Cairo University/Massachusetts Institute of Technology Technological Planning Program

Performance of Parraffinic-Waxy Asphalt Cements In Egyptian Road Construction

Volume I Literature Review and Background of the Problem in Egypt

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Sponsored By
United States Agency for
International Development

TAP Report 80-4 June 1980

AG-AAC-006
263006 1
PN-ATN-866
ISN-47156

PERFORMANCE OF PARAFFINIC-WAXY ASPHALT CEMENTS IN EGYPTIAN ROAD CONSTRUCTION

VOLUME I

LITERATURE REVIEW AND BACKGROUND OF THE PROBLEM IN EGYPT

TAP Report 80-4

JUNE, 1980

263-0061-C-00-104-00

PREFACE

This report is one of a series of publications which describe various studies undertaken under the sponsorship of the Technology Adaptation Program at the Massachusetts Institute of Technology.

The United States Department of State, through the Agency for International Development, awarded the Massachusetts Institute of Technology a contract to provide support at M.I.T. for the development, in conjunction with institutions in selected developing countries, of capabilities useful in the adaptation of technologies and problem-solving techniques to the needs of those countries. This particular study describes research conducted in conjunction with Cairo University, Cairo, Egypt.

In the process of making this TAP supported study some insight has been gained into how appropriate technologies can be identified and adapted to the needs of developing countries per se, and it is expected that the recommendations developed will serve as a guide to other developing countries for the solution of similar problems which may be encountered there.

Fred Moavenzadeh

Program Director

FOREWORD

A four-year research program entitled, "Performance of Paraffinic-Waxy Asphalt Cements in Egyptian Road Construction," sponsored jointly by the United States Agency for International Development and a group of Egyptian road construction companies was initiated in June, 1979 by the Massachusetts Institute of Technology, MIT, and Cairo University, CU. The final objective of the project is to improve the performance of pavements constructed with the Egyptian paraffinic-waxy asphalts.

The first year research is principally aimed at achieving a better understanding of the important factors affecting the use of Egyptian asphalts in road construction. In particular, the work includes:

1. An intensive literature survey to benefit from the experience of others dealing with temperature-sensitive asphalts, and help in establishing preliminary quality control criteria for Egyptian waxy asphalts in pavement construction;

2. A careful planning of sampling, laboratory, and preliminary field evaluation programs to determine the properties of Egyptian asphalts. This includes the selection of representative roadway sections and the assimilation of pavement history and distress evaluation data;

3. An evaluation of the physical and chemical characteristics of Egyptian asphalt cements; and

4. An evaluation of the properties of available Egyptian aggregates.

This report provides a comprehensive literature review related to the use of asphalt cements in road construction for the benefit of the Egyptian user (engineers, contractors, and regulating agencies) having a limited access to the international literature.

The research is supervised by Professors A. Osman, CU, and M. Baligh, MIT. The following individuals, listed alphabetically, have participated in the preparation of this report: A. Azzouz (MIT); F. Ezzat (Egyptian Petroleum Research Institute); A. Gadallah (CU); J. Gottwald (MIT); M. Noureldin (CU); L. Radwan (CU); and E. Sarhan (Ain Shams University)

ACKNOWLEDGEMENTS

The following individuals and/or organizations provided valuable contributions to this study:

Ministry of Transportation, The General Authority of Roads and Bridges

Eng. Ahmed Shawky
Chairman, The General Authority of Highways

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National Academy of Science, Egyptian Petroleum Research Institute

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Ministry of Industry, El-Nasr Petroleum Company, Alexandria

Eng. Said Kandil
Chairman

Matching funds were provided by the following Egyptian road construction companies:

1. The Arab contractors (Osman Ahmed Osman, and Co.):
   Eng. Hussein Osman

2. The Nile Company for Roads and Bridges:
   Eng. Ahmed El-Okaily

3. El-Nasr Contracting Company (Hassan Allam):
   Mr. Mohamed Fahmy Allam

4. The General Authority for Roads and Bridges;
   Eng. Ahmed Shawky

5. The Nile Company for Road Construction;
   Eng. Ahmed Moussa

6. The Nile Company for Desert Roads:
   Eng. Tharwat Sakr

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CHAPTER 1

INTRODUCTION

For more than half a century, asphalt cements used in Egyptian road construction were produced by distillation of crude oils from the fields in the Red Sea area. These asphalt cements were successfully used in hot asphaltic mixtures and produced roads with a good service record.

In the early seventies, the production from the Suez refinery was halted, and asphalt cements were produced from newly discovered crude oil fields in the Egyptian western desert. However, the new asphalts caused serious performance and construction problems. Asphalt concrete mixtures produced at normal mixing temperatures (275° to 300°F) were very fluid and caused difficulties in field laying operations. Rollers had to be delayed several hours behind the paver because of the remarkably slow setting time. Furthermore, field performance data indicated that pavements constructed with these asphalt cements showed a greater flushing tendency under traffic loads, especially during hot summer days. In addition, transverse cracks developed in some pavement sections after a few winter seasons. These performance problems were widespread, notably at many locations on the Cairo-Alexandria Expressway, which is one of the most important routes in Egypt. Some of these locations are Kafr Eldawar-Alexandria (Km 10.48 to Km 19.50), El Malatia-Abu Korkas, Damanhoor-Abu Hommas, and Toch-Banha sections. In most cases,

these problems were accompanied with severe creep deformations towards pavement edges and near the median curbs

Preliminary field core samples tested in the laboratory indicated that these construction and performance problems could be attributed to the considerable wax content in the asphalt cement. Studies by Metwally et al. (1975) showed that the wax content for the asphalt cements produced from the western desert region ranges from 5 to 15%, which is substantially higher than the generally accepted wax-content limit of 2.5 to 4%. At ordinary summer temperatures, waxy asphalt cements separate from the pavement layers and migrate vertically towards the surface and horizontally towards the pavement and median curbs. This mechanism led to successive deflections of the central portion of the highway and severe upheaves near pavement edges.

In some extreme cases, such as those of the Cairo-Alexandria Expressway, where 90 kilometers of the pavement surface layer had to be removed and a completely new wearing surface was reconstructed, the cost exceeded 9 million Egyptian pounds. Pavement service life dropped from 15 years to about 3 years due to the use of asphalts with high wax content. In addition, safety was indirectly affected by the inadequate pavement condition which represented a hazard to traffic.

The production of asphalt cements from the Egyptian western desert fields was halted during 1977 as a direct consequence of the aforementioned performance problems. However, road

construction in Egypt requires about 170,000 tons of bitumens per year (1977 data), of which about 90,000 tons are obtained from the eastern desert fields. The remaining 80,000 tons have to be obtained from the western desert fields.

The importance of the problem and its economic consequences have led the United States Agency for International Development, through its MIT - Cairo University Technological Adaptation program, and a group of Egyptian road construction companies to sponsor a four-year research project for the purpose of improving the performance of pavements constructed with the Egyptian paraffinic-waxy asphalts.

This volume is the first of a series of reports presenting the results of this research. It provides a comprehensive literature review related to the use of asphalt cements in road construction. The first six chapters of this report present current methods used for the production of petroleum asphalts along with their chemical, physical, and rheological properties. Chapter 7 is concerned with the use of waxy asphalt in road construction and summarizes the experience of other countries dealing with this problem. Finally, Chapter 8 presents a background of the problem in Egypt.

CHAPTER 2

PRODUCTION OF PETROLEUM ASPHALTS

2.1 Introduction

Asphaltic construction materials are a component of petroleum crude oil taken from the hundreds of thousands of oil wells throughout the world. The amount of asphalt that a crude oil may contain is quite variable, depending upon the American Petroleum Institute (API) gravity of the crude. The lower the gravity of the crude oil, the higher the asphalt content (see Fig. 2.1). For instance, a 15 API gravity crude would produce approximately 60 per cent asphalt and 40 per cent lighter petroleum products, such as gasoline, kerosene, fuel oil, lubricating oil, etc., whereas a 35 API gravity crude may produce only 10 per cent asphalt and about 90 per cent of the lighter fractions.

The crude oil is transported by pipelines, tank cars, or barges to the refineries where it is separated into its various components by a continuous-flow refining process.

In the refining of asphalt, two different processes are used: steam and vacuum distillation method and solvent extraction method. Another refining method used to obtain a higher percentage of motor fuel is the "cracking" process, which, by intense heat and high pressures, brings about a chemical change producing a bituminous type of material not widely used for paving.

2.2 Distillation Processes

Figure 2.2 shows a petroleum-asphalt flow chart. All distillation of petroleum is fractional. The asphalt-base petroleum will produce asphalt by a physical process. During the distillation, several different fractions are separated from the petroleum as shown in Table 2.1. When the distillation process is controlled so that overheating and subsequent chemical changes do not take place, the asphalt residue that remains is called a straight-run asphalt.

In general, the distillation process is a two-step operation. In the first operation, the crude oil is pumped through a tube still heater which will bring the crude oil, under pressure, up to a temperature of about 550°F. This crude is then released into the bottom of an atmospheric fractionating column. Upon being exposed to atmospheric pressure, the more volatile fractions, such as naptha, rise to the top of the fractionating column where the vapors condense and are caught in a trap as illustrated in Fig. 2.3. Traps arranged in the lower levels of the fractionating column catch the less volatile materials as they condense after rising to a position in the column where the temperature will cause condensation. The temperature of each trap is fixed at a temperature just below the boiling point of a liquid of a certain composition; thus, the nature of the materials collected in the traps is determined by this temperature. The so-called topped crude oil does not volatilize under atmospheric pressure.

For most crude oils, a second step must be used in order to produce asphalt because most crudes contain relatively high percentages of high-boiling-point fractions that cannot be distilled in an atmospheric distillation unit. The second step of the distillation process is illustrated in Fig. 2.4. As can be seen, it makes use of a second fractionation column. The problem involves removing the high-boiling-point fractions without heating the hot topped crude oil to a degree that will cause chemical changes or cracking to take place. This is accomplished by two methods. First, steam is introduced at the bottom of the fractionation column in such a way as to become intimately mixed with the hot topped crude as it is released into the chamber. Thus the boiling point of the various fractions becomes a combination of the boiling points of the oils that must be vaporized and of water. The second procedure, an aid for the use of lower temperatures, is the application of a partial vacuum to the fractionation column. The greater the vacuum applied, the lower the boiling point of the fractions to be separated from the hot topped crude oil. By controlling temperature, amount of steam, and the amount of vacuum, the exact quality of asphalt cement desired may be obtained. For example, the higher the temperature, the harder the resulting asphalt cement. The same would be true if a high vacuum were applied or a large amount of steam were introduced. If these factors are adjusted so that only a small amount of these "nonvolatile" fractions are removed, a soft asphalt cement is produced.

2.3 Air Blown Asphalts

An air-blowing process is sometimes used to improve an asphalt material by forcing air through an asphalt stock at temperatures of 400 to 550°F. A reaction takes place in which oxygen from the air combines with hydrogen of the hydrocarbon molecule to form water, which is emitted as steam. As a result, the hydrocarbons polymerize* to form heavier and harder materials. The air-blowing process produces heat; hence, once the temperature is brought to the point of chemical change, further heat need not be added. Sometimes certain catalysts, such as ferric chloride or phosphorous pentoxide, are used to speed or promote the reaction. In general, the process causes the asphalt to become harder and less ductile than asphalts not treated by air blowing. The advantage of air blowing is that the final product is less susceptible to temperature than an untreated asphalt, i.e., the air-blown material will show less change in properties for a given change in temperature. This is especially desirable in producing roofing asphalts where extremely hot and cold temperatures are experienced; thus, all roofing asphalts undergo considerable air blowing. This is also a property desired in highway asphalts. Although hardening and loss of ductility are undesirable, most modern highway asphalts undergo a short air-blowing process to produce decreased temperature susceptibility.

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*Polymerization: a process of forming a polymer or compound of high molecular weight or the union of two or more molecules of a compount to form a more complex compount of higher molecule weight.

2.4 Solvent Extraction Processes

The solvent extraction process makes use of a selective solvent, such as propane, to separate the paraffinic oils from the topped crude oil residues. By careful control of operating conditions, the paraffinic oils are dissolved by the solvent and then removed, the resulting solution being lighter than the remaining topped crude. This process enables straight-run distillation to be used in the production of asphalt cement from mixed-base petroleums.

Basically, the various solvent extraction processes are similar. In each case the distillate is contacted with a selective solvant to provide a higher viscosity index raffinate and an aromatic extract, from both of which solvent is recovered. The aromatic extracts are dark oils containing asphaltic residues and are added to the bitumens to improve its quality.

2.4.1 Furfural Extraction

Furfural is a good solvent for aromatics and resins and is extensively used to improve the viscosity index and oxidation characteristics of distillate and de-asphalted lubricating oils. The aromatics and contaminants of a high aromatic content, such as higher molecular weight sulfur and nitrogen compounds and resinous materials, are extracted with furfural.

Furfural boils at 162°C under atmospheric pressure and is thus readily separated from the heavier lubricating oil fractions. Extraction temperature lies in the range of 30° to 130°C

and solvent ratios can be kept quite low, normally between 1.5 and 3.5. Furfural is unstable at higher temperatures, and therefore, it should not be heated above 232°C in the solvent recovery section of the plant. To the same end, it is usual to exclude air from the process. A flow diagram for a plant is given in Fig. 2.5. Flashing and steam-stripping are applied for the recovery of furfural from raffinate and extract, followed by azeotropic distillation to dry the furfural for re-use.

2.4.2 Phenol Extraction

Phenol is quite a popular solvent-refining agent in the manufacture of lubricating oils. Its use is limited to the refining of distillates, unless prior de-asphalting is practised and, in this respect, it is similar to furfural. Compared with furfural, phenol has the advantage of better thermal stability, but phase separation may be more difficult. Asphaltenes interfere with phenol extraction and their presence promotes the formation of emulsions.

Extraction is usually carried out in a tower containing plates and an interesting feature of the process is the use of water as an "anti-solvent." The water, which actually contains some phenols, is injected into the lower part of the extraction tower and phenol of the desired water content is sent to the top. The action of water is to throw out the valuable raffinate phase from the solution in the solvent. Thus, the action is very similar to back-washing with extract or the maintenance of a

temperature differential across the column for the purpose of generating an internal reflux at the base of the column. Two liquid phases are formed, a raffinate and an extract dissolved in phenol. The raffinate phase contains the desirable paraffinic components of the feed and the extract phase contains the non-paraffinic components, Fig. 2.6. After the removal of the solvent from the extract, it is added to the straight-run bitumen.

2.4.3 Propane De-asphalting

Asphalt must be removed from feedstocks destined for lubricating oil manufacture in order to avoid emulsion difficulties in the solvent treating step.

Lubricating oil fractions, except for the heaviest grade, are obtained asphalt-free by vacuum distillation. Avoidance of thermal decomposition and consideration of economic distillation operation finally control the heaviest distillate that can be obtained. The applicaiton of propane de-asphalting to the vacuum distillation residue is a convenient method for overcoming this difficulty.

Liquid propane is a good solvent for paraffinic hydrocarbons, but the bitumens constituents, which should include the heavier aromatics, are not appreciably dissolved. Therefore, propane is an attractive solvent for the extraction of bright stock lubricating oil components from a residual stock.

With propane extraction, temperature lies in the range of 40° to 80°C and pressure ranges between 400 to 500 psi.

Solvent ratios are rather high, being usually 5 and 13 to 1 by volume.

The flow diagram of a typical propane de-asphaltic plant is shown in Fig. 2.7. Extraction with solvent takes place counter-currently in a tower equipped with contacting trays of a special design. A point of difference from most other solvent extraction processes is the installation of an internal steam heater at the feed end of the tower for the purpose of maintaining a higher temperature at the extract end. The reason is that propane is close to its critical point under the conditions of operation. Raising the temperature causes the propane to become more like a gas than a liquid; the solubility of paraffin falls and the selectivity is improved, contrary to the behavior of other solvents. The oil enters at the top and propane at the bottom of the column. The paraffinic components are preferentially dissolved in the propane and are withdrawn from the top. The bitumen is withdrawn from the bottom and added to the straight-run bitumen.

2.4.4 Propane Dewaxing

Propane is extensively used as a dewaxing solvent and is frequently competitive with the methyl ethyl ketone/benzene process. Compared with the latter process, propane dewaxing has the advantages of requiring a solvent of only one component and not requiring the installation of a separate refrigeration system, since chilling may be accomplished by the evaporation

of part of the solvent stream. Water removal is easily achieved, since water is relatively insoluble in propane. If a residual oil is to be processed, then a very neat operation may be carried out with propane, first applying propane de-asphalting and then following up with propane dewaxing without separating propane and oil in the stage intermediate between these two processes.

There are, however, certain disadvantages of the process. Propane is not a very selective solvent and thus dewaxing temperatures must be rather low in order to compensate for the relatively high solubility of wax in propane. High pressure equipment is required in order to maintain the propane in the liquid state. Careful control of the operating conditions is necessary in order to obtain readily filterable wax crystals. Gel formation is likely to occur at solvent ratio below 1.6:1.

A simplified flow scheme of a propane dewaxing plant is shown in Fig. 2.8. Hot feed is mixed with liquid propane, cooled by exchange and sent to a warm solution surge drum. From there, it is pressured into one of two batch chillers where the solution is cooled to the desired filteration temperature by auto-refrigeration. Some of the propane solvent vapor from the filters goes to the suction of the compressor. While cooling takes place in one chiller, the cold slurry in the other chiller is routed to the filter feed drum and the chiller is refilled with warm solution. The batch chillers are operated by an automatic sequence controller.

Wax is removed from the filtrate in two enclosed rotary drum filters. Filtrate and wax slurry from the filters are heated by condensing phenol in the exchangers and passed to high-pressure flash drums where most of the solvent is removed and returned to the propane condenser. Remaining solvent is removed in low-pressure flash drums and goes to the compressor suction, while the dewaxed oil is flash corrected and dried in a vacuum stripper.

2.5 Thermal Asphalts

Thermal or cracked asphalts differ from other asphalts in that they are products of a cracking process wherein chemical changes take place. This procedure is used when a topped crude is very low in asphalt content. The resulting asphalts are characterized by relatively high specific gravity, low viscosity, and high temperature susceptibility; their use in road asphalts is relatively uncommon.

2.6 Liquid Asphalts

Many times, especially in low-cost paving work, it is particularly convenient to work with an asphalt that is in liquid form at relatively low temperatures as compared to penetration-grade asphalt. This section discusses such liquid asphalt, namely, cutback liquid asphalts and emulsified asphalts. The cutback materials are formed by combining with asphalt cement the volatiles obtained from the first distillation stage in the production of asphalt. Asphalt emulsion is obtained by physically combining asphalt cement with water.

2.6.1 Cutback Liquid Asphalts

Cutback liquid asphalts are made by adding a solvent to an asphalt cement with the objective of producing a liquid asphalt that can be handled with equipment without the use of high temperatures. After the material is in place, it can revert back to a normal penetration asphalt cement by curing, a process in which the volatile component evaporates.

Cutback asphalts are classified according to their rate of curing and viscosity. Rapid-curing, medium-curing, and slow-curing asphaltic materials are designated by their initials, RC, MC, and SC, respectively. Thus the first two letters designate the type. The thinnest and most fluid grade is designated by the suffix number 30; however, this grade applies to the MC type only. The next most fluid grade is designated by the suffix number 70 and is common to RC, MC, and SC types. Other suffix numbers denoting higher viscosities for each of the three types are 250, 800, and 3000, respectively. These suffix numbers represent the minimum kinematic viscosity in centistokes at 140°F for the particular grade.

Rapid-curing cutback asphalts are manufactured by blending asphalt cement with a low-boiling-point solvent such as naptha or gasoline. An intermediate-boiling-point solvent of the kerosene range is blended with asphalt cements to produce medium-curing cutback asphalts. Slow-curing, SC, cutback asphalts may be manufactured by either of two processes, one by blending

asphalt cement with a high-boiling-point gas oil and the other by controlling the rate of flow and temperature of the crude during the first cycle of refining. Since the gas-oil portion of the SC cutback asphalt is a semivolatile material, it requires a much longer period for curing. In fact, SC materials taken from the bottom of the fractionating column are extremely slow-curing and may never completely cure.

2.6.2 Emulsified Asphalts

An emulsion may be defined as an intimate mixture of two immiscible liquids, one of which is dispersed in the other in the form of very fine droplets. An asphalt emulsion is a mixture of asphalt and water where asphalt is usually the dispersed phase and water the continuous phase. Asphalt emulsification is merely another means of liquefying an asphalt for use. There are many advantages in the use of asphalt emulsions, such as:

1. Can be used with cold as well as hot aggregate
2. Can be used with aggregate that is dry, damp, or wet
3. Eliminates the fire and toxicity hazards that attend the use of cutback asphalts

Emulsions also have their disadvantages, one of which is that they are easily subject to washing by rain. Furthermore, their manufacture is not as standardized as that of other liquid asphalts.

Emulsified asphalts are made by mechanically dispersing a hot asphalt cement in water that has been treated with an

emulsifying agent. Emulsified asphalts are classified according to the kind of emulsifying agent used. The two most commonly used types are anionic and cationic. There are three general grades for each of the two common types of emulsions. These grades are:

1. Rapid setting, RS
2. Medium setting, MS
3. Slow setting, SS

The rate of setting is controlled by the amount and type of emulsifying agent used.

