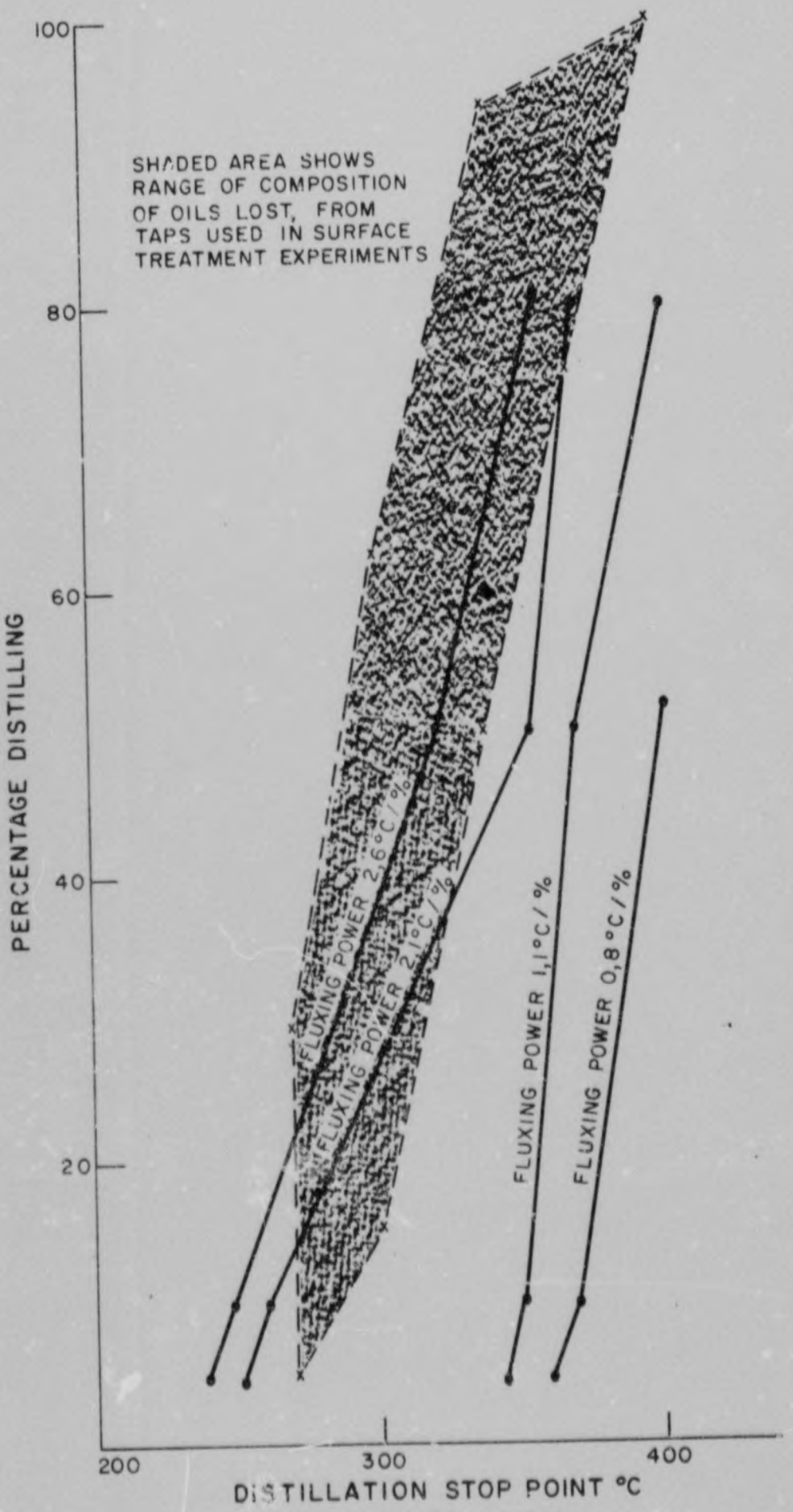

FIGURE 2-36

DISTILLATION CHARACTERISTICS OF TAR OILS OF VARIOUS FLUXING POWER USING 80°C (RING & BALL) SOFTENING POINT PITCHES

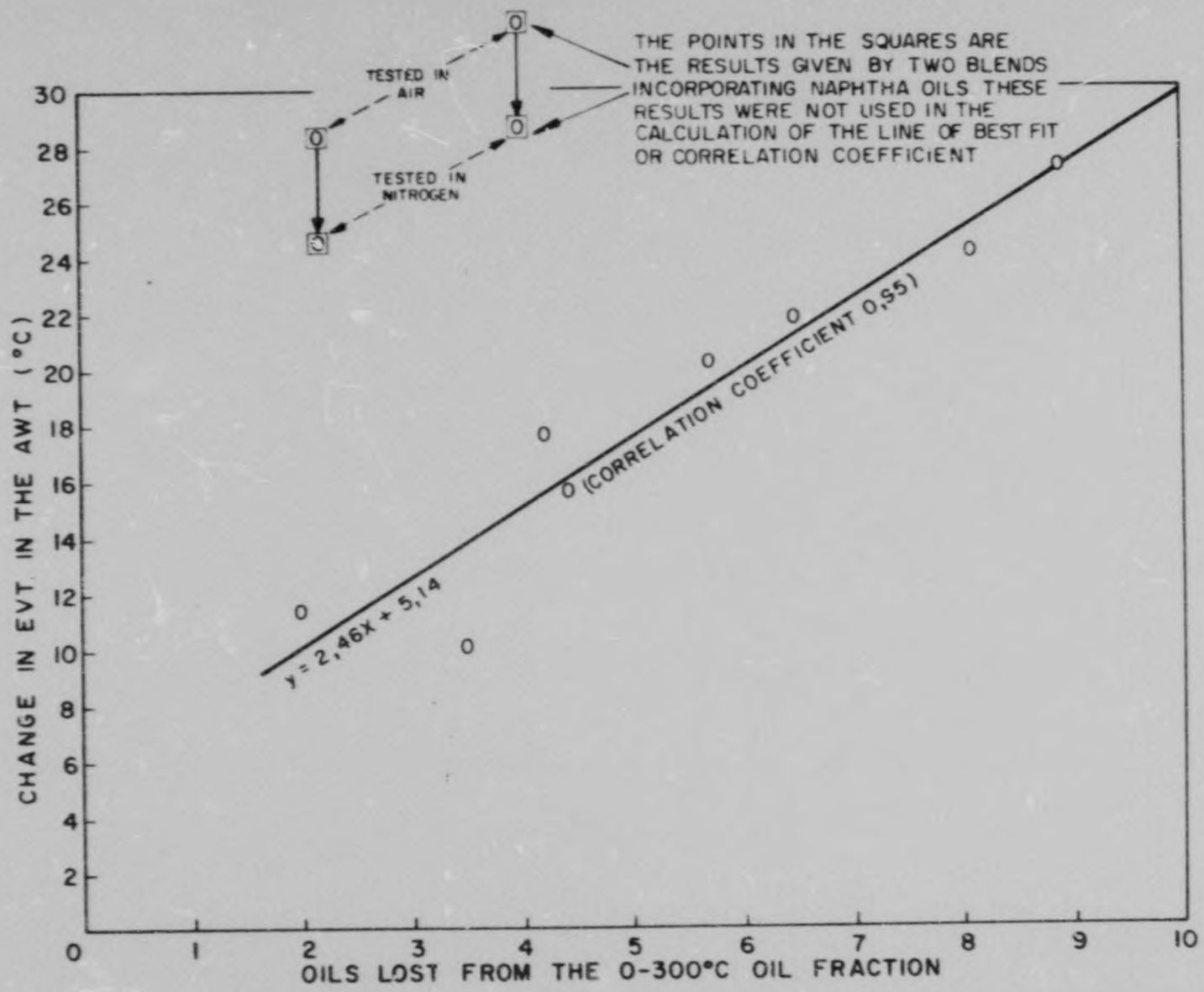

FIGURE 2-37

RELATIONSHIP BETWEEN OILS LOST (0-300°C FRACTION) AND CHANGE IN EVT IN THE ACCELERATED WEATHERING TEST

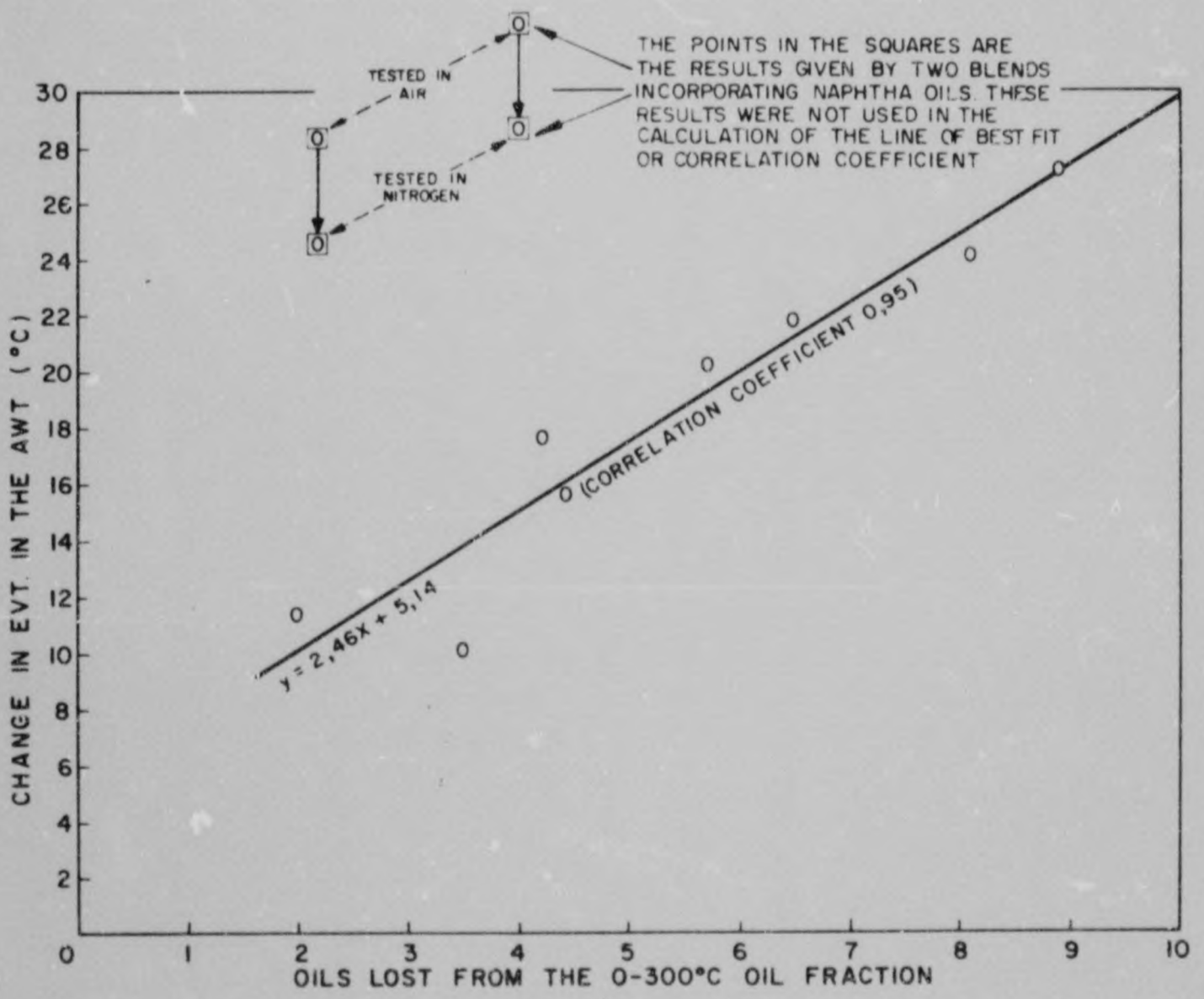

FIGURE 2-37

RELATIONSHIP BETWEEN OILS LOST (0-300°C FRACTION) AND CHANGE IN EVT IN THE ACCELERATED WEATHERING TEST

exist in coke-oven tars to a large extent, Lurgi and vertical-retort tars contain appreciable quantities of these and other reactive constituents.

This is substantiated by further pressure oxidation tests on Lurgi tars in which blends having less of the light oils rich in phenol had a lower oxidation susceptibility than those with a higher light-oil content. The composition of the high-volatile and low-volatile Lurgi tars were determined using the vacuum distillation test (ASTM D1160) and these results are given in Table 2 - 17. The oxidation test results are given in Figure 2 - 38.