Although all three grades of emulsions are produced in at least two viscosity ranges, the choice of grade depends upon the use to which the emulsion is put. RS emulsions, for example, are generally used for spray application work. They are rather unstable; that is, they contain relatively little emulsifying agent and slight disturbance will cause them to break or set. Medium setting grades of asphalt emulsions are used for mixing with fairly open-graded aggregates and can be used for penetration work in which the liquid asphalt is permitted to penetrate through a layer of aggregate, for seal coats and for surface treatments. Finally, slow-setting emulsions are used whenever high mixing stability is required. A common use of SS emulsions is in road mixes where the emulsions are mixed with existing roadbed material that may be granular, but that may have many fines.

Fraction	Product type	Boiling-point range, °F
Light distillate	Gasoline	100-400
Medium distillate	Kerosene	350-575
Heavy distillate	Diesel oil	425-700
Very heavy	Lubricating oil	Over 650
Residue	Asphalt	

Table 2.1 Fractions that make up petroleum (from Krebs and Walker, 1971)

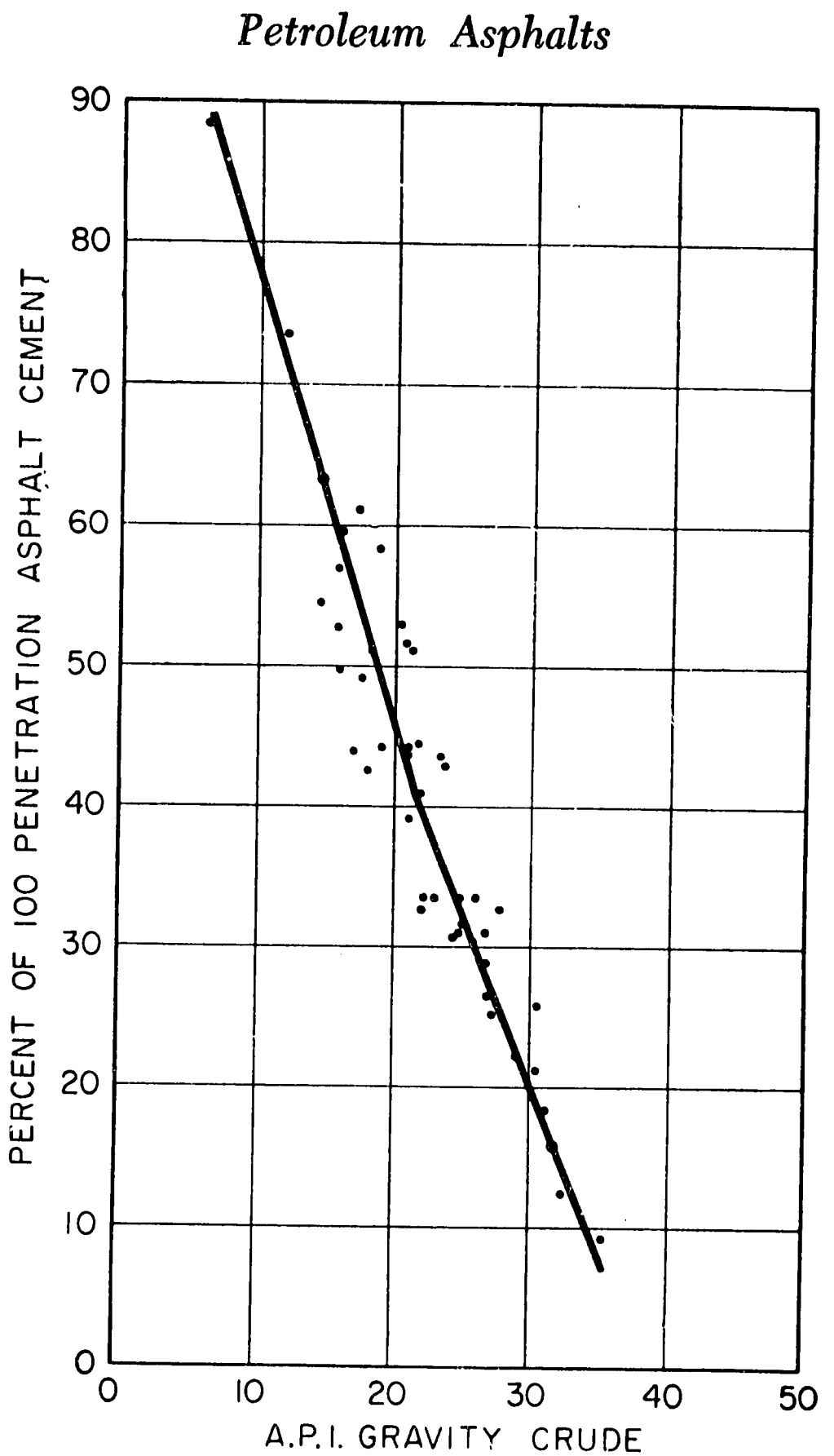


Fig. 2.1 API gravity crude (from Wallace and Martin, 1967)

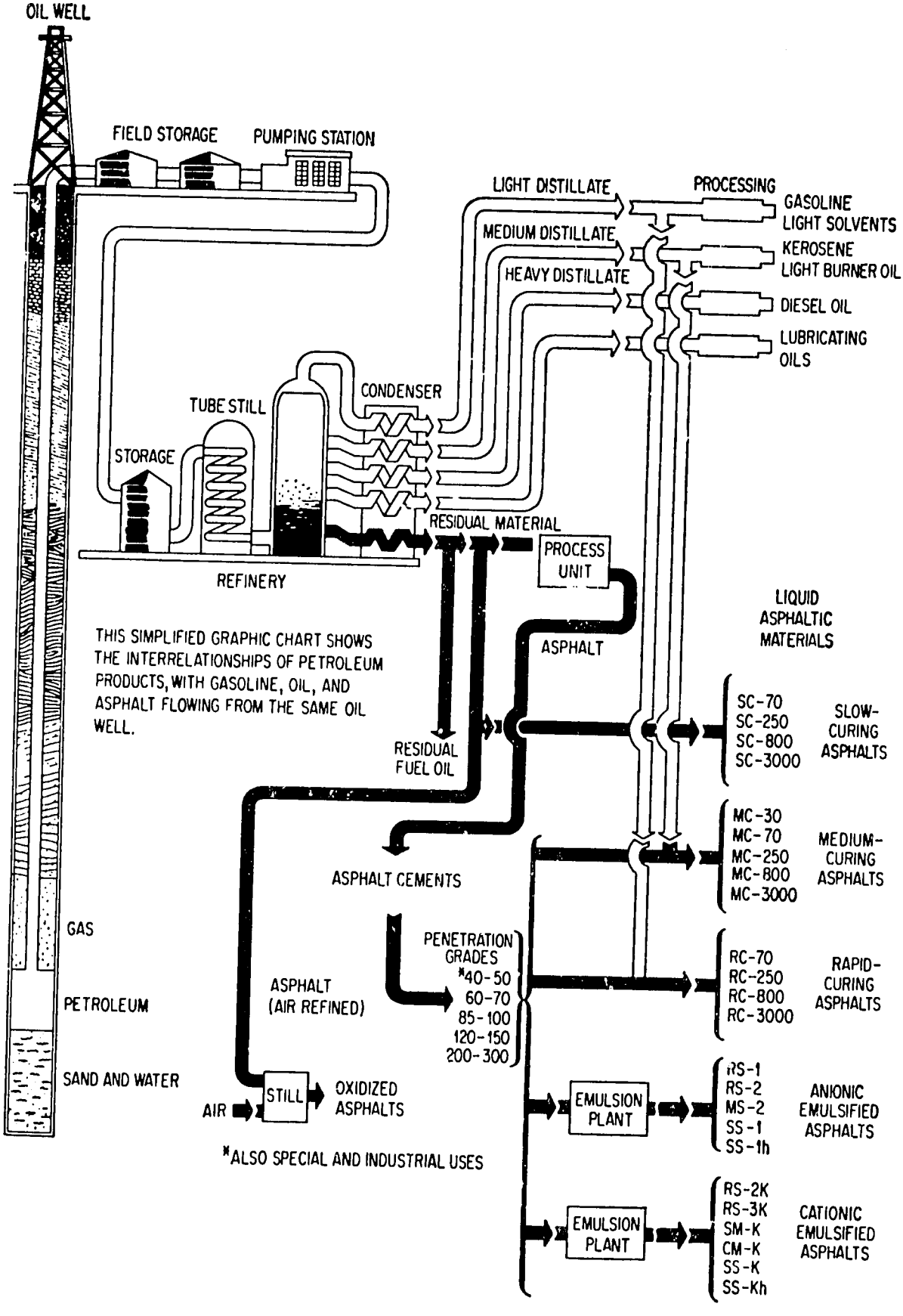


Fig. 2.2 Petroleum-asphalt flow chart (from Wallace and Martin, 1967)

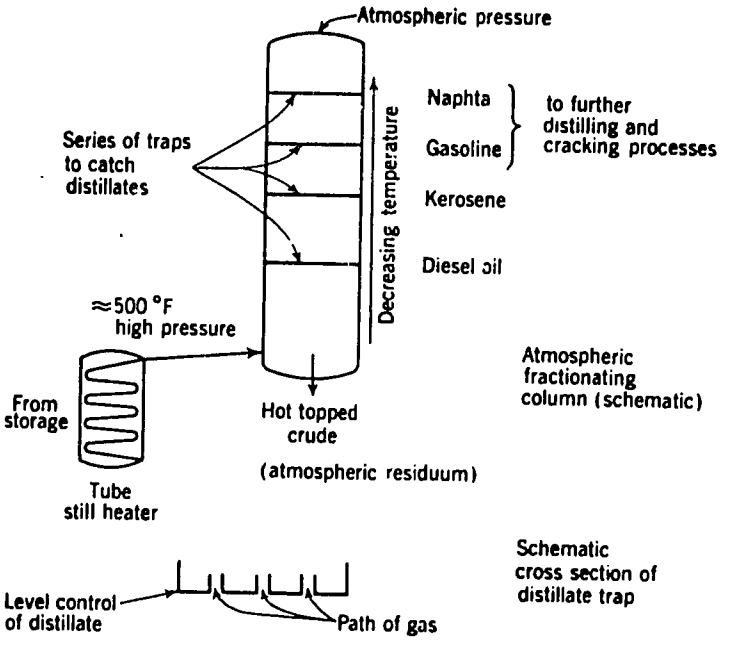


Fig. 2.3 Atmospheric-pressure distillation (From Krebs and Walker, 1971)

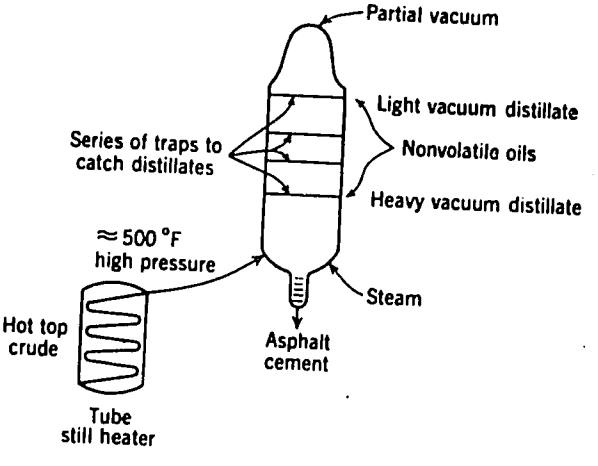


Fig. 2.4 Vacuum-steam distillation

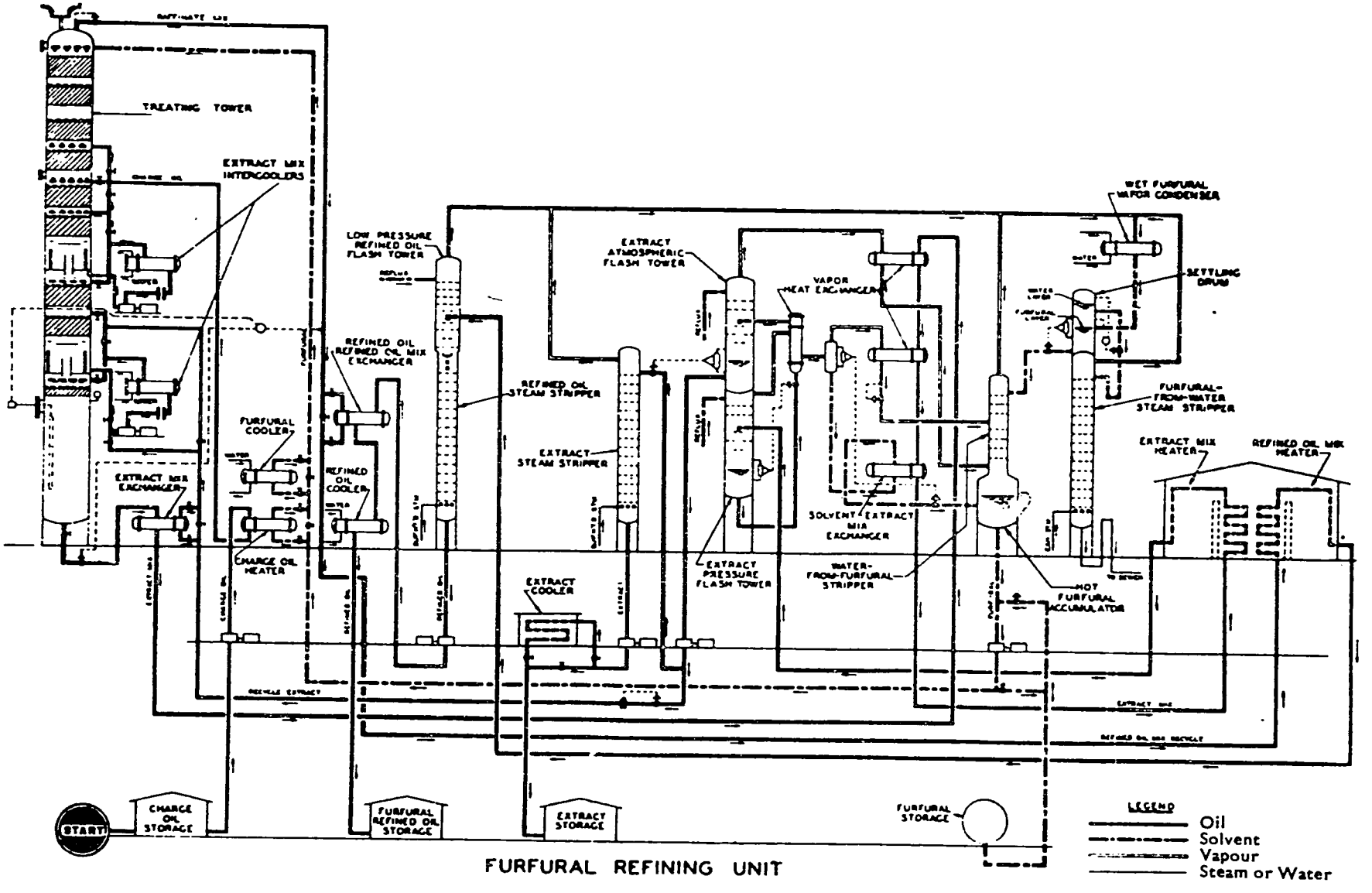


Fig. 2.5 Furfural extraction unit (from Berridge, 1973)

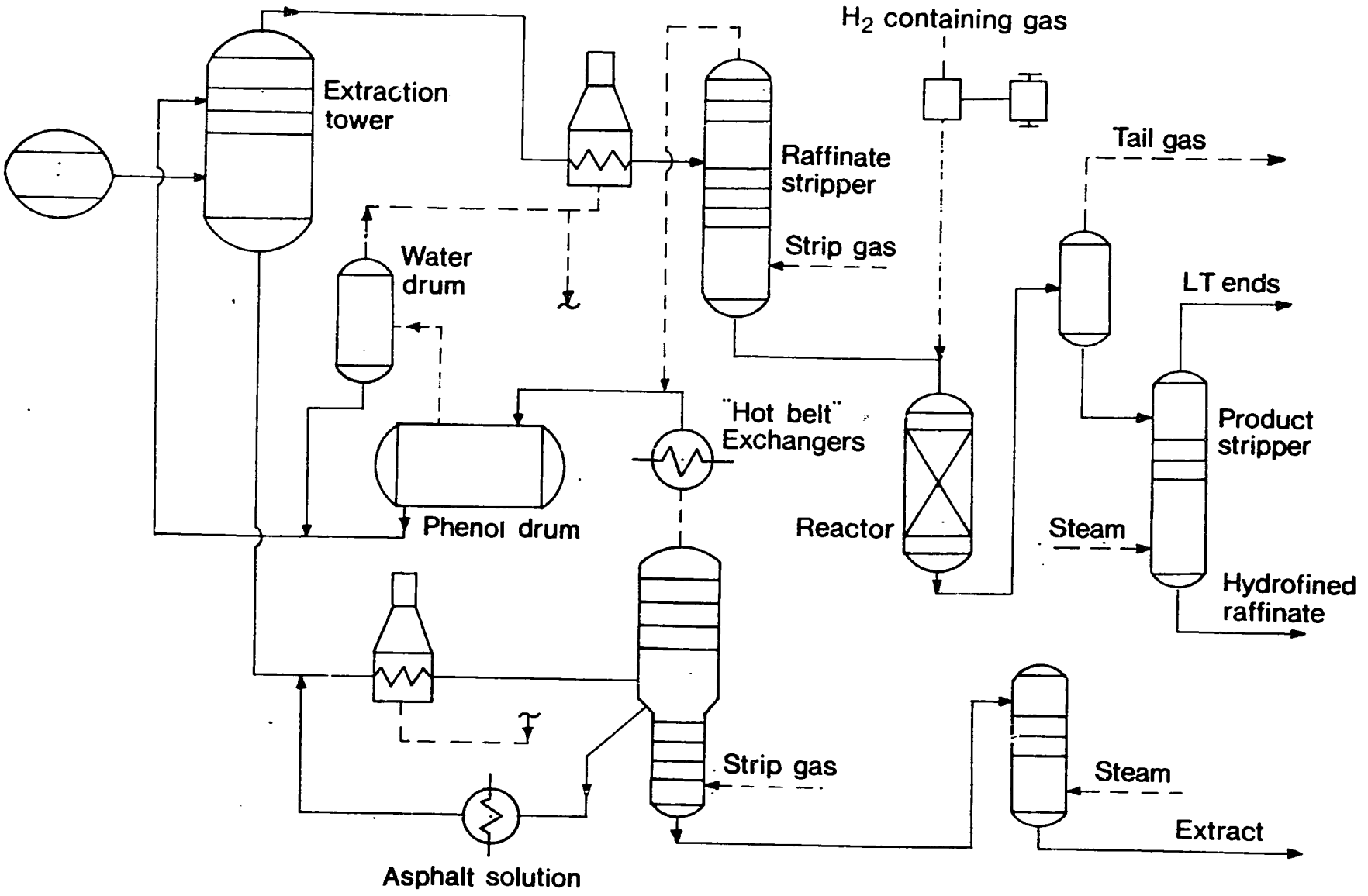


Fig. 2.6 The phenolfiner unit (from Berridge, 1973)

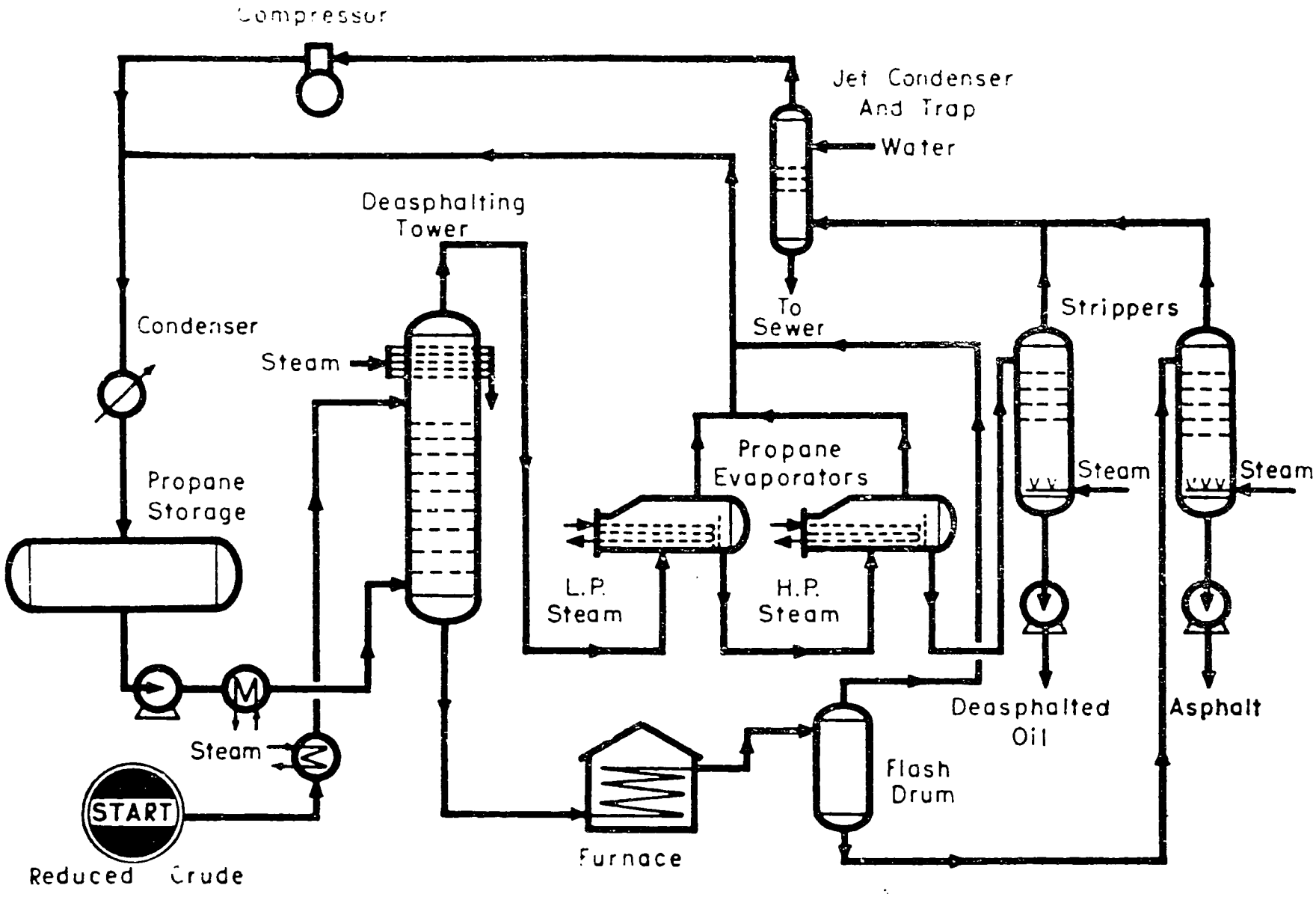


Fig. 2.7 Propane de-asphalting unit (from Berridge, 1973)

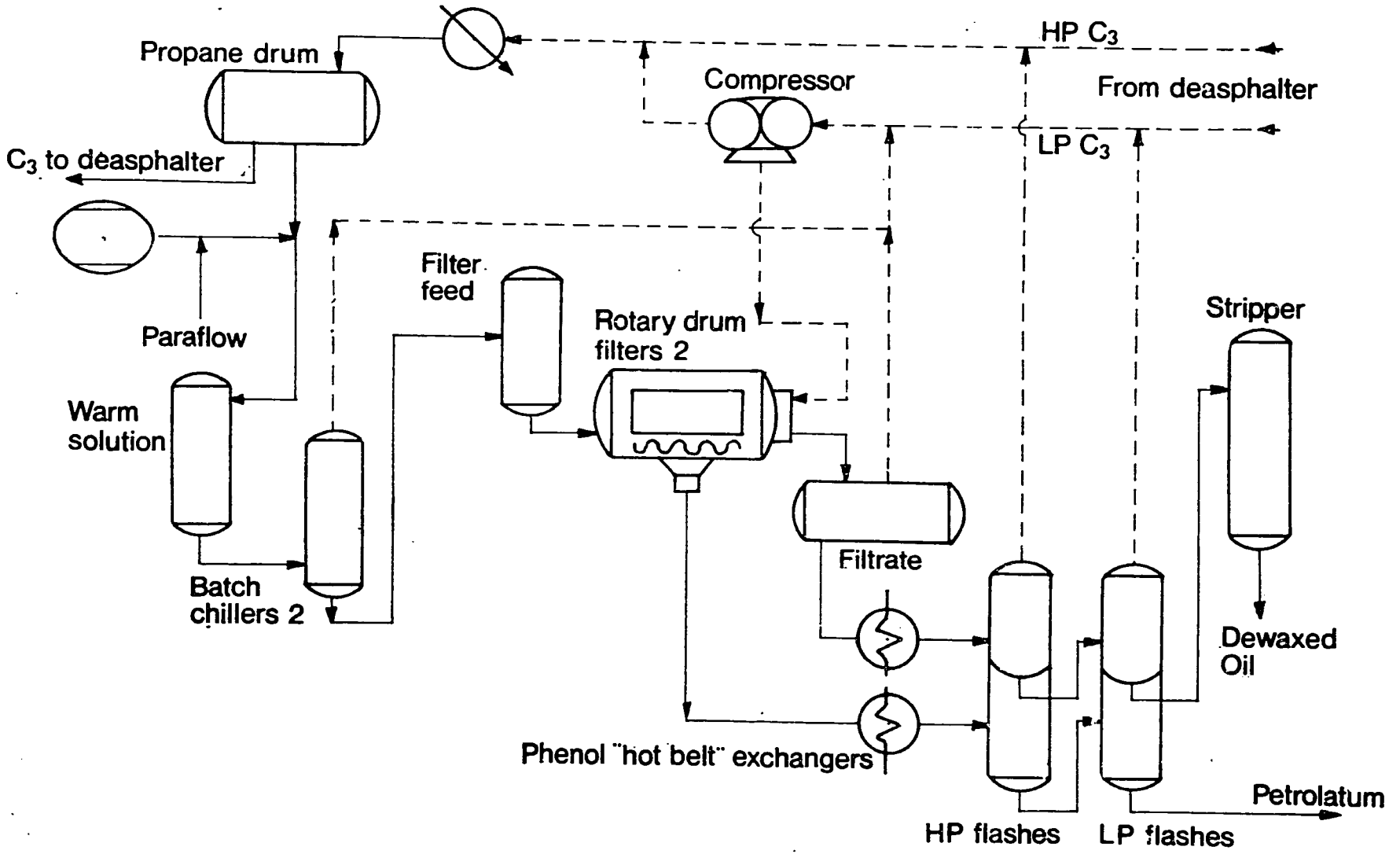


Fig. 2.8 Propane dewaxing unit (from Berridge, 1973)

CHAPTER 3

CHEMISTRY OF CRUDE OIL

Crude oil is not a uniform substance and its appearance and characteristics vary widely from one oilfield to another, and even from one well to another in the same oilfield. It may not be even a homogeneous substance as it can contain, besides dissolved gases, dissolved solids and colloidal suspensions. However, the elements present in the crude oil vary only between very narrow limits, as shown in Table 3.1.

3.1 Constituents of Crude Oil

As indicated by the high proportion of carbon and hydrogen, hydrocarbons are the main constituents of crude oils and account for over 75 per cent of the composition. The other elements present, sulfur, nitrogen, and oxygen, appear in the form of organic compounds which in some cases form complexes with metals, as in the case of metal prophyrins. Inorganic sulfur can be present as elementary sulfur or as hydrogen sulfide, dissolved in the oil. Heavy crudes of the younger formations have a low hydrocarbon content. The non-hydrocarbons are mainly concentrated in the heavy residues from the distillation of crudes.

3.1.1 Hydrocarbons

The hydrocarbons present in crude oils range from methane (one carbon atom in the molecule) up to molecules containing 60 or more carbon atoms, i.e., a range of molecular weights from 16 up to 850 or more.

The hydrocarbons are grouped into five main classes as follows:

1. Normal or straight chain paraffins (n-alkanes) - Saturated hydrocarbons formed by open chain as shown below:

$$CH_3 - CH_2 - CH_2 \ldots CH_2 - CH_3$$

These hydrocarbons are important constituents of light crude oil, particularly in the low-boiling point fractions, and their concentration decreases progressively with increasing mean molecular weight of the fractions.

2. Branched-chain paraffins (iso-paraffins or iso-alkanes) - Saturated hydrocarbons, with one or more alkyl side chains (R) as:

$$CH_3 - \overset{\overset{R}{|}}{CH} - CH_2 - \ldots - CH_2 - CH_3$$

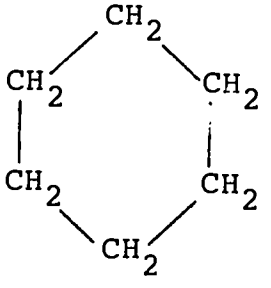
As with the normal paraffins, n-paraffins, the abundance of the branched-chain paraffins diminishes rapidly in the higher boiling fractions. In gasolines, iso-paraffins with a high degree of branching are very important constituents. Since both n-paraffins and iso-paraffins contain no ring structure, they belong to the same series with the general formula:

$$C_nH_{2n+2}$$

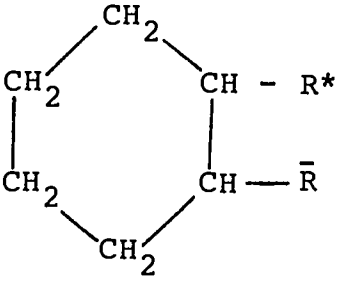
3. Napthenes (cycloparaffins, cycloalkanes) - Molecules with one or more saturated rings and possibly alkyl side chains. Cyclopentane and cyclohexane structures predominate

in petroleum. Also, traces of cycloheptane derivatives have been detected.

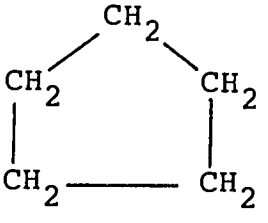
Different types of compounds that may exist in petroleum can be as follows:



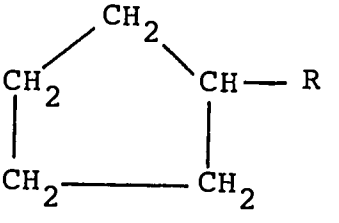
cyclohexane



alkylcyclohexane

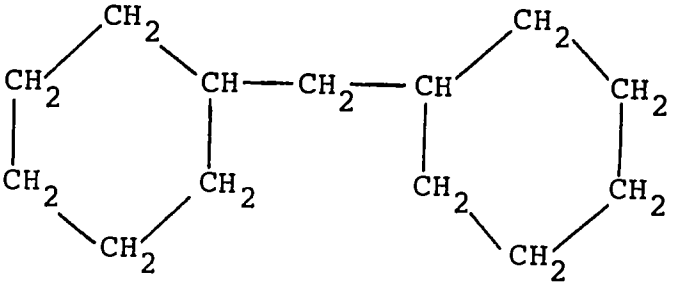


cyclopentane



alkylcyclopentane

Bicyclic naphtenes are important constituents of the kerosene and gas-oil fractions. Tricyclic, tetracyclic, and pentacyclic napthenes have been identified and isolated from lubricating oils.



isolated bicyclic

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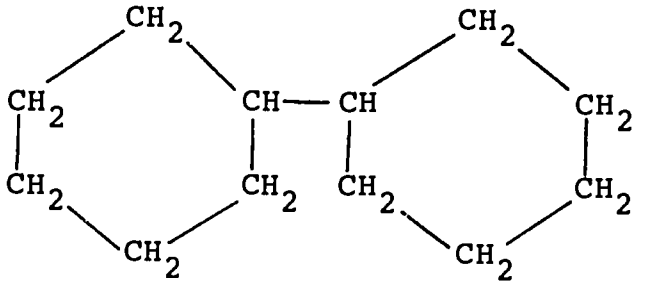
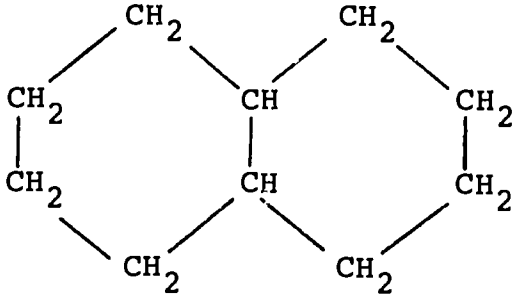
* R and $\bar{R}$ denote alkyl groups.



conjugated bicyclic



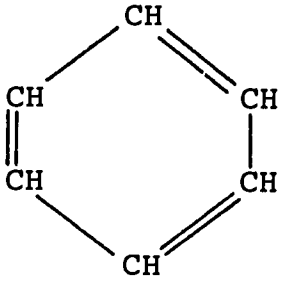
condensed bicyclic

The general formula for the pure ring napthenes is:

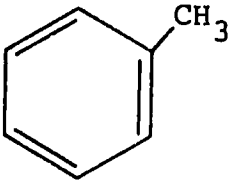
$$C_nH_{2n+2-2R_N}$$

where R_N is the number of naphthenic rings in the molecule.

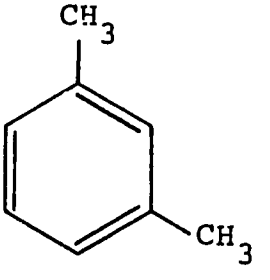
4. <u>Aromatics</u> - Hydrocarbons with at least one benzene ring in the molecule:



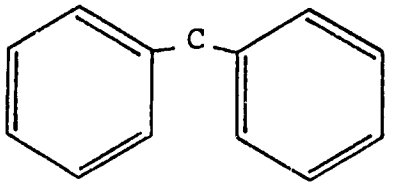
benzene ring
benzol



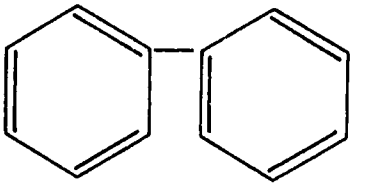
toluene



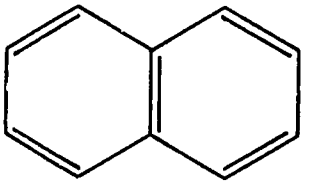
meta-xylene



isolated bicyclic



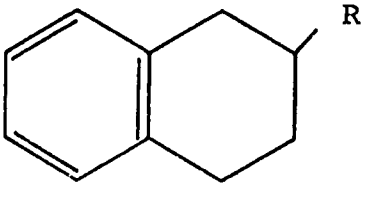
conjucated bicyclic



napthalene condensed bicyclic

Low molecular weight mononuclear aromatics are present in gasoline while the bicyclic ones are present in kerosene.

5. Mixed paraffin naphthenoarmatics - Compounds containing naphthenic rings, aromatic rings, and alkyl side chains in the same molecule



alkyl tetralin

3.1.2 Non-hydrocarbons

Crude oils contain appreciable amounts of organic non-hydrocarbons constituents, mainly sulfur-, nitrogen-, oxygen-containing compounds, and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil, but concentrate mainly in the heavier fractions and in the non-volatile residues.

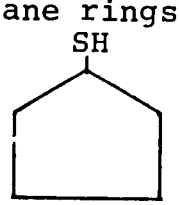
The presence of organic acids can promote metallic corrosion. In catalytic operations, poisoning of the catalyst can be caused by deposition of traces of metals (vanadium and nickel) or by chemisorption of nitrogen containing compounds on the catalyst.

1. Sulfur compounds - Organic sulfur compounds are present in all known crude oils, although their concentration can considerably vary. Generally, the higher the density of the crude oil, the greater the sulfur content. The total sulfur in the crude oil can vary from below 0.05% to about 5% or even more in heavy crudes.

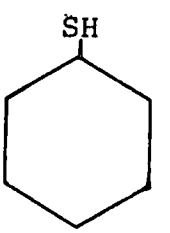
The distribution of sulfur in a given crude oil is not uniform, but increases with the increase in the molecular weight of the fractions concentrated in the distillation residues.

Hydrogen sulfide (H_2S) is often associated with petroleum gases. In the low boiling fractions of the crude, the main sulfur-bearing compounds present are the mercaptan, R - SH (R = alkyl group, i.e., CH_3-, C_2H_5-, etc.) which are corrosive compounds. Sulfides, R - S - R, and disulfides, R - S - S - R, are also found.

In the kerosene range, cyclic mercaptans with cyclopentane or cyclohexane rings are present.

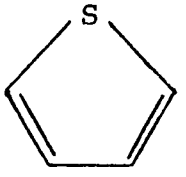


cyclopentane thiol

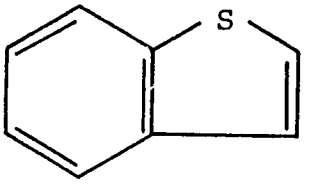


cyclohexane thiol

Thiophene and benzothiophene have been isolated from gasoline and kerosene, respectively.



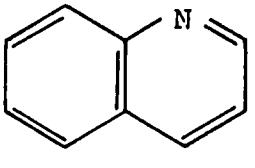
thiophene



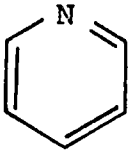
benzothiopene

2. Nitrogen compounds - Crude oils contain total nitrogen in the order of 0.1 up to 0.9%. With increasing boiling ranges, the nitrogen content increases and reaches a maximum in asphaltic distillation residues. Nitrogen compounds, unlike the sulfur derivatives, are relatively stable to heat and do not decompose in the normal refinery processes.

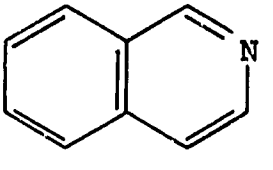
The majority of nitrogen compounds isolated from crude oil fractions belong to the basic group. Several basic nitrogen compounds have been isolated, as follows:



quinoline

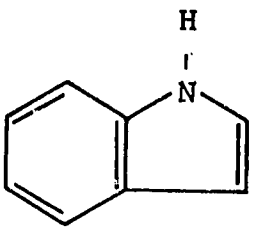


pyridine

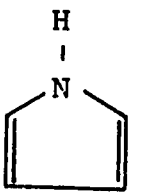


isoquinoline

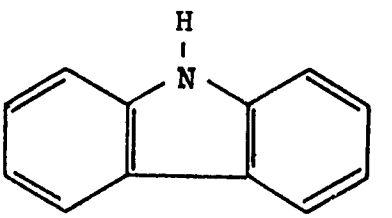
The non-basic nitrogen compounds identified consist mainly of derivatives of indoles, pyrrols, and carbazoles.



indole



pyrrole

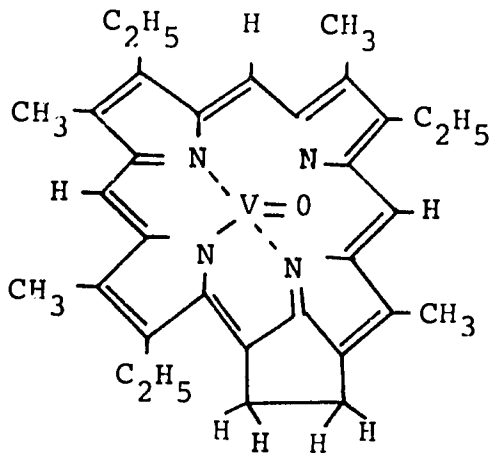


carbazole

The non-basic group of compounds known as porphyrins are also present.

3. Oxygen compounds - The total amount of oxygen in crudes is relatively low, varying from traces to a maximum of 2%. The oxygen content increases with the boiling range of the fraction. The greater portion of oxygen-containing constituents is concentrated in the residual oils. Oxygen is mainly present in the form of acidic compounds, such as organic acids, and, to a limited extent, phenols. For a given crude, the acidity is usually a maximum in the kerosene-gas oil range. The main acidic constituents are aliphatic carboxylic acids. Straight-chain acids containing from C_1 to C_{20} carbon atoms in the chain have been isolated. Monocyclic, bicyclic carboxylic and naphthenic acids are also present in kerosene and light gas oil fractions.

4. Metals - After burning, all crude oils leave an ash residue containing several metals from which vanadium and nickel occur in a very stable condition. Oil-soluble nitrogen complexes are in the form of porphyrins.



Vanadyl DPEP

(desoxophylloerythrin porphyrin)

The metal content of a crude appears in the distillation residues, associated with the asphaltic fraction.

3.2 Classification of Crude Oils

3.2.1 Introduction

Classifying crude oils is necessary to provide a guide to the quality, and hence value, of the oil. In the very early days, the kerosene fraction used for lighting purposes was the most valuable product. With the introduction of the internal combustion engines, gasoline became the most valuable fraction in the crude oil. The specific gravity of the crude oil provided a rough measure of the amount of the lighter fractions present; the lower the specific gravity (or the higher the API gravity, which is an inverse scale) the greater is the yield of light fractions obtained by simple distillation, and hence, the higher the price of the crude oil.

With the introduction of refining procedures, the rough guide provided by specific gravity was insufficient to classify the crude petroleum oils. Moreover, further information on the

nature of the oil and some indications of the chemical composition of both the crude oil and the various fractions which could be produced from it are necessary.

3.2.2 Classification According to the Base of a Crude Oil

The first attempt to provide such information was the use of the "base" concept of a crude oil. Crude oils were classified as paraffinic base, asphaltic base, and mixed base types. Paraffinic base crude oils are assumed to have gasoline of low knocking quality, good burning kerosene, high viscosity index lube oil, high wax content, and no asphalt. On the other hand, asphaltic crude oils are assumed to have gasoline of high knocking quality, kerosene of poor burning characteristics, lubricating oil of low viscosity index and asphalt suitable for commercial uses. The mixed base crudes are those which on distillation yielded residues containing both paraffin waxes and asphaltic material. This scheme was later enlarged to accommodate a fourth group of crudes, namely, a "hybrid base" group whose residue on atmospheric distillation contains asphaltic material with small amounts of paraffin wax. These were described as "naphthenic" crudes. Later on, it has been shown that this type of classification is not good enough to comprise all types of crude oils.

3.2.3 Classification According to the Wax Content of the Distillation Residue

Mallison (1927) suggested a classification system based on the wax content of the distillation residue. Crude oils are

considered to be asphaltic if the distillation residue contains less than 2% wax. On the other hand, a crude oil is considered paraffinic if it contains more than 5% wax.

3.2.4 Classification According to the U.S. Bureau of Mines

In 1935, Lane and Garton of the U.S. Bureau of Mines put forward a general scheme for the classification of crudes based on the specific gravity of two key fractions produced by a standardized method of fractionating the crude. The method starts by distilling the crude at atmospheric pressure. During this process, the fraction boiling between 240° and 275° is collected (Key fraction No. 1). The distillation is continued under a pressure of 40 mm of mercury. During this second step, the fraction boiling between 275° and 300°C is collected (Key fraction No. 2). The specific gravities of both fractions are determined, and based on these specific gravities (or API gravities), the crude is classified as belonging to one of the nine classes shown in Table 3.2.

The U.S. Bureau of Mines also developed the so-called correlation index, which is expressed as follows:

$$C.I. = 473.7d - 456.8 + 48640/k \qquad (3.1)$$

where

C.I. = correlation index

d = specific gravity at 60/60°F

k = average boiling point in degrees kelvin

Index values between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the fraction; from 15 to 20, a predominance of either naphthenes or mixtures of paraffins, naphthenes, and aromatics. Above 50 indicates the predominant aromatic character.