TABLE 2 - 17

COMPOSITION OF LURGI TARS USED IN THE PRESSURE OXIDATION TESTS

Oil Fraction	High-volatile	Low-volatile
Distillation % v/v		
0 - 200 °C	0,0	0,0
200 - 270 °C	7,7	1,9
270 - 300 °C	7,1	2,9
300 - 340 °C	14,8	8,8
Total to 340 °C	29,6	13,6
Pitch softening point °C (r&b)	73,2	46,8

As in the earlier pressure oxidation tests, the test conditions were standard except that the temperature was 30°C; at which all the binders had the same initial viscosity. The oxidation susceptibility of the Lurgi tar may be a function of the boiling range of the oils and this may be associated with the content of phenolic material in the tar blend.

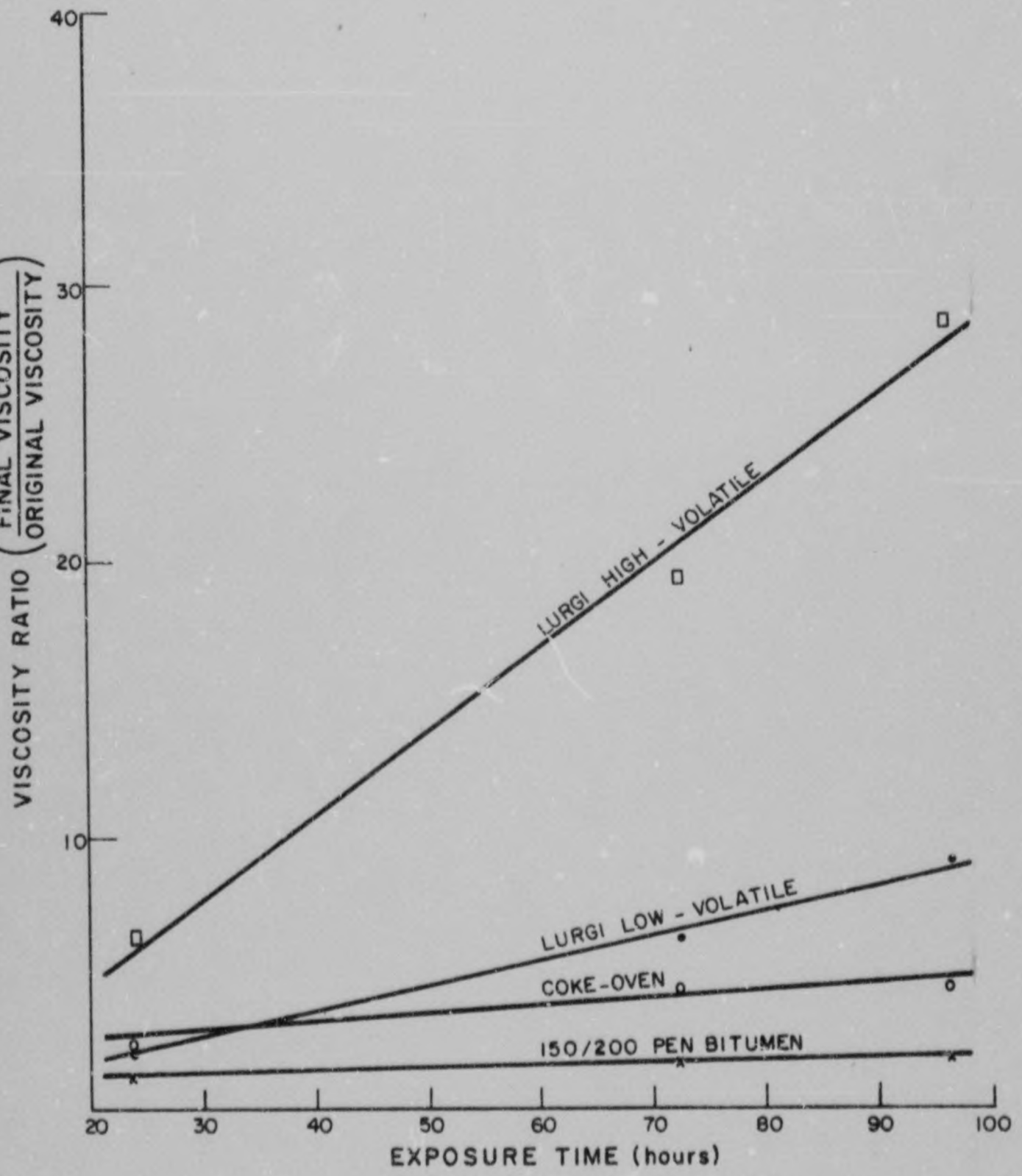

FIGURE 2-38

PRESSURE OXIDATION TEST RESULTS GIVEN BY HIGH-AND LOW-VOLATILE LURGI TAR, COKE-OVEN TAR AND BITUMEN.