3.2.5 Classification According to the Characterization Factor

The characterization factor developed by Watson et al (1935) is based on the data of pure hydrocarbons and on correlating the boiling point with the specific gravity according to the following expression:

$$K = T_B^{1/3} d \tag{3.2}$$

where T_B is the boiling point in degrees Rankine (degrees Fahrenheit plus 460), or the average boiling point in the case of a fraction, and d is the specific gravity at 60/60°F. Paraffinic hydrocarbons give values of K between 12.5 and 13.0; naphthenic hydrocarbons vary between 11.0 and 12.0 and aromatics vary from 9.8 to 12.0.

3.2.6 Classification According to the Carpatica Method

Creanga (1961) developed the so-called carpatica method of classifying crude oils. In this method, the crude oils are characterized by the two following indices:

1. Structural indices: indicating the chemical nature of the constituent hydrocarbons expressed as per cent of

carbon in paraffinic C_p, naphthenic C_N, and aromatic C_A structures, respectively, in relation to the total hydrocarbons present in the crude. The structural group values of the fractions boiling up to 200°C are calculated from the hydrocarbon type analysis (paraffins, naphthenes, and aromatics), while they are determined by n-d-m method (refractive index, density, and molecular weight) for the fractions boiling above 200°C. The structural indices are used for the classification of the crudes into classes according to Table 3.3.

2. Quality indices: expressed as the weight percentage of wax (c), resins and asphaltenes (r), sulfur (s), and fractions distilled up to 200°C (d). These indices give an indication of the subclasses or groups to which the crude oil belongs, according to Table 3.4.

Element	% wt
Carbon	83.9 - 86.8
Hydrogen	11.4 - 14.0
Sulfur	0.06 - 8.00
Nitrogen	0.11 - 1.70
Oxygen	0.5
Metals (Fe, V, Ni,...etc.)	0.03

Table 3.1 Elements present in crude oils (from King et al, 1973)

Class	Key fraction No. 1		Key fraction No. 2	
	SP.Gr. 60/60°F	°API	SP.Gr. 60/60°F	°API
1. Paraffinic	<0.825	≥40	<0.876	≥30
2. Paraffinic-Intermediate	<0.825	≥40	0.876-0.934	20-30
3. Intermediate-Paraffinic	0.825-0.860	33-40	<0.876	≥30
4. Intermediate	0.825-0.860	33-40	0.876-0.934	20-30
5. Intermediate-Naphthenic	0.825-0.860	33-40	>0.934	≤20
6. Naphthenic-Intermediate	>0.860	≤33	0.876-0.934	20-30
7. Naphthenic	>0.860	≤33	>0.934	≤20
8. Paraffinic-Naphthenic	<0.825	≥40	>0.934	≤20
9. Naphthenic-Paraffinic	<0.860	≤33	<0.876	≥30

Table 3.2 Classification of crude oils according to the U.S. Bureau of Mines

Nomination of the class	Chemical characteristics of the hydrocarbons
1. Paraffinic	$C_p^t \geq 72$
2. Paraffinic-Naphthenic	$C_p^t \geq 50,\ C_p^t + C_N^t \geq 90$
3. Paraffinic-Aromatic	$C_N^t \geq 50,\ C_p^t + C_A^t \geq 90$
4. Paraffinic-Naphthenic-Aromatic	$C_p^t \geq 50,\ C_N^t > C_A^t,\ C_A^t > 10$
5. Paraffinic-Aromatic-Naphthenic	$C_p^t \geq 50,\ C_A^t > C_N^t > 10$
6. Naphthenic-Aromatic	$C_p^t < 50,\ C_N^t > C_A^t$
7. Aromatic-Naphthenic	$C_p^t < 50,\ C_A^t > C_N^t$

where C_p^t = per cent carbon in paraffinic chains

C_N^t = per cent carbon in naphthenic rings

C_A^t = per cent carbon in aromatic rings

Table 3.3 Classification of crude oils according to carpatica method (structural indices)

Quality index	Characteristics wt %
Non-waxy	$C < 2$
Waxy	$C > 2$
Poorly resinous	$r < 10$
Resinous	$10 \leq r < 25$
Asphaltic	$r \geq 25$
Non-sulfurous	$s < 0.5$
Sulfurous	$s \geq 0.5$

C = percent wax

r = percent resins and asphaltenes

s = percent sulfur

Table 3.4 Classification of crude oils according to carpatica method (quality indices)

CHAPTER 4

CHEMISTRY OF BITUMEN

4.1 Introduction

The composition and structure of bitumens are complex, but separation into fractions of distinctive chemical types is possible by both chemical and physical methods.

The asphaltic components of petroleum are separated by a light hydrocarbon solvent into a soluble maltenes portion and insoluble asphaltenes (Table 4.1).

The structure and properties of these two portions vary, not only with crude oil source, but also with the type of solvent used for this precipitation.

The term "maltenes" denotes a mixture of the total resins and oils obtained as filterates from asphaltene precipitation.

4.2 Constituents of Bitumen

4.2.1 Oils

The oily component is the fraction that is soluble in cyclohexane with which it can be eluted from alumina. It consists of paraffinic straight chain, iso-, and cycloparaffin and aromatic components. The paraffinic constituents are the fraction soluble in petroleum ether 40-60°C boiling range (aromatic and sulfur free). Aromatics are the fraction that is soluble in petroleum ether 40-60°C boiling range, but is adsorbed in alumina and eluted by benzene.

The paraffinic constituents are hydrocarbons having a low refractive index (1.45 to 1.46 at 80°C) as well as wax molecules. The aromatic oil molecules consist of aromatic nuclei connected to aliphatic or cyclic saturates. This gives a structure which is, to a great extent, naphtheno-aromatic.

The oils are composed of the lowest molecular weight hydrocarbons in bitumen.

Asphalts have been considered to be derived from petroleum hydrocarbons by reactions of oxidation, dehydrogenation, and sulfurization. The oils are formed at first, followed by resins, then carboxylic acids, and eventually asphaltenes. The oil fraction has the lowest percentage of heteroatoms, especially that containing sulfur and oxygen.

4.2.2 Resins

The term "resins" denotes the material eluted from various solid adsorbents (silico gel and alumina) after oil elution. They have an aromatic character, and do not contain any pure paraffinic or naphthenic hydrocarbon. The proportions of heteroatoms are relatively higher than that in oil. Their molecular weights are much higher than those of the oils. According to different authors, the molecular weight varies between 1,000 and 3,800.

The resins in asphalts could be either hydrogenated to oils or dehydrogenated by the so-called "oxidation reactions" to form the next high molecular weight material known as asphaltenes.

4.2.3 Asphaltenes

Asphaltenes are present in asphalt in the form of hard, solid, friable, brown-black constituents which are the heaviest compounds of the condensed structure. It is not possible to know exactly the structural shape of asphaltene molecules. Erdman (1965) provides a review of the literature including detailed structural knowledge of petroleum asphaltenes. Mass spectroscopic techniques (Clerk and O'Neal, 1960), nuclear magnetic resonance spectroscopy (NMR), electron spin resonance (ESR), as well as x-ray diffraction and electron microscopy (Dickie and Yen, 1966), have all been used to define the indistinct outlines of the asphaltene molecules. The data suggested that the molecular weight of these materials might be as high as 1 to 5×10^3 (Dean and Whitehead, 1963; Winnifford, 1963). The asphaltene molecule would appear to carry a core of stacked flat sheets of condensed aromatic rings. Approximately 5 of these sheets, each with some 16 condensed rings, are stacked one above the other with a repeated distance of 3.55 to 3.70°A (°A = Angestrome = 1×10^{-8}cm) giving an overall height for the stack of 16 to 20°A. The average sheet diameter would appear to be 8.5 to 15°A. The stacked aromatic sheets show some disorder, probably induced by chains of aliphatic and/or naphthene ring systems which, linking the edges of the aromatic sheets, tend to be held apart. The repeated distances between these saturated connecting groups appear to be 5.5 to 60°A, and the average number

carbon atoms in the rings of both the aromatic and napthene ring systems would appear to be 6. The condensed aromatic sheets contain oxygen, sulfur, and nitrogen atoms, and these elements are probably associated with the free radical sites (Ferris et al, 1966) detected by ESR. These sites may well be the centers at which complexed, non-porphyrin, vanadium and nickel are located, since Sugihara and his coworkers (1965) have shown a correlation between sulfur and metal removal from the asphaltenes.

4.2.4 Waxes

Wax is an extract obtained from oils by organic solvents. It is a mixture of organic hydrocarbons, white, yellow, to brown in color.

Petroleum waxes are generally classified as paraffin wax and microcrystalline wax.

Paraffin Wax - Normal alkanes are the major constituents of distillate wax. Varying proportions of branched-chain paraffins (iso-alkanes) and cycloalkanes are also present (Minchin, 1948; Buchler, 1927).

Waxes with n-alkane contents up to 98% were found. Aromatics are present only in traces, 0.1% or less, most of them of the monocyclic type.

A. Wax Analysis Methods

The analysis of paraffin wax was done by Bengen's discovery (1949) that urea could form adducts with n-alkanes. I was found that for complex formation to be possible in case of iso-alkanes, a methyl side group must be accompanied by a straight chain of at least 10-13 carbon atoms, and that in the case of ethyl, this must be at least 24 carbon atoms in length.

Carbon number distribution, as well as hydrocarbon type distribution, could be determined by high-temperature mass-spectrometry (O'Neal, 1953).

High temperature gas liquid chromatography (GLC) is another interesting technique (Ogilvie et al, 1958) for carbon number distribution determination. This is particularly so when GLC is combined with selective methods for separating the wax components according to their types. The linde molecular sieve type 5°A is, under certain conditions, a selective absorbent for n-paraffins (Dean, 1966). By recovering the n-paraffins from the sieves and analyzing them by GLC, an accurate picture of their carbon number distribution can be obtained. The distribution of iso-paraffins in the wax can also be determined from another GLC run on the whole wax.

B. Transition Point

It has been noticed that at temperatures below the apparent solidification point of the wax, changes in crystal structure

frequently take place. The temperature at which this occurs is known as the transition point (see Fig. 4.1).

Straight chain alkanes in the range from 20 up to 36 carbon atoms show transition points in the solid phase (Gray, 1948; and Schaerer et al, 1955). The transitions are accompanied by a change in the refractive index (Johnson, 1954), specific gravity (Sayer et al, 1944), and the absorption in the infrared region (Martin et al, 1958).

A large heat of transition is necessary to convert the β-modification, which is stable at lower temperatures, into the α-modification, stable at high temperatures, up to the melting point.

Microcrystalline Wax - The knowledge of the composition of microcrystalline waxes is less advanced than it is for distillate waxes. The part giving urea adduct varies considerably and values between 3 and 60% have been found.

Data on the composition of microcrystalline waxes are given by Ridenour et al (1958). Besides straight chain alkanes, they found branched-chain alkanes, monocyclopentyl, monocyclohexyl, and dicyclohexyl paraffins, aromatics, and polycycloparaffins.

More recent data on the structure of the saturated fractions of residual waxes show that these fractions are mainly composed of multiple-branched iso-paraffins and monocycloparaffins. The method of analysis applied is a combination of pyrolysis, hydrogenation, and gas liquid chromatography.

4.3 Identification Methods

It is necessary to utilize the major analytical techniques available for identifying individual components in mixtures isolated from bitumen samples. Ultraviolet, visible, infrared and nuclear magnetic resonance spectroscopy, electron microscope, and gas liquid chromatography are the more important methods employed in studying bitumen components.

Infrared analysis readily identifies functional groups (Colthup et al, 1964). These groups absorb characteristically in the infrared region of the electromagnetic spectrum. It is helpful for identifying hydrocarbons. Infrared analysis requires relatively large amounts of samples: for example, 1 mg. of pure material.

Compounds containing chromophores absorb in the ultraviolet region of the spectrum. Hetero and conjugated systems readily absorb ultraviolet radiation with high extinction coefficients in many cases (Mair et al, 1966; Commins, 1966). Aromatic hydrocarbons have characteristic absorption in the ultraviolet region as well as fluorescence, which often help identify the particular compound.

Nuclear magnetic resonance determines proton environment, enabling the analyst to identify many organic compounds. Some of the problems with isomers are solved with NMR spectroscopy. The percentages of the following five types of protons (Williams and Chamberlain, 1963) could be calculated.

1. Paraffinic methyl (aliphatic, cyclic and gama or farther removed from aromatic ring, unsaturated linkage or heteroatoms)
2. Paraffinic methylene or methine (aliphatic, cyclic and beta or farther removed from aromatic ring...) plus methyl beta to aromatic ring
3. Methyl alpha to aromatic ring
4. Methylene or methine alpha to aromatic ring
5. Aromatic (benzenoid)

Gas liquid chromatography is used for the identification of individual components of n-paraffinic hydrocarbons in waxes (Ogilvie et al, 1958). It is used to determine the carbon number distribution in oils, to differentiate among different crude oils, and to distinguish between two samples of the same type.

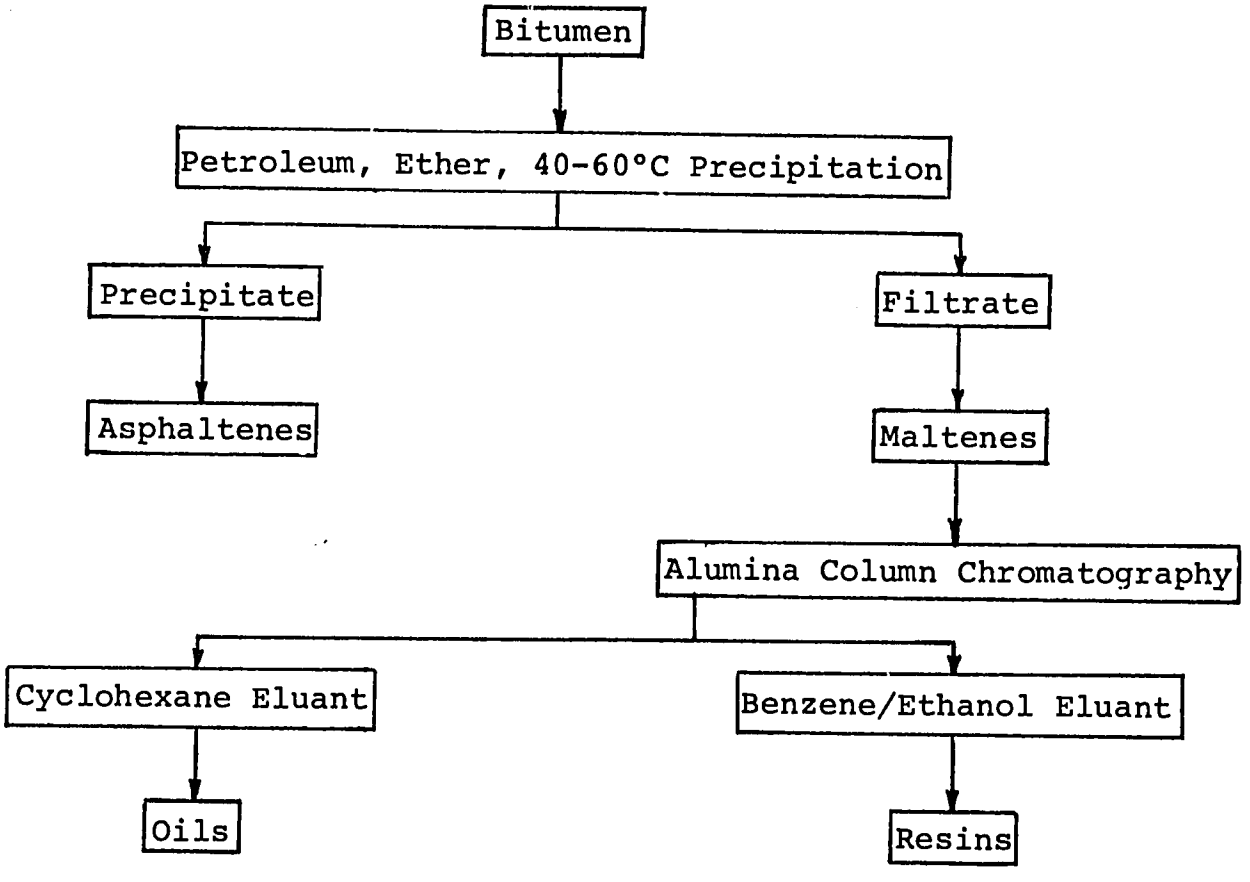
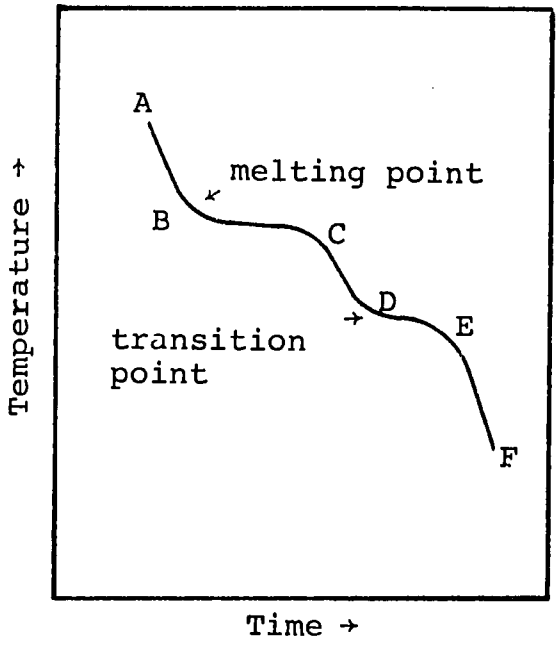
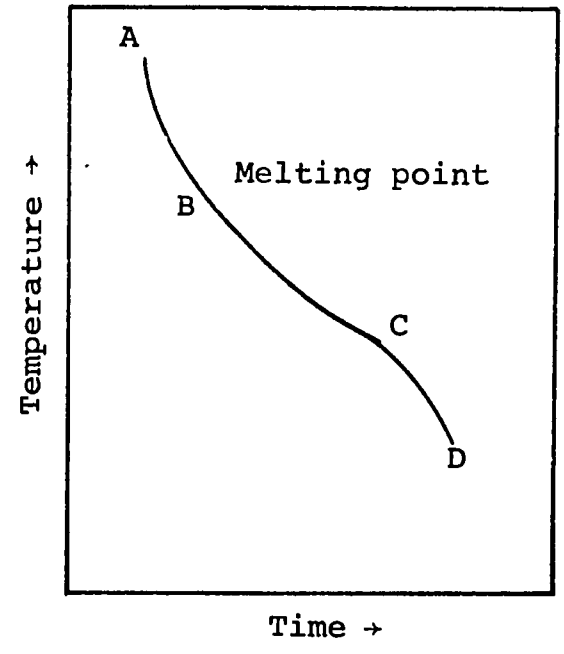


Table 4.1 Separation of bitumen constituents



Cooling Curve of a Paraffin Wax



Cooling Curve of a Micro-crystalline Wax

Figure 4.1 Cooling curves of a paraffin and microcrystalline wax

CHAPTER 5

PHYSICAL PROPERTIES OF ASPHALTIC MATERIALS

The quality and suitability of an asphalt for any given use are practically well-defined by evaluating the following major four properties:

1. Consistency
2. Durability, or resistance to weathering
3. Rate of curing
4. Adhesion and resistance to water action

5.1 Consistency

Consistency is the general term used to describe the degree of fluidity or plasticity of an asphalt at any particular temperature. The consistency of an asphalt considerably varies with temperature and it is, therefore, necessary to use a standard temperature when comparing the consistency of one asphalt cement with another.

5.1.1 Measurements of Consistency

The consistency of asphaltic materials ranges from that of a very thin liquid, just a little thicker than water, to that of a stiff semisolid resembling sealing wax. Because of this wide variation, no one instrument can satisfactorily measure the consistency of all asphaltic materials. Four methods of measuring consistencies are usually used (Wallace and Martin, 1967):

1. Penetration Test
2. Viscosity Tests (Saybolt-Furol, Kinematic Viscosity,...etc.)
3. Float Test
4. Softening-Point Test (usually specified for air-blown asphalts)

Penetration Test - The penetration test measures the hardness or stiffness of a bituminous material under a given set of circumstances. The results of the test are expressed as the distance, in tenths of a millimeter, that a standard needle penetrates vertically into a sample of the asphalt under known conditions of loading, time, and temperature. Standard penetration, which is implied unless other conditions are stated, is for a load of 100 g applied for 5 sec at a temperature of 77°F (see Fig. 5.1). The relation of penetration value to consistency is an inverse one, that is, the higher the penetration, the softer the asphalt.

Common penetration grades of asphalt cements are 40-50, 60-70, 85-100, 120-150, and 200-300. Generally speaking, lower penetration grades will be used in the warmer climates in order to avoid softening under high summer temperatures. Conversely, higher penetration grades may be used in the north so that excessive brittleness does not occur during cold winter weather.

Viscosity Test - Viscosity is the broad, general term for consistency. It is a measure of the resistance to flow. Thus, the higher the viscosity of a liquid, the more nearly it approaches

a semisolid in consistency. Viscosity can be measured either by the Furol viscosity test or by the kinematic viscosity test.

a. Fural Viscosity Test - Fural viscosity is a specific test which is used to measure the viscosity of liquid as-asphaltic materials. The Furol-viscosity value is the number of seconds required for 60 cu cm of the material to flow through an orifice of given size at a specific temperature (see Fig. 5.2). Thus, the higher the Furol viscosity at a given temperature, the more viscous the material.

b. Kinematic Viscosity Test - The kinematic viscosity test utilizes a gravity-flow capillary viscometer (Figs. 5.3 and 5.4). The viscometer is mounted in a thermostatically controlled, constant-temperature bath. The Zeitfuchs cross-arm viscometer (Fig. 5.3) is more suitable for liquid asphalts, whereas the Cannon-Manning viscometer (Fig. 5.4) is more suitable for asphalt cements. A suitable, clear oil must be used in the bath when tests are made at 275°F.

With the viscometer mounted in the bath, asphalt is poured into the large opening of the viscometer until it reaches the filling line (Fig. 5.3). The filled tube remains in the bath at test temperature for a specified period of time to make sure that the tube and asphalt are at proper temperature. A slight pressure is applied to the large opening of the tube, or a slight vacuum to the small opening, thus causing asphalt to start flowing over the

siphon section just above the filling line. Gravity causes the asphalt to flow downward in the vertical section of capillary tubing. A timer is started when the asphalt reaches the first timing mark and stopped when it reaches the second. The time interval, multiplied by a calibration factor for the tube, gives the kinematic viscosity in units of centistokes. The calibration factor is determined by using standard calibrating oils of known viscosity characteristics.

Float Test - This test is used for measuring the consistency of some asphalts which are more viscous than a Grade 3000 liquid asphalt, as well as those which have a penetration higher than 300.

In making the float test, the asphalt is placed in a small mold which is open at both ends. It is then chilled, attached to the bottom of an aluminum saucer, and placed in a water bath at 122°F (see Fig. 5.5). The number of seconds required for water to force its way through the asphalt plug is the float-test value. Thus, the higher the float-test value, the stiffer is the asphalt.

Softening-Point Test - The simplest, most direct method of determining the temperature-susceptibility characteristic of asphalts is afforded by the ring-and-ball softening point. An asphalt cement having a higher softening point for a given penetration at 77°F is less susceptible to consistency change

due to temperature. In making the test, asphalt is first placed in a small ring and chilled. The ring is then immersed in water or glycerin; a small steel ball is placed on the asphalt, and heat is applied to the liquid. As the temperature is raised, a point is reached at which the asphalt softens and allows the ball to sink to the bottom of the container. The temperature at which this occurs is the softening point (see Fig. 5.6).

5.2 Durability Characteristics

Paving asphalts must remain plastic to satisfactorily perform as binders. However, when asphalt is exposed to the weather in a thin film, it eventually loses much of its plasticity and becomes brittle because of chemical and physical changes. Durability of an asphalt is its resistance to change in properties when subjected to processing (e.g., mixing with aggregate) and weathering, and is manifested primarily by a resistance to hardening with time.

5.2.1 Mechanisms of Hardening

A number of factors contribute to the ability of a paving asphalt to resist hardening with time. These factors (Monismith, 1961) are:

1. Oxidation
2. Volatilization
3. Polymerization
4. Thixotropy

5. Separation
6. Synersis
7. Photooxidation

Oxidation - It is the chemical reaction of oxygen in the air with asphalt. The rate of oxidation is primarily a function of the character of the exposed surface area of the asphalt and temperature. At elevated temperatures, oxygen causes a dehydrogenation of the asphalt which results in a formation of asphaltenes. On the other hand, at normal temperatures, the oxidation process is slow and oxygen is primarily absorbed by the asphalt. The oxidation process usually results in forming a film of hard material at the surface of the asphalt. If this film remains undisturbed, further reaction of oxygen with the material will be prevented. However, if the film is cracked, new surfaces of asphalt will be exposed and additional oxidation takes place. Oxidation is believed to be one of the primary causes of hardening of the asphalt in both the plant and in the road.

Volatilization - It is the evaporation of lighter hydrocarbons in the asphalt. Elevated temperatures will accelerate this process. Many studies concluded that volatilization is one of the primary agencies of hardening of asphalt materials, especially in the plant mixing operations where high temperature is combined with violent agitation. To a certain extent, the rate of volatilization would appear to depend on asphalt source and the refining procedure (Monismith, 1961).

The rate of hardening due to the above two factors, oxidation and volatilization, is directly proportional to the exposed surface area of the asphalt and inversely proportional to the volume. Therefore, it is the effect of the surface area-volume ratio that explains why a large mass of asphalt may be kept in a storage tank at a temperature of 150°C (300°F) for several weeks or even months without undue hardening, whereas this same asphalt, when agitated in a pugmill at the same temperature will lose several points in penetration in less than one minute (Wallace and Martin, 1967). In the first case, the exposed surface area to volume ratio is very small, while in the second case this ratio is enormous. It should be noted that this principle is recognized in asphalt pavement mix design methods. For adequate stability, a pavement must contain small air voids. However, the greater these air voids become, the more area is exposed to oxidation. Therefore, these air voids are usually specified to be as small as practicable in most of the design methods of asphaltic concrete pavements.

Polymerization - It is a combining of like molecules to form larger molecules (Monismith, 1961). In the case of asphaltic materials, polymerization can be defined as the combining of smaller molecular weight hydrocarbons into larger molecular weight hydrocarbons. Several studies have shown a considerable evidence that resins are the most susceptible asphalt component to change and that polymerization mainly involves the conversion of resins to asphaltenes with only minor changes occurring in the oily

fractions. This change can be detrimental, since it tends to make the asphalt more brittle and, consequently, the pavement more susceptible to cracking.

Thixotropy - Thixotropy, or age hardening, is a progressive hardening due to a rearrangement of the molecules to form a gel-like structure in the asphalt. This hardening action takes place rapidly during the first few hours and then gradually decreases. After about a year, the rate of hardening is almost negligible. This type of hardening, however, is reversible and can be partially, or even totally, eliminated by reheating or mechanically working the asphaltic material. Usually, hardening due to thixotropy occurs in areas where the pavement is subjected to little or no traffic, causing the gel-like structure to form within the asphalt.

Separation - According to Monismith, 1961, separation is the term used to describe the removal of the oily constitutes, resins, or asphaltenes from an asphalt as caused by the selective absorption of some aggregates on which an asphalt film has been placed. This action may cause the asphalt to either harden or soften.

Syneresis - This is the exudation reaction occurring in asphalts in which, due to the formation of a structure within the material, a thin oily liquid containing either dispersed or dissolved intermediate and heavier bodies is exuded to the surface. With the elimination of some of the lighter oils, the asphalt will

progressively harden with time. This reaction in its less extreme form is referred to as the "staining tendency" of the asphalt. While this reaction is mainly associated with highly-blown asphalts, it may occur in paving asphalts in its less extreme forms.

Photooxidation - Photooxidation is the breaking of asphalt molecules into water and water-soluble products due to the effect of the actinic rays of the sun. The reaction is essentially one of oxidation, accelerated by the action of light (Wallace and Martin, 1967).

Fortunately, the destructive rays are able to penetrate only a few molecular layers past the surface of the asphalt. Therefore, photooxidation must be considered to be of secondary importance in the deterioration of thick pavements. However, it considerably contributes to the weathering of light seal coats and very thin asphalt surfaces (Wallace and Martin, 1967).

5.2.2 Durability Tests

The most widely used test for evaluating the durability of paving asphalts is the Thin-Film Oven, TFO, test developed by Lewis and Welborn (1941). The TFO test is not a test per se. It is a procedure intended to subject a sample of asphalt to hardening conditions approximating those which occur in normal, hot-mix plant operations. Penetration tests, made on the sample before and after the TFO test, are considered to be a measure of these hardening conditions.

The TFO test is made by placing a 50-cu cm sample of asphalt cement in a cylindrical, flat-bottom pan 5.5 in. in inside diameter and 3/8 in. deep. The asphalt layer is about 1/8 in. deep. The sample and container are placed on a rotating shelf in a ventilated oven and maintained at a temperature of 325°F for a period of 5 hr. The shelf rotates at approximately 5 to 6 rpm. For other durability tests and procedures, the reader is referred to Wallace and Martin (1967).

5.3 Rate of Curing

Curing is defined, in the case of asphaltic materials, as the increase in consistency of an asphalt due to the progressive loss of solvent by evaporation. The rate of curing is an important characteristic in manufacturing and using cut-back asphalts for paving purposes.

5.3.1 Factors Affecting Curing Time

The important factors affecting the curing time of an asphaltic material can be grouped into two categories:

1. Factors due to inherent properties of the asphalt
2. External factors

The important inherent properties of the asphalt that affect curing time are:

a. Volatility, or evaporation rate of the solvent - The effect of volatility of the solvent is self-evident, because it forms the essential difference between RC, MC, and SC asphalts.

b. Amount of solvent contained in the cutback - It is apparent that the less solvent contained in a cutback, the less the time required for it to cure out by evaporation of this solvent.

c. Penetration of the base asphalt - The curing time increases with increasing penetration, or increasing softness, of the asphalt.

The important external factors that affect curing time are as follows:

a. Temperature

b. Surface area exposed (ratio of surface area to volume)

c. Wind velocity past the surface

5.3.2 Curing Tests

Considering the variety of the factors affecting curing time, it is practically impossible to predict the exact curing time to be expected in the field. It is the external factors which are unpredictable and uncontrollable. Therefore, if these external factors are kept constant, a test may be made that reflects the comparative curing time of asphaltic materials (Wallace and Martin, 1967).

The curing index (Martin, 1949), developed by the Texas Highway Department, serves as such a test. In fact, however, it is not a test, but rather an interpretation of the standard distillation results that yields a number, called the curing index, which is expressed in hours.

The apparatus used for performing the standard distillation test is shown in Fig. 5.7. Two hundred centimeters of the cutback to be tested is placed in the flask and the apparatus assembled as shown. Heat is applied until the material boils, causing the condensed solvent to collect in the graduated cylinder. The volume of solvent contained in the graduate is observed and recorded at the following temperatures, in degrees Fahrenheit, 320, 347, 374, 437, 500, 600, and 680. This distillation, in effect, yields the solvent and base asphalt which the refiner used in making the cutback.

Wallace and Martin (1967) present the procedure used to interpret the results of the distillation test, as well as other approaches aimed at determining the curing times of asphalts.

5.4 Adhesion and Resistance to Water Action

The durability of an asphalt pavement is greatly dependent upon the ability of the asphalt to adhere to the aggregate. Generally, asphalt cannot be considered an ideal adhesive. However, if some precautions are taken, it is adequate.

Few problems may arise when asphalt is mixed with aggregates in the absence of water. On the other hand, because aggregates are wetted more easily by water than by an asphalt, the presence of water can lead to significant problems, either in the initial coating of damp or wet aggregate or in maintaining an adequate bond between the binder and the aggregate. Failure of a bond already formed is commonly referred to as "stripping," which is

brought about by the displacement of the asphalt binder from the aggregate surface by water.

5.4.1 Adhesion in the Absence of Water

To obtain good adhesion, it is first necessary for the binder to wet the aggregates. For practical purposes, it is necessary that wetting should occur almost instantaneously and, therefore, too high a viscosity may cause some difficulties. This is particularly important if the aggregate is dusty because of the tendency of the dust layer on the aggregate, rather than the aggregate itself, to be coated by the binder. Consequently, if the viscosity is too high, the binder may not reach the surface of the aggregate.

In some cases, when a binder weathers and becomes brittle, rupture of the binder/aggregate bond may take place so that the binder comes away from the stone surface. However, even with binders which have become brittle, it is customary for any failure under mechanical stress to be a failure in cohesion rather than adhesion, occurring within the film of binder rather than at the binder/stone interface.

5.4.2 Adhesion in the Presence of Water

At least three theories are used to describe the water resistance of asphalt-coated aggregates (Monismith, 1961). These theories are:

1. Chemical reaction concept - acidic components of asphalt react with basic minerals of aggregate to form water insoluble compounds

2. Mechanical concept - emphasizes the role of surface roughness and porosity

3. Surface energy concept - adhesion resulting from interfacial energy relationships at the aggregate, asphalt, water, and air interfaces

According to the chemical reaction concept, when a solid is wetted by a liquid, adsorption occurs at the surface and is followed by a chemical reaction between adsorbed material and constituents of the solid phase. To achieve a good adhesion, the asphalt must contain certain acid or polar compounds and must produce a water insoluble reaction compound. While acidic stones (e.g., quartz) cannot react with an acid oil, basic oxides (e.g., limestones) can react and achieve good adhesion.

Based on the mechanical theory, the composition of the rock is important only to the extent that it affects surface texture. It is thought that the rougher the surface texture, the better is the adhesion. Porous aggregates usually show better adhesion to asphalt, due also in part to mechanical interlock.

The surface energy concept makes use of the classical theory of wetting to explain adhesion. In the presence of water, the

chemical theory states that (Monismith, 1961):

$$\gamma_{SW} - \gamma_{SB} = \gamma_{WB}\cos\Theta \tag{5.1}$$

where:

γ_{SW} = aggregate-water interfacial tension

γ_{SB} = aggregate-asphalt interfacial tension

γ_{WB} = asphalt-water interfacial tension

Θ = contact angle

Figure 5.8 shows that the smaller the contact angle, the greater is the possibility that the asphalt will flow over the surface of the aggregate and form the desired bond.

Thus, the work required to displace water by an asphalt is directly proportional to the interfacial energy between asphalt and water and is also related to the angle of contact. This theoretical treatment is not rigorous because it has been simplified by omitting one term in the equation, the surface pressure of the adsorbed layer of water. A fuller treatment of the general problem is given by Gregg (1951). Displacement of the water by the asphalt will be made easier if the interfacial energy (asphalt/water) is reduced and Θ is increased. In the case of a normal asphalt, Θ is always less than 90° and so the factor $(1 + \cos\Theta)$ is always > 1, i.e., an appreciable amount of work is required to make the asphalt binder displace the water and, as a result, the asphalt tends to collect in drops on the surface. However, as Blott et al have shown (1954), it is possible to produce wetting if a very high pressure is applied.

The values of γ_{SW} and Θ can both be altered by adding certain chemicals to the system. A similar effect is obtained when a cationic surface-active agent is dissolved in the asphalt. The agent is strongly adsorbed at the stone surface and the contact angle is increased, as well as the interfacial tension between binder and water being reduced, so that spreading of the binder against the water is able to take place.

A more practical approach to explain the adhesion phenomenon seems to be that using the principle of polarity. Asphalts are generally rather weakly polarized. In other words, mineral aggregates, particularly those formed from freshly broken stones, ordinarily exhibit some degree of polarity. This tendency depends upon the chemical and mineralogical structure of the material, upon its surface condition, and upon other factors of its physical condition (Monismith, 1961).

Therefore, since water molecules are all dipoles and are thus very active electrically, it is clear why water presents such a problem to the paving technologists with respect to stripping failures. Two situations may exist:

1. If an aggregate particle is already coated with water, it is impossible for the normal asphalt cement to displace the water and bond the aggregate particles.

2. If the particle should be coated with an asphalt, it is still possible for the water to later strip the bitumen from the aggregate.

In some cases, however, an aggregate-asphalt combination may exhibit polar tendencies which are considerably stronger than the polar action of the same aggregate with water. In such a case, the asphalt would displace water on the surface of the stone and little stripping action might be expected. Also, the polar tendencies of some asphalt materials tend to increase with age, due to orientation of polar materials within the main body of the asphalt. As a result, a certain mixture might happen to be weakly water-resistant shortly after its preparation, but would later have satisfactorily adhesion as polar orientation proceeded.

As a conclusion, it would appear that all three concepts are necessary to explain the behavior of asphalt and aggregate in the presence of water because chemical reactions may take place, mechanical interlock occurs, and surface energy relationships influence adhesion.

5.5 Specifications

Tables 5.1 through 5.6 present the asphalt cement specifications as provided by the Asphalt Institute (1979). Table 5.1 provides the standard specification for penetration graded asphalt cements. In 1957, a Highway Research Board committee recommended the development of a more fundamental means of measuring the consistency of asphalt cements, as a replacement for the empirical penetration test. In 1971, the American

Association of State Highway Officials (AASHO) adopted the specifications shown in Tables 5.2 through 5.4 for five viscosity grades of asphalt cements. It should be noted that Table 5.2 should be used if not otherwise specified. Tables 5.5 and 5.6 present the asphalt cement specifications according to the American Society for Testing and Materials, ASTM.

Standard Specification for
Penetration Graded Asphalt Cement

1. SCOPE

AASHTO DESIGNATION: M 20-70

1.1 This specification covers the following 5 penetration grades of asphalt cement for use in highway construction: 40 to 50, 60 to 70, 85 to 100, 120 to 150, and 200 to 300. For asphalt cements graded by viscosity see AASHTO M 226.

2. MANUFACTURE

2.1 Asphalt cement shall be prepared by the refining of crude petroleum by suitable methods.

3. PROPERTIES

3.1 The asphalt cement shall be homogeneous, free from water, and shall not foam when heated to 175C (347F).

3.2 The various grades of asphalt cement shall conform to the requirements given in Table 1.

4. METHODS OF SAMPLING AND TESTING

4.1 Sampling and testing of asphalt cement shall be in accordance with the following standard methods of the American Association of State Highway and Transportation Officials:

Sampling	T 40
Water	T 55
Penetration	T 49
Solubility in Trichloroethylene	T 44
Ductility	T 51
Flash point	T 48
Thin film oven test	T 179
Spot Test	T 102

Requirements for a Specification for Asphalt Cement
AASHTO M 20

	Penetration Grade									
	40-50		60-70		85-100		120-150		200-300	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Penetration at 25C (77F) 100 g, 5 sec	40	50	60	70	85	100	120	150	200	300
Flash point, Cleveland Open Cup	450	...	450	...	450	...	425	...	350	...
Ductility at 25C (77F) 5 cm. per min., cm	100	...	100	...	100	...	100	...	...	...
Solubility in trichloroethylene percent	99	...	99	...	99	...	99	...	99	...
Thin-film oven test, 1/8 in. (3.2 mm), 163C (325F) 5 hour										
Loss on heating, percent	...	0.8	...	0.8	...	1.0	...	1.3	...	1.5
Penetration, of residue, percent of original	58	...	54	...	50	...	46	...	40	...
Ductility of residue at 25C (77F) 5 cm. per min., cm	...	...	50	...	75	...	100	...	100	...
Spot test (when and as specified (see Note 1) with):										
Standard naphtha solvent	Negative for all grades									
Naphtha-xylene solvent, percent xylene	Negative for all grades									
Heptane-xylene solvent, percent xylene	Negative for all grades									

NOTE: The use of the spot test is optional. When it is specified, the Engineer shall indicate whether the standard naphtha solvent, the naphtha-xylene solvent, or the heptane-xylene solvent will be used in determining compliance with the requirement, and also, in the case of the xylene solvents, the percentage of xylene to be used.

Table 5.1 AASHTO Specification for asphalt cements

(Grading based on original asphalt)

TEST	VISCOSITY GRADE				
	AC-2.5	AC-5	AC-10	AC-20	AC-40
Viscosity, 60 C (140 F), poises	250 ± 50	500 ± 100	1000 ± 200	2000 ± 400	4000 ± 800
Viscosity, 135 C (275 F), Cs-minimum	80	110	150	210	300
Penetration, 25 C (77 F), 100 g., 5 sec.-minimum	200	120	70	40	20
Flash Point, COC, C (F)-minimum	163(325)	177(350)	219(425)	232(450)	232(450)
Solubility in trichloroethylene, percent-minimum	99.0	99.0	99.0	99.0	99.0
Tests on residue from Thin-Film Oven Test:					
Viscosity, 60 C (140 F), poisees-maximum	1000	2000	4000	8000	16000
Ductility, 25 C (77 F), 5 cm per minute cm-minimum	100 [1]	100	50	20	10
Spot test (when and as specified)[2] with:					
Standard naphtha solvent	Negative for all grades				
Naphtha-Xylene-solvent, % Xylene	Negative for all grades				
Heptane-Xylene-solvent, % Xylene	Negative for all grades				

[1] If ductility is less than 100, material will be accepted if ductility at 15.6 C (60 F) is 100 minimum.

[2] The use of the spot test is optional. When it is specified, the Engineer shall indicate whether the standard naphtha solvent, the naphtha-xylene solvent or the heptane-xylene solvent will be used in determining compliance with the requirement, and also, in the case of xylene solvents, the percentage of xylene to be used.

Table 5.2 AASHTO specification for asphalt cement graded by vicosity at 60°C (140°F)

(Grading based on original asphalt)

TEST	VISCOSITY GRADE				
	AC-2.5	AC-5	AC-10	AC 20	AC-40
Viscosity, 60 C (140 F), poises	250 ± 50	500 ± 100	1000 ± 200	2000 ± 400	4000 ± 800
Viscosity, 135 C (275 F), Cs-minimum	125	175	250	300	400
Penetration, 25 C (77 F), 100 g, 5 sec.-minimum	220	140	80	60	40
Flash Point, COC, C (F)-minimum	163(325)	177(350)	219(425)	232(450)	232(450)
Solubility in trichloroethylene, percent-minimum	99.0	99.0	99.0	99.0	99.0
Tests on residue from Thin-Film Oven Test:					
Loss on heating, percent-maximum (optional)[3]		1.0	0.5	0.5	0.5
Viscosity, 60 C (140 F), poises-maximum	1000	2000	4000	8000	16000
Ductility 25 C (77 F), 5 cm per minute, cm-minimum	100 [1]	100	75	50	25
Spot test (when and as specified)[2] with:					
Standard naphtha solvent	Negative for all grades				
Naphtha-Xylene-solvent, % Xylene	Negative for all grades				
Heptane-Xylene-solvent, % Xylene	Negative for all grades				

[1] If ductility is less than 100, material will be accepted if ductility at 15.6C (60 F) is 100 minimum.

[2] The use of the spot test is optional. When it is specified, the Engineer shall indicate whether the standard naphtha solvent, the naphtha-xylene solvent, or the heptane-xylene solvent will be used in determining compliance with the requirement, and also, in the case of xylene solvent, the percentage of xylene to be used.