940-01-4-160/2

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PART 3

Tars as surface treatment binders

INDEX TO PART 3

INTRODUCTION TO PART 3

From the preceding investigations and discussions it is evident that to improve the performance of tars in surfacings it is necessary to improve both their weathering resistance and their rheological properties.

The investigation (Part 2, chapter 5) of the weathering in the Highveld climate of coke-oven tars in single-surface treatments showed conclusively that hardening is mainly brought about by the loss (by evaporation) of volatile oils. It is apparent that much improvement can be made at the manufacturing stage by increasing the proportion of heavy plasticising oils and reducing the volatile oil content.

Over the years a number of modifying agents have been used to improve the temperature susceptibility of viscosity of tars, and Karius and Dickinson, (1959) found that the rheological properties of coke-oven tars could be substantially improved by the addition of fine particles of coal and long-chain polymers. Vastly improved performance in South African experiments resulted, although it was found that in cases where performance was satisfactory very low-volatile tar blends had been used (Jamieson,1974a).

Local tar producers eventually rejected the idea of producing coal- and polymer-in-tar dispersions because of production costs. Interest in the addition of other polymers to tar continued and eventually centred on polyvinyl chloride (PVC) which is the cheapest and most abundant plastic material (Ansart, 1967) and which had been under investigation by several authorities in Europe (Rofidal, 1967; Kuhnel and Wilman, 1969 and Ansart, 1971). These authors claimed that the binder had outstanding initial advantages in surface treatments and its superior cohesive properties reduced "whip-off" of stones thereby almost eliminating windscreen damage.

Another development in Europe was the modification of tar by the addition of bitumen. Blending of the two materials has been tried for many years but in recent times it has received a fresh impetus which may be due to improved production techniques with a consequent reduction in handling problems and an improvement in the performance of these blends.

Multiple-seal constructions are popular in South Africa particularly for new constructions in rural areas, and it was thought that unmodified

tars might be satisfactory for use in lower layers where weathering could be prevented.

The author's investigations on PVC/tar covered all aspects of manufacture, handling, application, testing and evaluation. In the case of tar/bitumen blends, however, the production and handling aspects were left to the manufacturers and the author's work has concentrated on evaluating blend properties, developing testing techniques and studying performance. The use of unmodified tars in multiple surface treatments was investigated by studying their performance in experimental sections.

3.1. MODIFICATION WITH POLYVINYL CHLORIDE (PVC)

Resume'

Tar containing 1,5 per cent PVC is cheaper than bitumen in interior regions of the country. The compatibility of PVC with road binders varies and is greatest with coke-oven tars. The affinity of PVC for hydrocarbons has been studied using gas-chromatographic subtraction-loop techniques. The properties of local coke-oven tars modified with PVC are shown and a modified ductilometer method for determining the ductility-tenacity is described.

The commercial production of PVC/tar is straight-forward and PVC addition has a beneficial effect upon the proportions of volatile and plasticising oils in the blend, provided heavy- flux-oils are used. Although the polymer may degrade if excessive storage temperatures are used, low-volatile PVC/tars may be safely stored at 110°C for eight days without damage to the polymer.

Road experiments have been constructed to evaluate the behaviour of the binder in surface treatments and from the results, together with observations made on commercial work, it is shown that where conditions are optimised, the minimum service life required for economic parity with bitumen can be obtained. From this practical work, guidance is given on the design and construction of PVC/tar surface treatments.

Polyvinyl chloride (PVC) was first prepared in Germany in about 1930 since when manufacturing plants have been set-up in most industrialised countries including South Africa. It may be manufactured either by the reaction of acetylene with hydrochloric acid gas, or by that of ethylene with chlorine gas. The product is a powder the nature of which can be controlled by the conditions under which the gaseous components are combined. Variations in molecular mass, particle size, shape and texture are possible and the polymer may be supplied in either powder or latex form. The molecular mass, or K-value (molecular mass in 000's) is significant in preparing PVC/tars.

The higher the K value the more elastic is the resultant binder, percentage of PVC added, but on the other hand these polymers are more expensive and more difficult to disperse in the tar. Thorough dispersion is essential to obtain the full benefit of the additive. Although various forms of PVC, including remnants ("sweepings") from PVC fabricating processes, have been used for the preparation of PVC/tar in Europe (Wilman, 1970), a grade known as "Corvic" D60/11* has been found to be most suitable and this has been used exclusively in these investigations. It has been blended with tar in concentrations of up to 5 per cent (higher concentrations may be possible) though common commercial binders used for surface treatment work contain 1,5 per cent.

At PVC concentrations of 1,5 per cent, PVC/tars have a price advantage over bitumen in many areas of South Africa. The cost of PVC/tar at major centres in the country has been calculated on the same basis as that employed in Part 1, Chapter 2. The suppliers of PVC/tar are Dundee Road Products whose works are situated at Wasbank (Natal) and in future it is anticipated that Iskop may supply the binder from their works at Vanderbijlpark. These centres have been used as the points of supply in the calculations. The current price of "Corvic" D60/11* is approximately R735/tonne and hence at a concentration of 1,5 per cent the increase in cost of the tar is about R11/tonne. The same assumptions regarding the transportation costs and the hot(spraying) temperatures were made as in the previously described calculations. The price of PVC/tar at major centres was compared with the calculated cost of bitumen at these centres and as a result it is estimated that PVC/tar should be cheaper in the areas (hatched) indicated in Figure 3 - 1. This comprises a great deal of the interior including the most densely populated part of South Africa.

3.1.1 Compatibility of PVC with bituminous binders

PVC powder cannot be combined with equal effect with all bituminous binders. Complete dispersion of PVC in petroleum bitumens and tars of vertical-retort and Lurgi-retort origin is not possible, and even after prolonged mixing the undispersed particles of powder can be seen like particles of inorganic filler in these binders. In coke-oven tars complete dispersion of the powder occurs if the powder is added slowly