[3] The use of loss on heating requirement is optional.

Table 5.3 AASHTO Specifications for asphalt cement graded by vicosity at 60°C (140°F)

(Grading based on residue from Rolling Thin Film Oven Test)

TESTS ON RESIDUE FROM AASHTO TEST METHOD T 240[1]	VISCOSITY GRADE				
	AR-10	AR-20	AR-40	AR-80	AR-160
Viscosity, 60 C (140 F), poise	1000 ± 250	2000 ± 500	4000 ± 1000	8000 ± 2000	16000 ± 4000
Viscosity, 135 C (275 F), Cs-minimum	140	200	275	400	550
Penetration, 25 C (77 F), 100 g, 5 sec.-minimum	65	40	25	20	20
Percent of original Pen., 25 C (77 F)-minimum	—	40	45	50	52
Ductility, 25 C (77 F), 5 cm per min., cm minimum	100[2]	100[2]	75	75	75
TESTS ON ORIGINAL ASPHALT					
Flash Point, COC, C (F)-minimum	205 (400)	219 (425)	227 (440)	232 (450)	238 (460)
Solubility in Trichloroethylene, percent-minimum	99.0	99.0	99.0	99.0	99.0

[1] AASHTO T 179 (Thin-Film Oven Test) may be used, but AASHTO T 240 shall be the referee method.
[2] If ductility is less than 100, material will be accepted if ductility at 15.6 C (60 F) is 100 minimum.

Table 5.4 AASHTO specifications for asphalt cement graded by viscosity at 60°C (140°F)

	Penetration Grade									
	40-50		60-70		85-100		120-150		200-300	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Penetration at 77°F (25°C) 100 g, 5 s	40	50	60	70	85	100		150	200	300
Flash point, °F (Cleveland open cup)	450	...	450	...	450	...		...	350	...
Ductility at 77°F (25°C) 5 cm/min, cm	100	...	100	...	100	...	100	...	100	...
Retained penetration after thin-film oven test, %	55+	...	52+	...	47+	...	42+	...	37+	...
Ductility at 77°F (25°C) 5 cm min, cm after thin-film oven test	...	...	50	...	75	...	100	...	100	...
Solubility in trichloroethylene, %	99.0	...	99.0	...	99.0	...	99.0	...	99.0	...

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Table 5.5 ASTM specifications for asphalt cement for use in pavement construction

NOTE—Grading based on original asphalt.

Test	Viscosity Grade				
	AC-2.5	AC-5	AC-10	AC-20	AC-40
Viscosity, 140°F (60°C), P	250 ± 50	500 ± 100	1000 ± 200	2000 ± 400	4000 ± 800
Viscosity, 275°F (135°C), min, cSt	80	110	150	210	300
Penetration, 77°F (25°C), 100 g, 5 s, min	200	120	70	40	20
Flash point, Cleveland open cup, min, °F (°C)	325 (163)	350 (177)	425 (219)	450 (232)	450 (232)
Solubility in trichloroethylene, min, %	99.0	99.0	99.0	99.0	99.0
Tests on residue from thin-film oven test:					
Viscosity, 140°F (60°C), max, P	1250	2500	5000	10,000	20,000
Ductility, 77°F (25°C), 5 cm/min, min, cm	100[a]	100	50	20	10

[a] If ductility is less than 100, material will be accepted if ductility at 60°F (15.5°C) is 100 minimum at a rate of 5 cm/min.

NOTE—Grading based on original asphalt.

Test	Viscosity Grade				
	AC-2.5	AC-5	AC-10	AC-20	AC-40
Viscosity, 140°F (60°C), P	250 ± 50	500 ± 100	1000 ± 200	2000 ± 400	4000 ± 800
Viscosity, 275°F (135°C), min, cSt	125	175	250	300	400
Penetration, 77°F (25°C), 100 g, 5 s, min	220	140	80	60	40
Flash point, Cleveland open cup, min, °F (°C)	325 (163)	350 (177)	425 (219)	450 (232)	450 (232)
Solubility in trichloroethylene, min, %	99.0	99.0	99.0	99.0	99.0
Tests on residue from thin-film oven test:					
Viscosity, 140°F (60°C), max, P	1250	2500	5000	10,000	20,000
Ductility 77°F (25°C), 5 cm/min, min, cm	100[a]	100	75	50	25

[a] If ductility is less than 100, material will be accepted if ductility at 60°F (15.5°C) is 100 minimum at a rate of 5 cm/min.

NOTE—Grading based on residue from rolling thin-film oven test.

Tests on Residue from Rolling Thin-Film Oven Test:[a]	Viscosity Grade				
	AR-1000	AR-2000	AR-4000	AR-8000	AR-16000
Viscosity, 140°F (60°C), P	1000 ± 250	2000 ± 500	4000 ± 1000	8000 ± 2000	16000 ± 4000
Viscosity, 275°F (135°C), min, cSt	140	200	275	400	550
Penetration, 77°F (25°C), 100 g, 5 s, min	65	40	25	20	20
% of original penetration, 77°F (25°C), min	...	40	45	50	52
Ductility, 77°F (25°C), 5 cm/min, min, cm	100[b]	100[b]	75	75	75
Tests on original asphalt:					
Flash Point, Cleveland Open Cup, min, °F(°C)	400 (205)	425 (219)	440 (227)	450 (232)	460 (238)
Solubility in trichloroethylene, min, %	99.0	99.0	99.0	99.0	99.0

[a] Thin-film oven test may be used but the rolling thin-film oven test shall be the referee method.
[b] If ductility is less than 100, material will be accepted if ductility at 60°F (15.5°C) is 100 minimum at a rate of 5 cm/min.

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Table 5.6 ASTM specifications for asphalt cement, vicosity graded at 140°F (60°C)

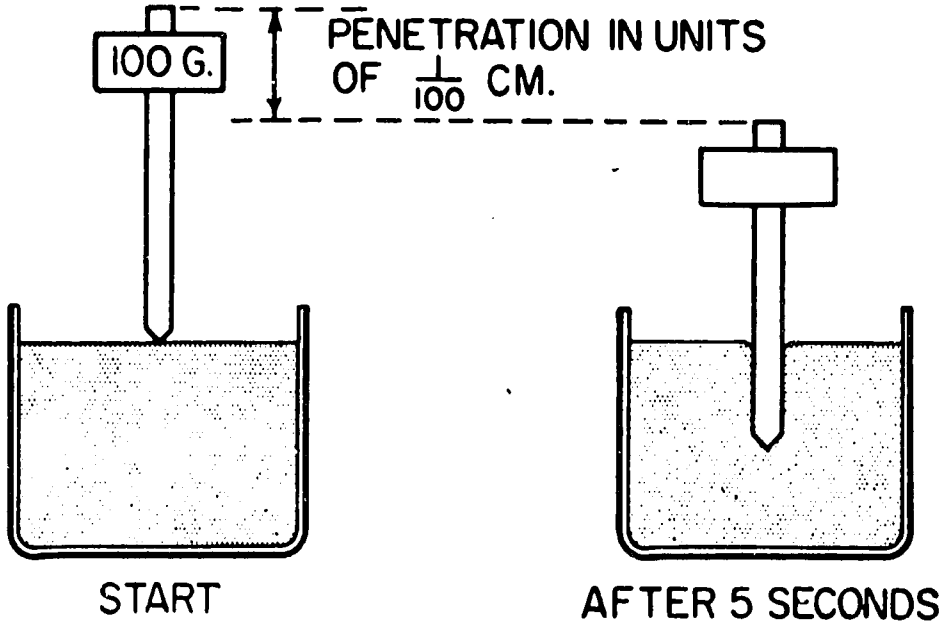


Fig. 5.1 Penetration test (from Wallace and Martin, 1967)

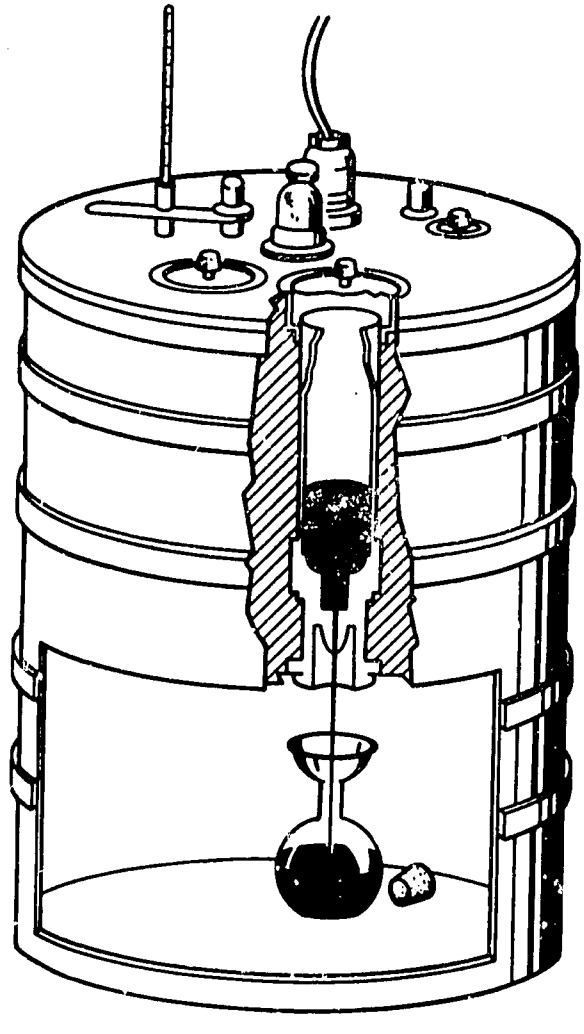


Fig. 5.2 Furol viscosity test (from Wallace and Martin, 1967)

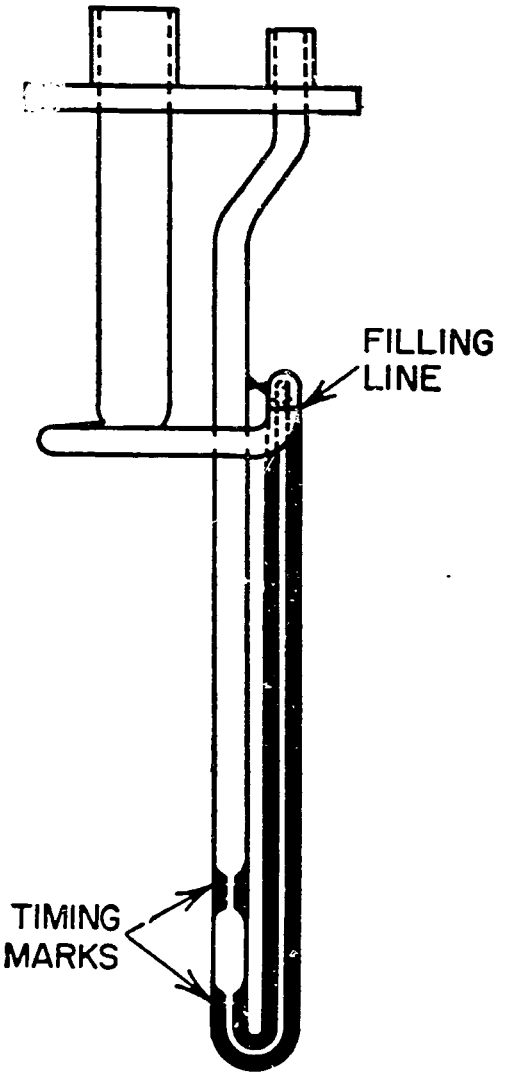


Fig. 5.3 Zeitfuchs cross-arm viscometer (from Wallace and Martin, 1967)

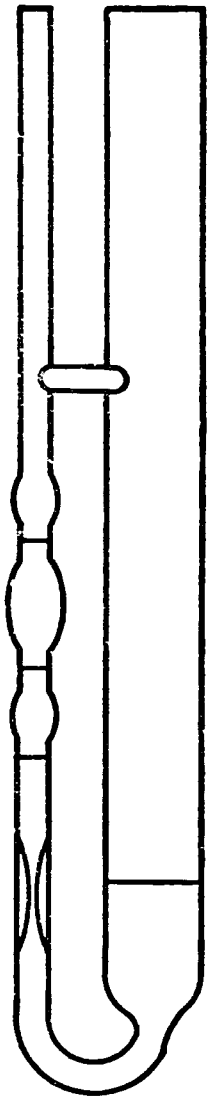


Fig. 5.4 Cannon-Manning vacuum viscometer designed for viscosity measurements of asphalt (from Wallace and Martin, 1967)

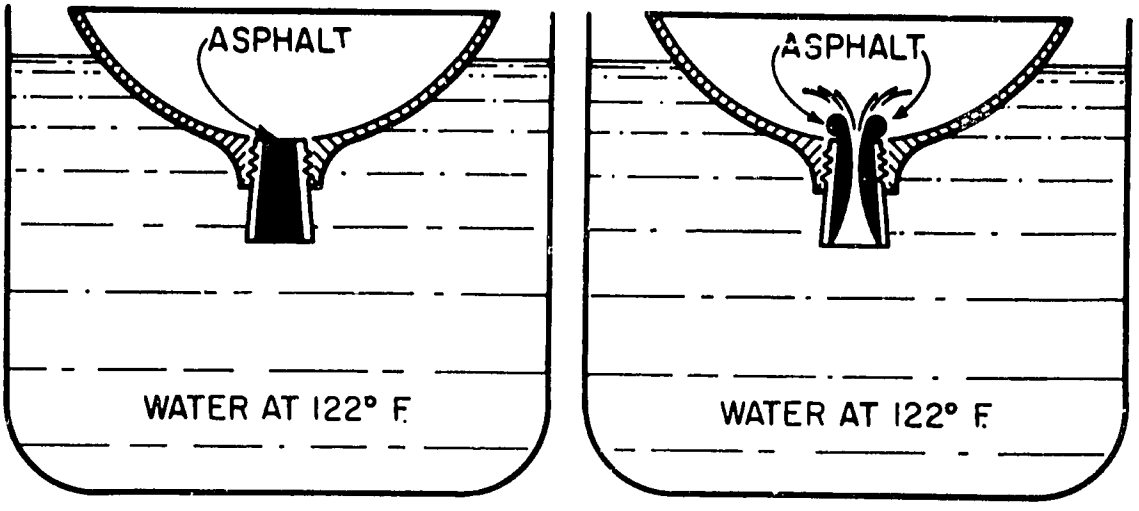


Fig. 5.5 Float test (from Wallace and Martin, 1967)

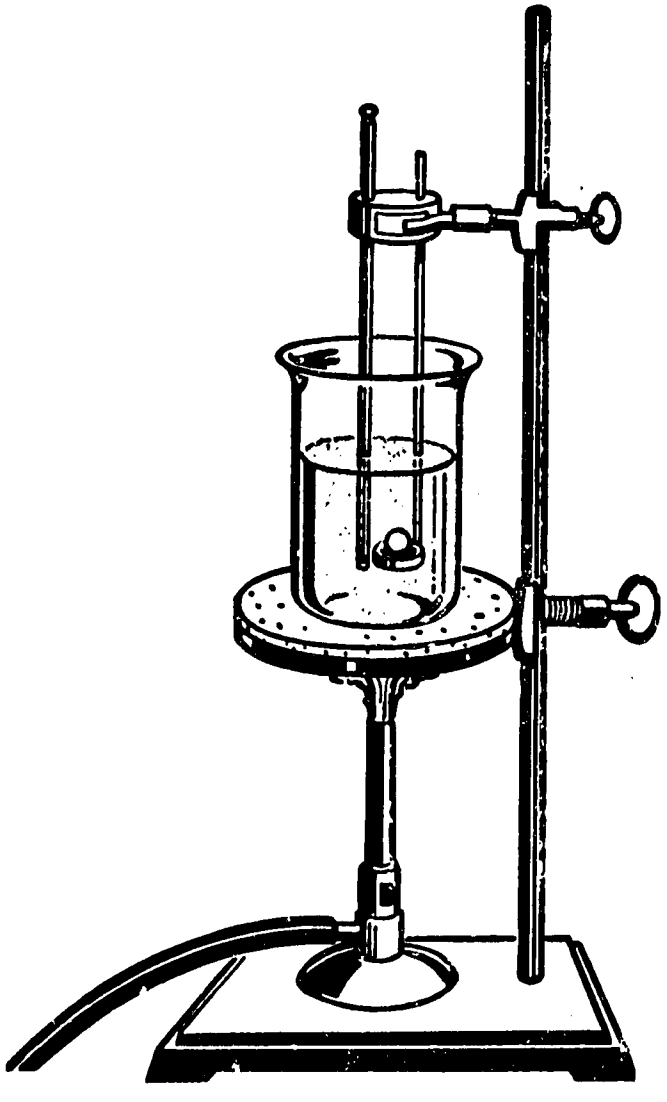


Fig. 5.6 Softening-point test (from Wallace and Martin, 1967)

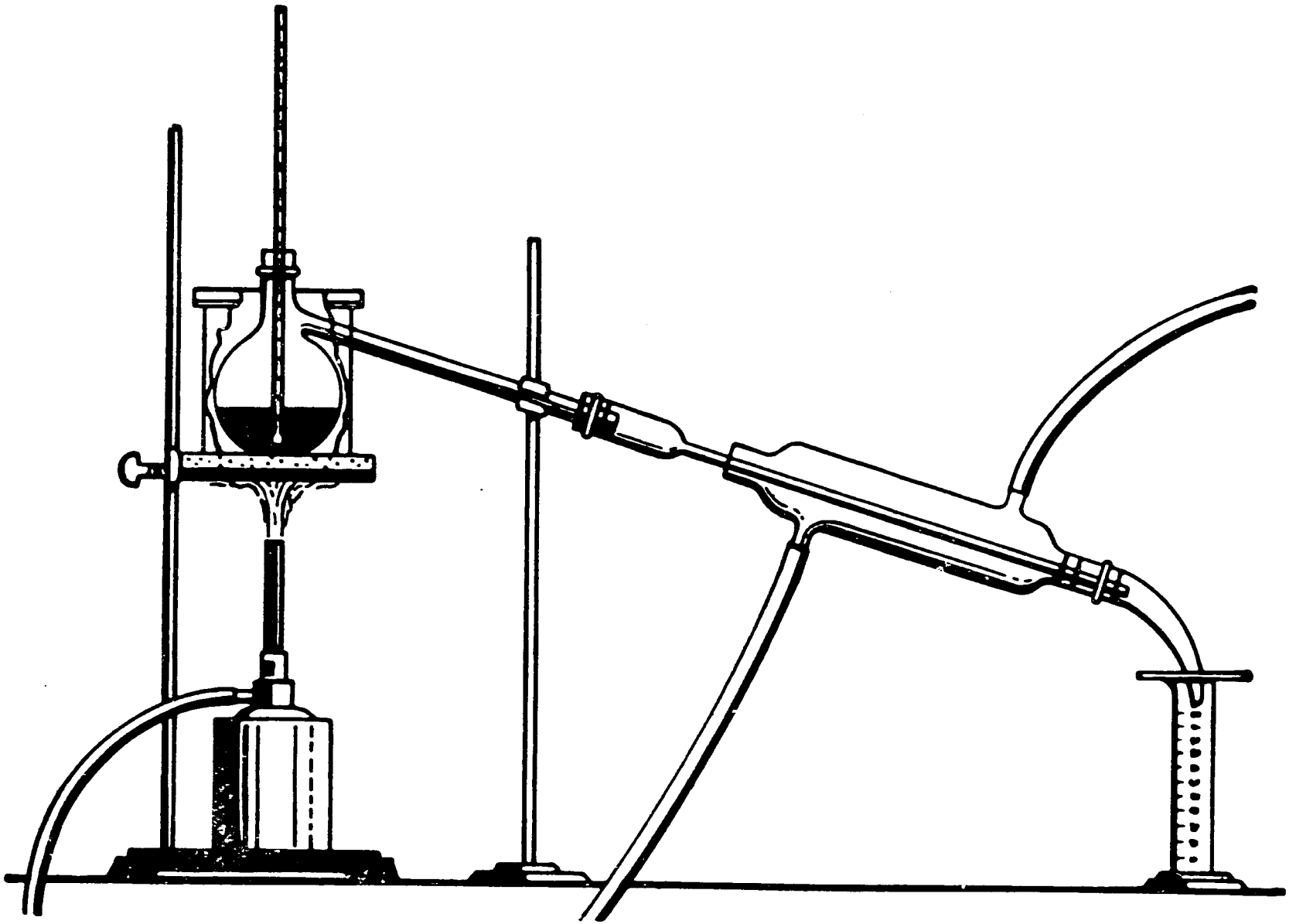


Fig. 5.7 Distillation test (from Wallace and Martin, 1967)

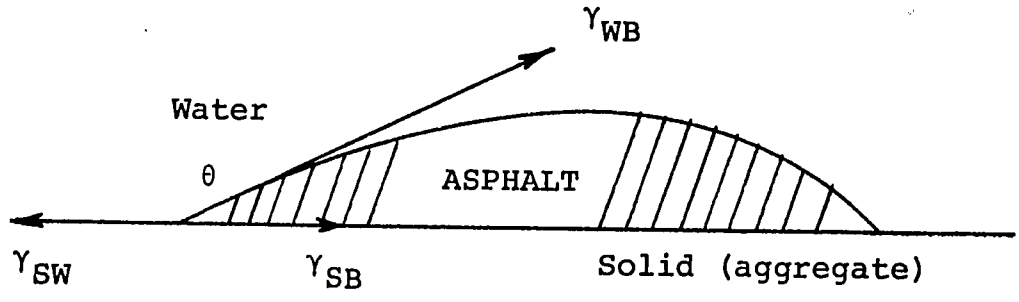


Figure 5.8 Contact angle in an aggregate, asphalt and water system (Monosmith, 1961)

CHAPTER 6

RHEOLOGICAL CHARACTERISTICS OF ASPHALTIC MATERIALS

6.1 Introduction

Asphalts, like many other materials, are rheological materials; that is, their deformation characteristics are time dependent. In addition, asphalt is a thermoplastic material since its consistency varies with temperature. This behavior under load and the effects of time and temperature are important when considering the use of asphalts in pavement construction.