* Denotes a molecular mass of 60 000

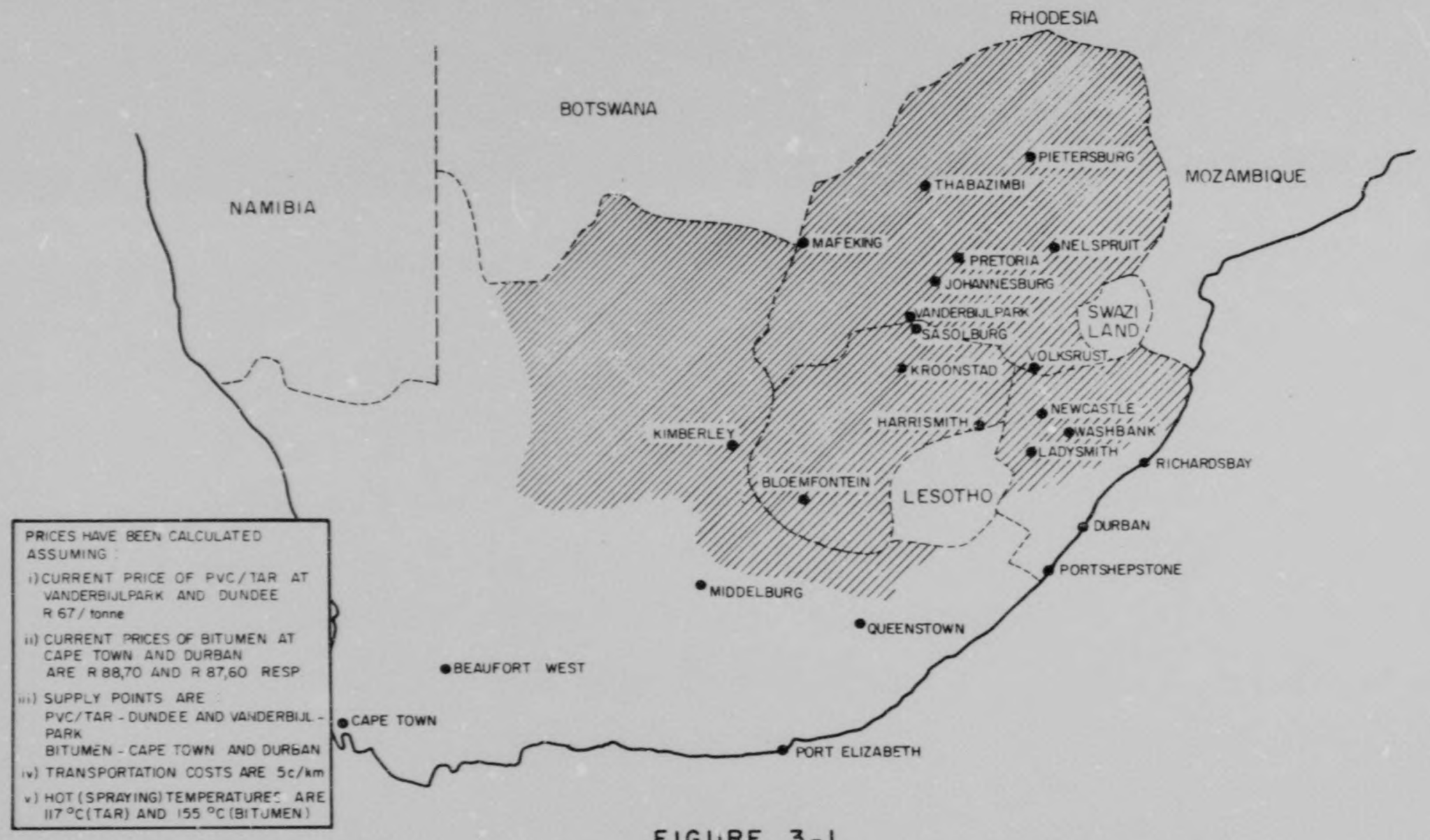

FIGURE 3-1

AREAS OF SOUTH AFRICA WHERE PVC/TAR (CONTAINING 1,5 PER CENT PVC) IS CHEAPER THAN BITUMEN, ASSUMING SUPPLY POINTS OF PVC/TAR ARE WASHBANK AND VANDERBIJLPARK.

and it is possible that some chemical bonding takes place between the polymer and hydrocarbon molecules in the tar.

3.1.1.1 Affinity of PVC for hydrocarbon types

The affinity of various organic types for PVC has been studied using a gas-chromatographic subtraction-loop technique, Preliminary investigations in gas chromatography showed that the PVC powder could be used as a stationary phase for certain separations. However, complete retention of certain types of compound occurred and it was realised that this selectivity exhibited by the PVC could be used to study its behaviour towards various organic types. Accordingly a subtraction loop containing the powder was fitted between the column outlet and the detector inlet and the behaviour of compounds and mixtures of compounds when injected into the chromatograph was studied and compared with their behaviour in a normal (without a subtraction loop) chromatographic system. Details of the technique and of the effect of the loop on chromatograms of various organic mixtures are given in Appendix A 1.3

Table 3 - 1 shows that of the hydrocarbons, the PVC had the greatest affinity for aromatic types. From Appendix A 1.3 however, it is evident that this affinity may be qualified by the configuration of the molecule*. (For example n-chain compounds containing terminal functional groups were substantially absorbed whereas branched molecules tended to be eluted .)

From the results of this study, it would be expected that PVC would have the greatest affinity for bituminous binders which were highly aromatic and or where functional groups were present, but that this affinity would be lessened by the presence of substituted alkyl groups or chains. This is consistent with the known constitution of bitumen and the chemical characteristics of local tars, as determined in Part 2 Chapter, 2.2, and their compatability with PVC as shown in Table 3 - 2.

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* It will be apparent that PVC powder has a potential in gas chromatography as an aid to the identification of aromatics in mixtures with n-, iso- and cycloparaffins. This has been suggested (Jamieson, 1972) and it has been shown that its effectiveness for this purpose is comparable with molecular sieve 5A. Its behaviour is different, however, in that it selectively removes aromatics whereas the molecular sieve 5A removes the n-paraffins. N.B. Its usefulness is confined to the arrangement where the loop is fitted between the column and the detector. For pre-column subtraction it was found to be unsuccessful.