Asphalts are neither purely elastic nor purely viscous in behavior. When they are loaded extremely rapidly, they exhibit elastic behavior, and when they are loaded very slowly, viscous behavior. For an intermediate range of loading rates, they exhibit a combination of elastic and viscous behavior and may be referred to as viscoelastic materials. Several models, such as the Kelvin, Maxwell, Burgers, and Voigt models (Jongepier and Kuilman, 1969; Monismith, 1961), have been used to describe the response of such materials. These models are based on representing the elastic behavior by a spring and the viscous behavior by a dashpot, and by combining the spring and dashpot in various configurations, representation of the time dependent behavior can be obtained. However, these models are sometimes very complicated and engineers have often found that they, even the simple ones, do not adequately represent the actual behavior of asphalt cements.

Various investigations have pointed out that the behavior of asphalt cements can be satisfactorily represented by means of the stiffness concept (Heukelom and Klomp, 1964; Van der Poel, 1954). The stiffness modulus is an extension of Young's modulus of elasticity for a purely elastic solid, but specifies the time of loading and temperature and, thereby, recognizes the visco-elastic nature of the material.

The stiffness modulus of a bituminous material can be measured experimentally over a wide range in load conditions from creep behavior to dynamic loading. In addition, there are different ways to indirectly backfigure the stiffness moduli using charts and/or monographs correlating routine test data and stiffness values (Heukelom, 1969; Mcleod, 1969; Van der Poel, 1954).

6.2 Effects of Rate of Loading

Asphalts are materials whose stress-strain characteristics are time dependent. For relatively slow rates of loading, a number of asphalts behave as viscous materials and are Newtonian in behavior. Other asphalts, under the same loading conditions, are non-Newtonian in behavior.

The deviation from the Newtonian behavior is a function of how well the asphaltenes are dissolved in the oil-resin phase. If there are either a small proportion of asphaltenes or the asphaltenes are well dissolved in the oil-resin phase, asphalts will exhibit Newtonian behavior at low rates of shear. As the asphaltenes become less well dissolved, e.g., increase in amount

through air blowing, they tend to act in clusters. At low shear rates, the effect of this action is to give relatively higher shear stresses and high viscosities. As the shear rate increases, however, the tendency is to reduce the effect of the agglomeration and thus lower the viscosity of the material.

As the rate of loading increases, all asphalts become more elastic in behavior. At very rapid rates, the materials may be almost completely elastic. Saal and Labout (1950) have suggested three groupings for asphalts based on their behavior under load. Essentially, these groupings are based on how well the asphaltenes are dissolved in the oil-resin phase.

The first group, called the "sol type" materials, are those in which the asphaltenes are well dissolved. At very rapid rates of loading, the material would behave elastically; at very slow rates, the material would behave as a Newtonian material.

The second classification would be for the asphalts of the "elastic sol type" which exhibits ideal elasticity, retarded elasticity, and viscous flow. The third classification, "gel asphalts," would apply to the air-blown materials. These materials exhibit no permanent deformation under low stress. As was pointed out previously, the asphaltenes in these materials are poorly dissolved and therefore tend to agglomerate and introduce a structure to the material which would tend to explain this type of behavior.

In general, asphalts display different characteristics under load, depending upon the load rate and the chemical composition of the material.

6.3 Effects of Time

Asphalts may increase in viscosity with time when allowed to remain in an unloaded condition. The change is termed thixotropy. In the case of air-blown asphalts, where the increase in viscosity is quite marked, and where the asphaltenes are poorly dissolved in the oil-resin phase, a structure will gradually develop with time which results in an increase in viscosity. Either large shearing deformations or heat will tend to destroy this structure and the asphalt will again exhibit the same initial viscosity. From this we could infer that Newtonian materials should exhibit little thixotropy and that, as the material deviates from Newtonian behavior, the tendency toward thixotropic change will increase.

6.4 Effects of Temperature

Asphalt is a thermoplastic material, i.e., the material changes its consistency with changes in temperature. As was noted in Chapter 5, the variation in consistency with temperature is important in order to carry out proper road design and construction.

A number of techniques are available for defining the temperature-viscosity relationships of asphalts. Three will be cited in this discussion.

The first is the penetration ratio (pen. ratio). This technique consists of determining the consistency of an asphalt cement at 77°F and 39.2°F by the standard penetration test (see Chapter 5 for a description of the test). The pen. ratio is then calculated from the relationship:

$$\text{pen. ratio} = \frac{\text{pen. @ 39.2°F}}{\text{pen. @ 77°F}} \times 100 \qquad (6.1)$$

By setting a minimum value for this ratio, an attempt is made to control the change in viscosity with change in temperature (temperature susceptibility) and to preclude excessive hardening of asphalt in the low temperature range. The pen. ratios for three different 85-100 penetration asphalt cements are shown in Fig. 6.1. In this figure, it will be noted that the material with the highest pen. ratio shows the least change in viscosity with change in temperature.

A second technique is to specify the slope of the temperature vs. viscosity relationship for asphalts when the viscosity is plotted in absolute units (e.g., poises). Two relationships have been suggested and both are merely attempts to define straight-line relationships between temperature and viscosity.

The first of these is the Walther formula which states:

$$\log \log[\text{viscosity} + \text{constant}] = \qquad (6.2)$$
$$\log \text{absolute temperature (°Kelvin)} + \text{constant...}$$

When comparing viscosities of asphalts at a given temperature, it is necessary to select a specific shear rate. The

viscosities of non-Newtonian asphalts are a function of shear rate and therefore, for a comparison, the same shear rate must be used. As with the penetration ratio comparison, sample B (the air-blown material) shows the least change in viscosity with change in temperature (Fig. 6.1).

The second relationship based on absolute units is the Waterman formula:

$$\log \text{viscosity} = \frac{\text{constant}}{(\text{absolute temperature})^x} + \text{constant} \qquad (6.3)$$

where the exponent, x, has a value of 3.5 to 4 for most asphalts. In both cases the comparison of temperature susceptibility would be made on the basis of the numerical value of the slope of the line. The steeper the slope, the more temperature susceptible the material.

The third technique for measuring the temperature susceptibility of asphalts is also based on the measurement of consistency at two temperatures. In this case, the measurements are the penetration at 77°F and the ring-and-ball softening point temperature (see Chapter 5 for details). From these two measurements, Shell researchers (Pfiffer and Van Doormal, 1936) have developed a simple measure of temperature susceptibility called the <u>penetration index</u> (P.I.). The chart from which the P.I. can be determined is shown in Fig. 6.2.

It has been found that the penetration index is not so much a measure of the temperature susceptibility of viscosity for

bitumens, but rather gives a measure of their deviation from Newtonian behavior. Bitumens normally used for road construction have a P.I. between -2 and +2. Bitumens with a P.I. below -2 are substantially Newtonian and usually characterized by brittleness at low temperatures. Coal tar pitches also fall within this group. Bitumens with an index greater than 2 are usually less brittle, show marked time dependent elastic properties and have a non-Newtonian behavior at large strains. Air-blown asphalts usually fall within this group.

Of these three methods, the second has the apparent advantage that the viscosity of the asphalt is expressed in the same units at all temperatures and thus permits a comparison in one set of units.

As has been noted, the air-blown asphalts are least temperature susceptible. Generally speaking, the greater the proportion of asphaltenes and the less well these are dissolved in the oil-resin phase, the less temperature susceptible the material.

6.5 Asphalt Stiffness Modulus

Van der Poel (1954) has developed a simplified procedure to describe the viscoelastic behavior of asphalts. Recognizing the linearity between stress and strain for small deformations for a range of loading times, he has developed a relationship between stress and strain called the stiffness modulus.

The stiffness modulus can be determined over a range in loading conditions from creep behavior to dynamic loading. Thus

it is possible to characterize the stiffness of an asphalt over a wide time scale. At very short loading times, dynamic application, the stiffness value would approach the modulus of elasticity. By this technique, it is also possible to include the effects of temperature.

To simplify the determination of the stiffness modulus, a nomograph has been prepared (Fig. 6.3) from which the stiffness of the asphalt at a given temperature, time of loading, and stress can be determined using only the results of the penetration and ring-and-ball softening point tests. From the penetration value and the softening point temperature, the penetration index, P.I., for the asphalt can be obtained. The P.I. together with the time of loading and softening-point temperature minus test temperature are used to estimate the stiffness modulus using the nomograph.

It has to be emphasized, however, that this nomograph cannot be used to predict the behavior of very waxy bitumens. It is known that, especially for soft bitumens, the ring-and-ball temperature is greatly influenced by the presence of paraffin wax. The nomograph was developed using bitumens which contained a maximum wax content of 2% (specification D.I.N. 1999).

Heukelom in his work (1969 and 1973) developed a "bitumen test data chart" (BTDC) for analyzing the effect of temperature on the mechanical behavior of asphaltic bitumens. The presented test data chart (Fig. 6.4) can be used for distinguishing

between different types of bitumen, especially those containing high wax content and blown asphalts.

In addition, Heukelom's "BTDC" could be used for appraising the data used for entering Van der Poel's stiffness nomograph. Through this appraisal, the stiffness nomograph range of application can be extended to cover different types of asphalts.

Heukelom suggested a modification of the Van der Poel method for estimating the stiffness modulus of asphalt cements. His modification can be summarized as follows:

1. Plot the viscosity and penetration values on the "Bitumen Test Data Chart."

2. A "corrected ring-and-ball softening point, T_N, can be found by extended the penetration branch or the viscosity branch, depending upon the temperature region in which one is interested (see Fig. 6.4).

3. The Pfiffer and Van Doormaal P.I. is then replaced by Q, which can be calculated as follows:

$$Q = 20 \cdot \frac{T_{2p}-T_N-111}{T_{2p}-T_N+222} \qquad (6.4)$$

where T_{2p} = temperature at which the viscosity is equal to 2.0 poises; this temperature can be determined from the Bitumen Test Data Chart

T_N = corrected softening point

4. Use the Van der Poel nomograph to estimate the stiffness modulus for the particular time of loading and temperature.

Mcleod (1967) developed another method for estimating the stiffness modulus of asphalt cements. This method is based on the relationship between asphalt viscosity at 275°F (or at 140°F) and its penetration at 77°F. Mcleod believed that this relationship provided a very reasonable basis for expressing differences in temperature susceptibility of asphalt cements. He demonstrated that for asphalt cements of the same penetration at 77°F, there were remarkable differences in their viscosities at 275°F. As this approach for evaluating asphalt temperature susceptibility was different from those employed by Van der Poel and Heukelom, Mcleod used the term "Penetration-Viscosity Number," PVN.

Mcleod's method for estimating the stiffness modulus of an asphalt cement may be summarized as follows:

1. The penetration-viscosity number, PVN, can be estimated from Fig. 6.5 using the following equation:

$$PVN = \frac{\log L - \log x}{\log L - \log M} \cdot (-1.5) \qquad (6.5)$$

where x = viscosity in centistokes at 275°F for the asphalt cement for which PVN is to be determined

L = viscosity in centistokes at 275°F for a PVN of 0.0, determined from Fig. 6.5 for the penetration at 77°F of the given asphalt cement

M = viscosity in centistokes at 275°F for PVN of -1.5, determined from Fig. 6.5 for the penetration at 77°F of the given asphalt cement

2. The ring-and-ball softening point temperature ($T_{R\&B}$) is called the "base temperature" by Mcleod and is determined from the nomograph shown in Fig. 6.6 rather than by actual testing.

3. The modulus of stiffness of the asphalt is then determined using Mcleod's modification of Heukelom and Klomp's nomograph (1964) as shown in Fig. 6.7.

6.6 Rehologic Behavior of Asphalt Concrete Mixes

A number of experimental methods have been developed to describe the relationship between stress and strain for asphalt mixes. Two of these methods, the dynamic complex modulus and the modulus of resilient deformation, are similar. The concept and definition of the dynamic complex modulus for asphalt concrete have been presented by Papazian (1962). Seed et al. (1962) developed the background and the concept of the modulus of resilient deformation. In both tests, vertical stresses are applied to a specimen and the resultant vertical strains measured. A modulus is calculated as the ratio of stress to the recoverable or resilient strain under repeated loading conditions. By the complex modulus test procedure, in-elastic as well as elastic behavior may be measured.

The stiffness modulus is another concept for describing the relationship between stress and strain for asphalt mixes. Deacon (1965) presented the stiffness concept and calculated

it from repeated beam flexture tests by measuring the beam's central deflection. Deacon measured the total deflection (recoverable and permanent), from which he computed the stiffness modulus. It is expected, therefore, that the stiffness modulus would differ from both the modulus of resilient deformation and the complex modulus.

The tests discussed above are expensive, complicated and, therefore, may not be available for different pavement design agencies. For this reason, and in order to effectively evaluate the modulus or strength properties of the paving materials, researchers have often attempted to correlate these properties to some standard or conventional tests. Some of these attempts showed some degree of correlation with a wide scatter. This scatter is expected and is due to either the inconsistency of the properties of the specimen tested or the experimental inaccuracies associated with the conventional tests. It should be recognized that these correlations should be used only when actual test data are not available.

The following brief discussion of some of these approaches at least indicates that there is some potential for such correlations.

Nijboer (1957) has suggested a method for estimating the asphalt mixture stiffness as correlated to the ratio of the Marshall stability and the Marshall flow value. Nijboer's formula was limited to a loading time of four seconds at high

service temperatures (60°C). McLeod (1967) also developed a similar procedure and suggested that the stiffness-Marshall correlation was valid for a range of mixtures.

Shook and Kallas (1969) investigated the relationship between the flexural modulus and several routine or standard tests including the Marshall stability, Marshall flow value, Hveem stability, Hveem cohesiometer value, ultimate tensile strength, elongation in direct tension, and elongation in indirect tension or the split-tension test. Even though several corrections were made in regard to air-voids in the specimens, no practical degree of correlation was found between the resilient modulus and most of these other conventional test values. However, fairly good correlations were obtained using the results of the ultimate tensile strength of the Marshall stability/flow ratio as related to the resilient modulus.

Hadley, et al. (1970) investigated possible correlations between the stiffness or resilient modulus and Poisson's ratio determined for the indirect tension test at 75°F and a standard beam test at 140°F. They found reasonable correlations, for a general range of test conditions, between the modulus of elasticity and cohesiometer values, and between Poisson's ratio and stability.

One of the more useful as well as convenient methods for estimating resilient modulus of asphalt treated mixtures is

based on the stiffness concept of Van der Poel (1954). Van der Poel and later Heukelom and Klomp (1964) concluded in their studies that there is a relation between the modulus of the mix, S_{mix}, and the modulus of the binder, S_{bit}, irrespective of the combination of loading time and temperature underlying the value of S_{bit}.

Based on the stiffness modulus of the asphalt cement, the stiffness modulus of the asphalt concrete mixtures can be determined by the following relationship, which was first developed by Van der Poel and later modified by Heukelom and Klomp (1964):

$$S_{mix} = S_{bit} \left[1.0 + \left(\frac{2.5}{n}\right)\left(\frac{C_v}{1.0 - C_v}\right)\right]^n \qquad (6.6)$$

where

S_{mix} = stiffness of asphalt concrete mixtures, kg/cm^2.

S_{bit} = stiffness of asphalt cement, kg/cm^2.

$$n = 0.83 \log_{10} \frac{4 \times 10^5}{S_{bit}}$$

C_v = volume concentration of the aggregate in the mixture, defined as follows:

$$\frac{\text{Volume of compacted aggregate}}{\text{Volume of (asphalt + aggregate)}} = \frac{100 - \%\ \text{VMA}}{100 - \%\ \text{air voids}}$$

where

VMA = voids in mineral aggregate.

When dealing with asphalt concrete cores cut from a pavement or a compacted laboratory sample, the previous equation for C_v can be replaced by an equivalent equation as follows:

$$C_v = \frac{1}{1 + c} \tag{6.7}$$

where

$$c = \frac{W_s}{W_g} \quad \frac{G_g}{G_s} = \frac{\text{\% of asphalt by weight of aggregate}}{100.0} \left[\frac{G_g}{G_s}\right]$$

where

W_s = weight of asphalt

W_g = weight of aggregate

G_s = specific gravity of asphalt

G_g = specific gravity of aggregate

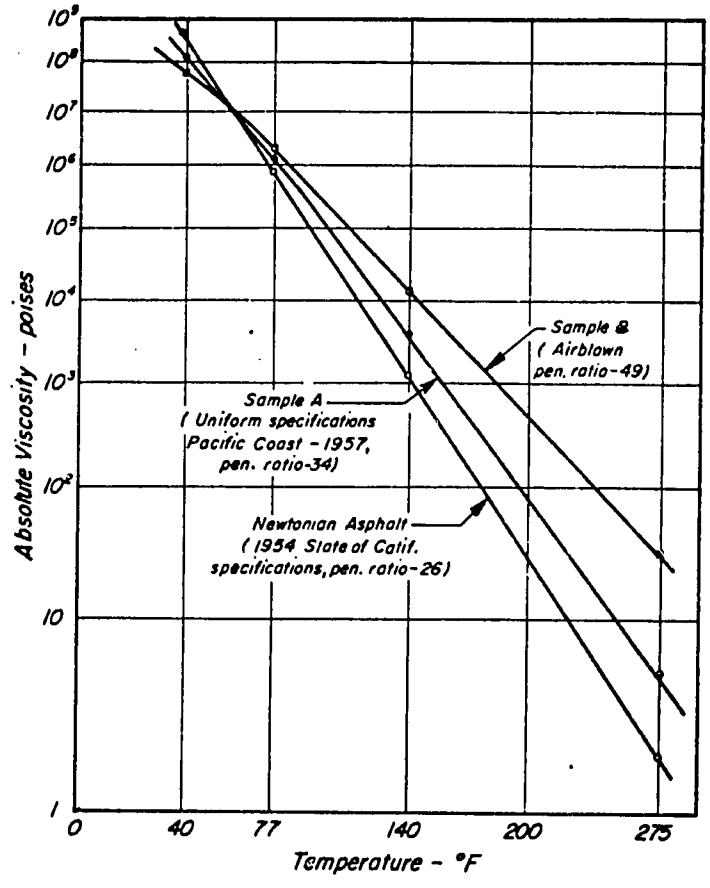
A chart for solving the equation of S_{mix}, for a range of C_v values from 0.6 to 0.94 is presented in Fig. 6.8. Heukelom and Klomp stated that the relation of S_{mix} is applicable to well-compacted mixtures with about 3 percent air voids and C_v values between about 0.7 and 0.9. For mixtures with air voids greater than 3.0 percent, Van Draat and Sommer (1966) derived a correction to be applied to the C_v value. The corrected C_v (C_v') is determined as follows:

$$C_v' = \frac{C_v}{1 + H} \tag{6.8}$$

where

H = actual percent air voids - 3.0% .

The nomograph suggested by Heukelom and Klomp seems to indicate a fairly good approach to predicting stiffness over a range of temperatures and times of loading, at least for a range of conventional mixes. However, there have been incidences where this nomograph fails to predict experimental data with any reasonable degree of certainty. There may be some asphalt cementing materials which do not follow the stiffness concepts originally developed by Van der Poel. These may be based on different viscosity relationships, sources of the asphalt, or other factors. Also, the low asphalt content as used in some of the leaner asphalt treated bases may cause the stiffness to deviate somewhat from that predicted by Heukelom and Klomp.



NOTE: Vicosity is measured at a shear rate of 5×10^{-2} sec^{-1}.

Figure 6.1 Temperature-vicosity relationship for asphalt cements (Monismith, 1961)

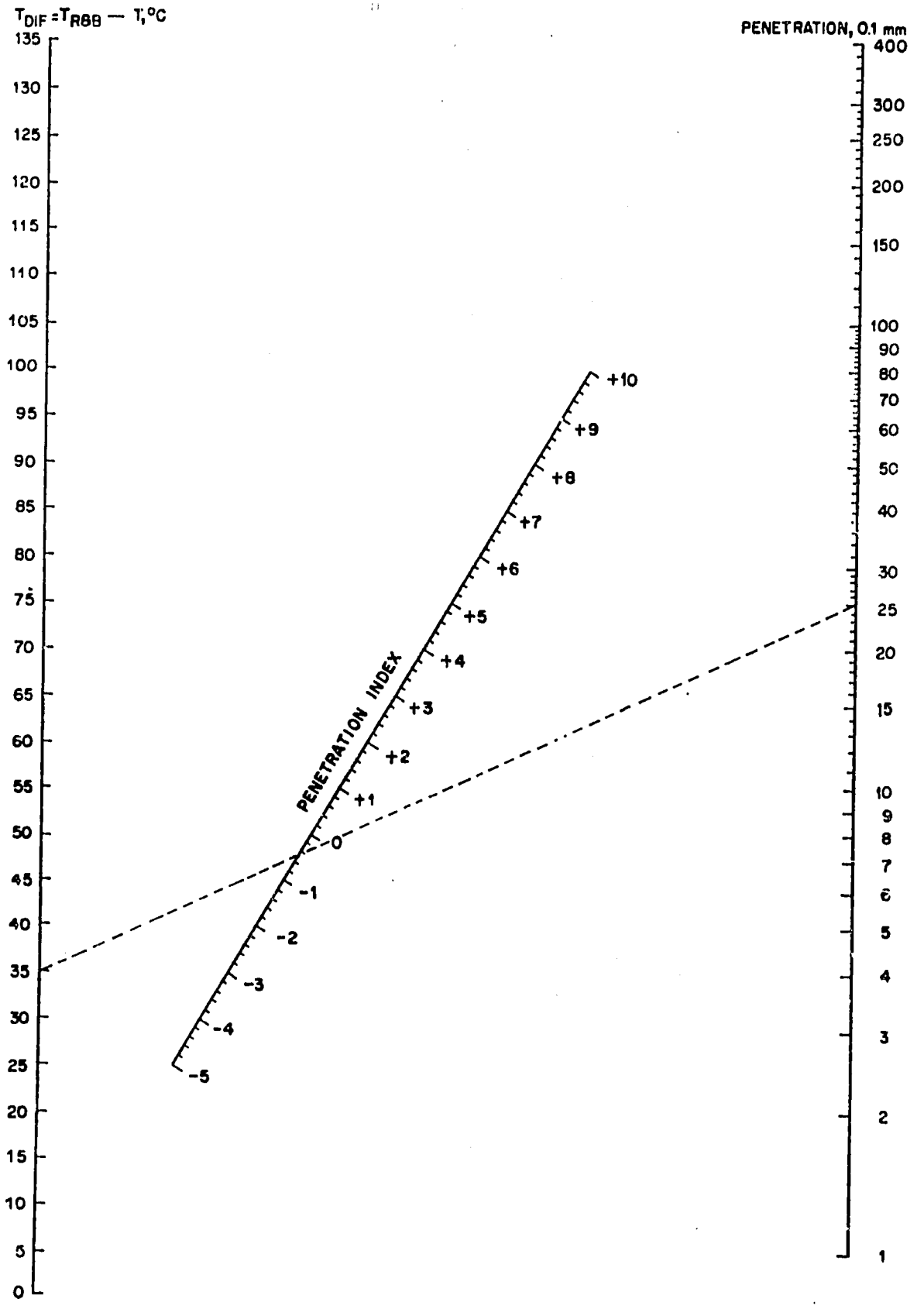


Figure 6.2 Nomograph for determining Pfeiffer and Van Doormial's Penetration Index

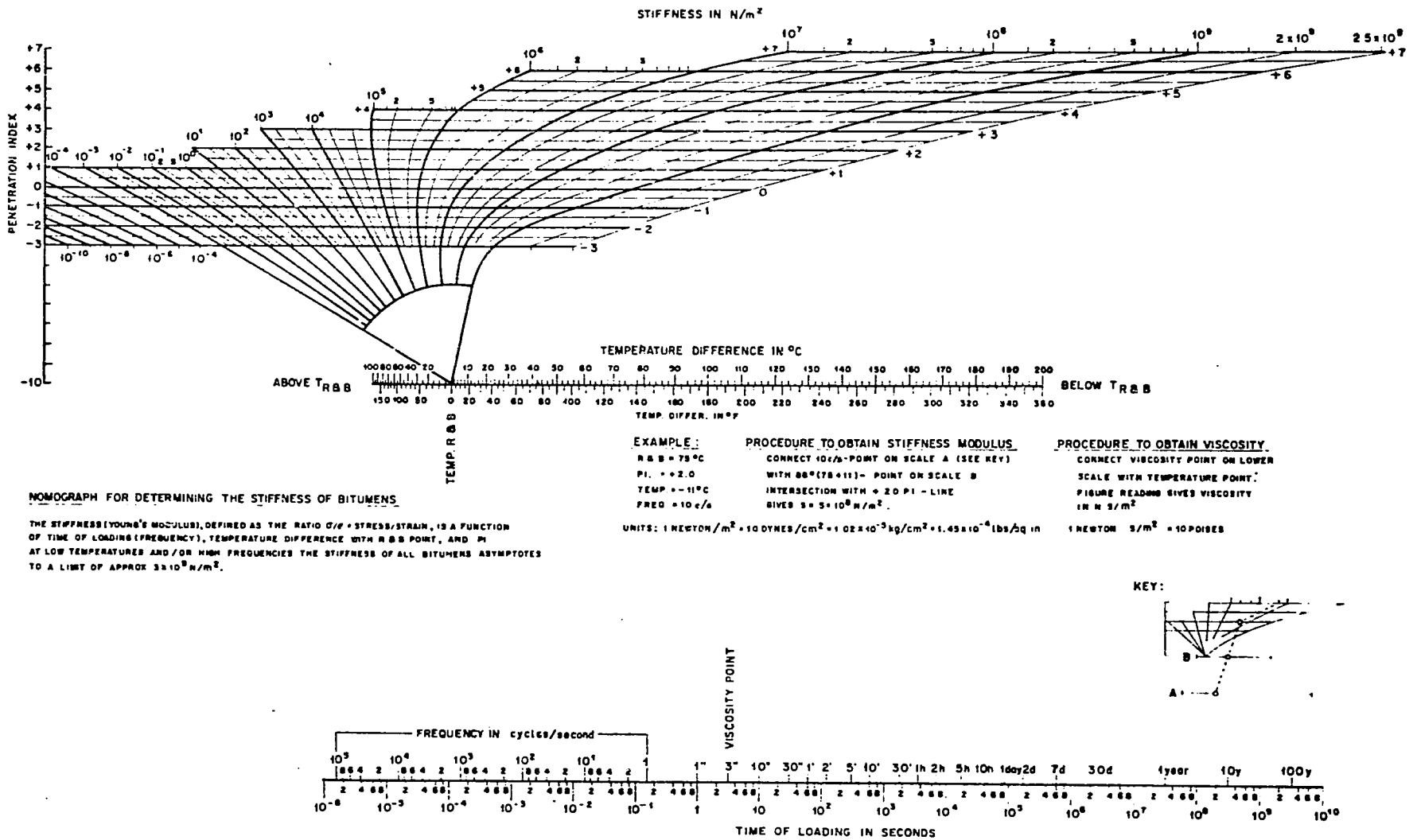


Figure 6.3 Van Der Poel's nomogram for determining stiffness modulus of bitumens.

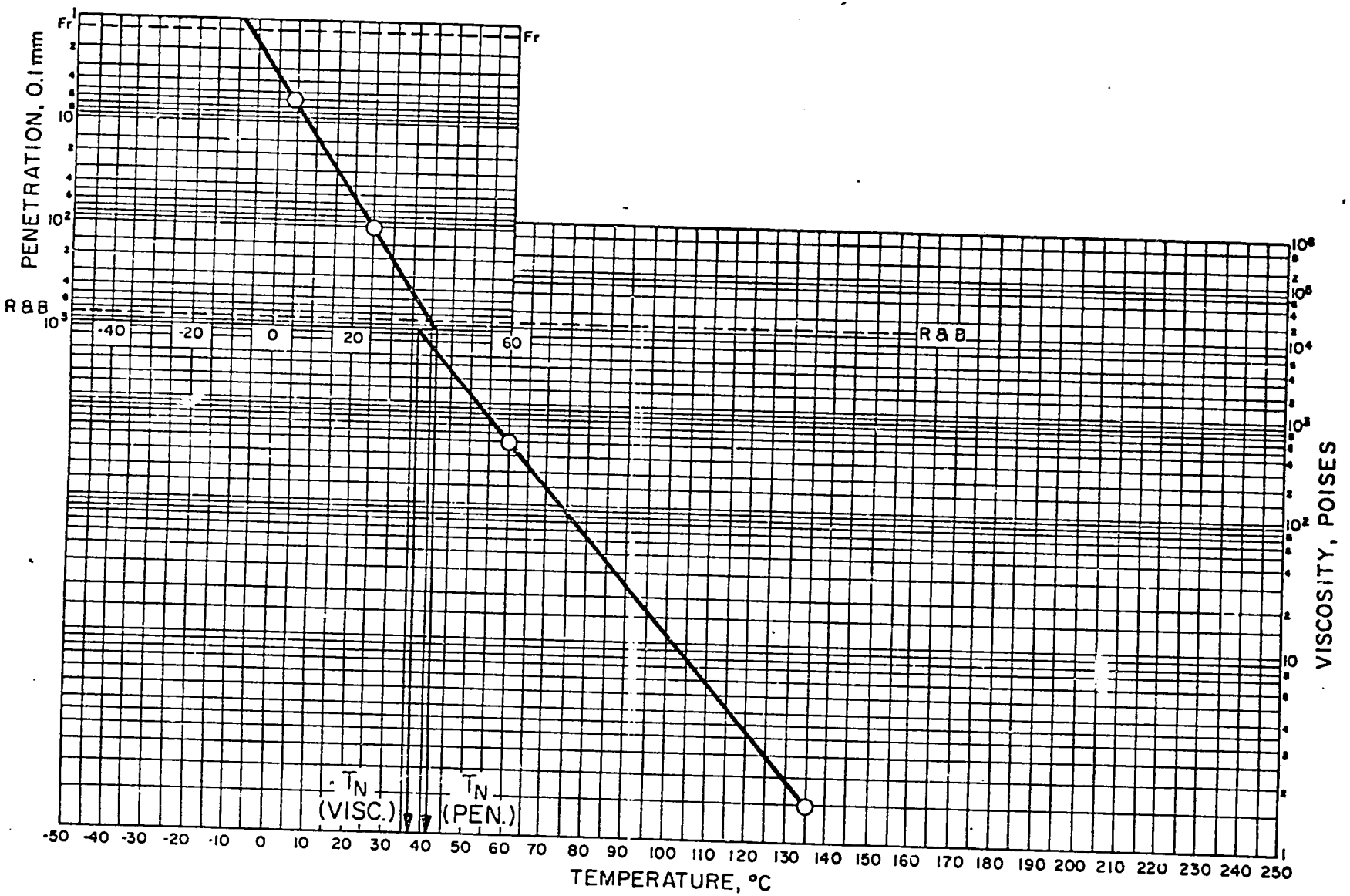


Figure 6.4 Heukelom's bitumen test data chart (Heukelom, 1969)

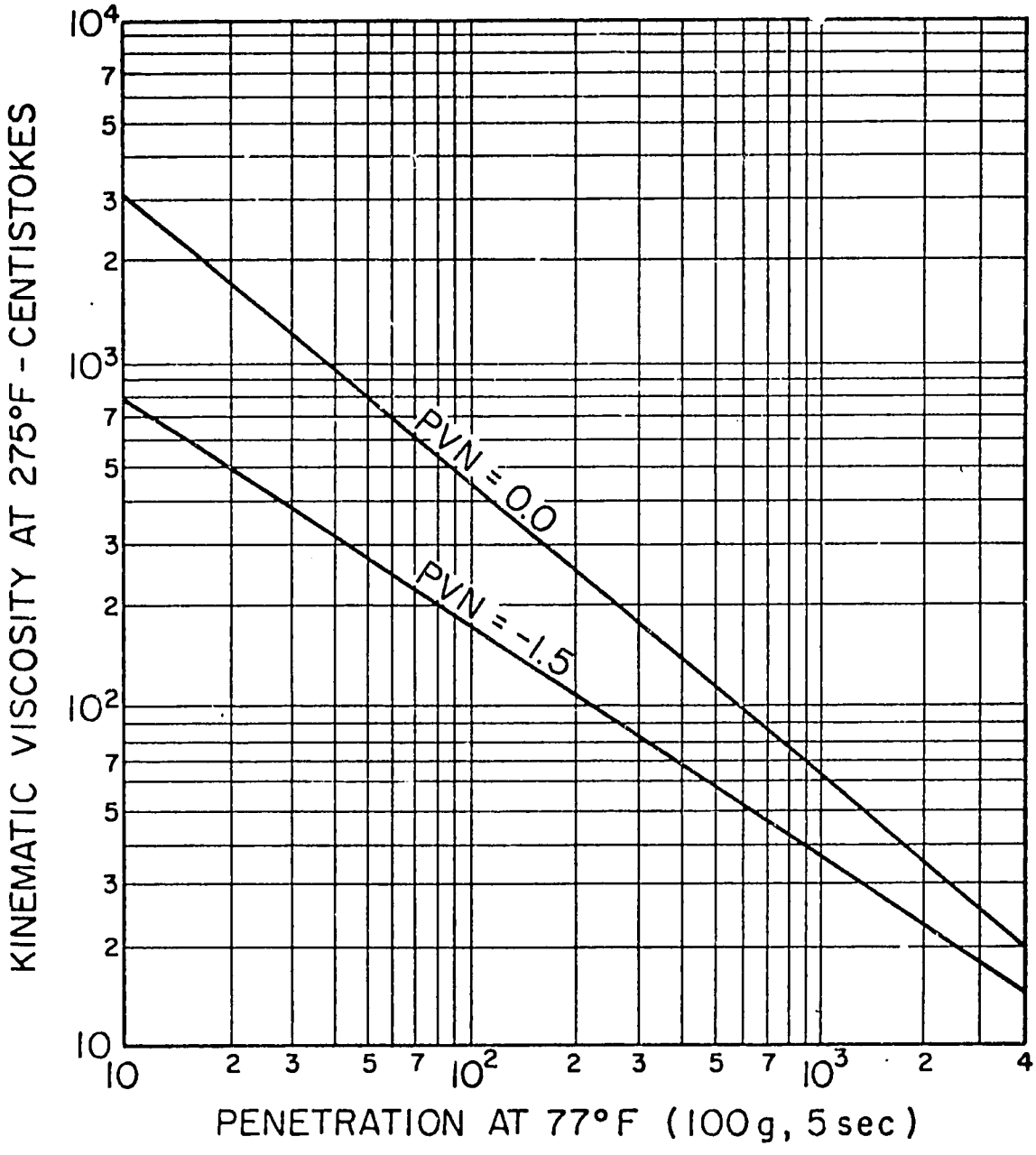


Figure 6.5 McLeod's chart for estimating the penetration vicosity number PVN, of an asphalt cement

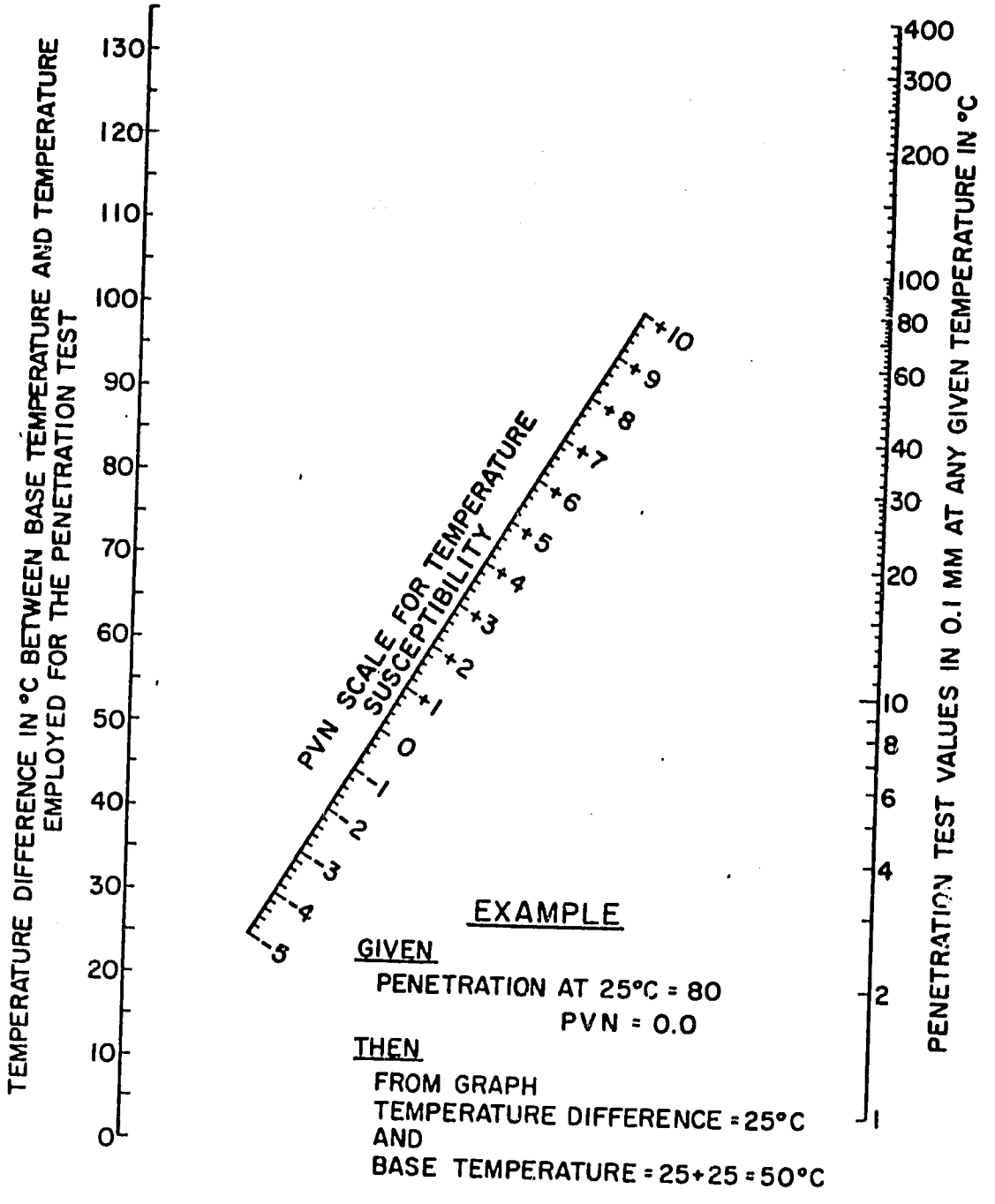


Figure 6.6 Suggested modification of Heukelom's version of Pfeiffer's and Van Doormaal's nomograph for relationship between penetration, penetration vicosity number and base temperature (McLeod, 1969)

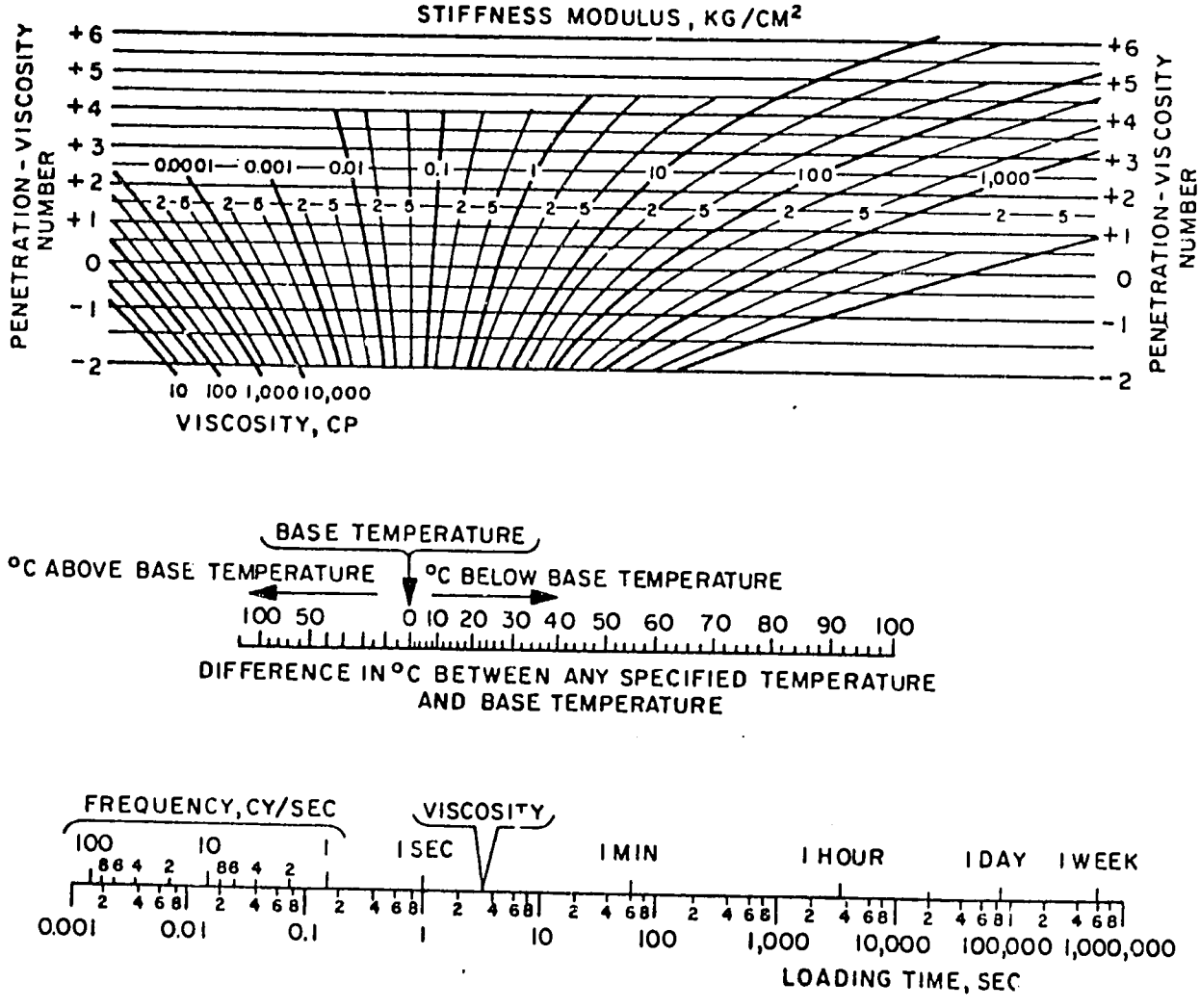


Figure 6.7 Suggested modification of Heukelom's and Klomp's version of Van Der Poel's nomograph for determining modulus of stiffness of asphalt cements

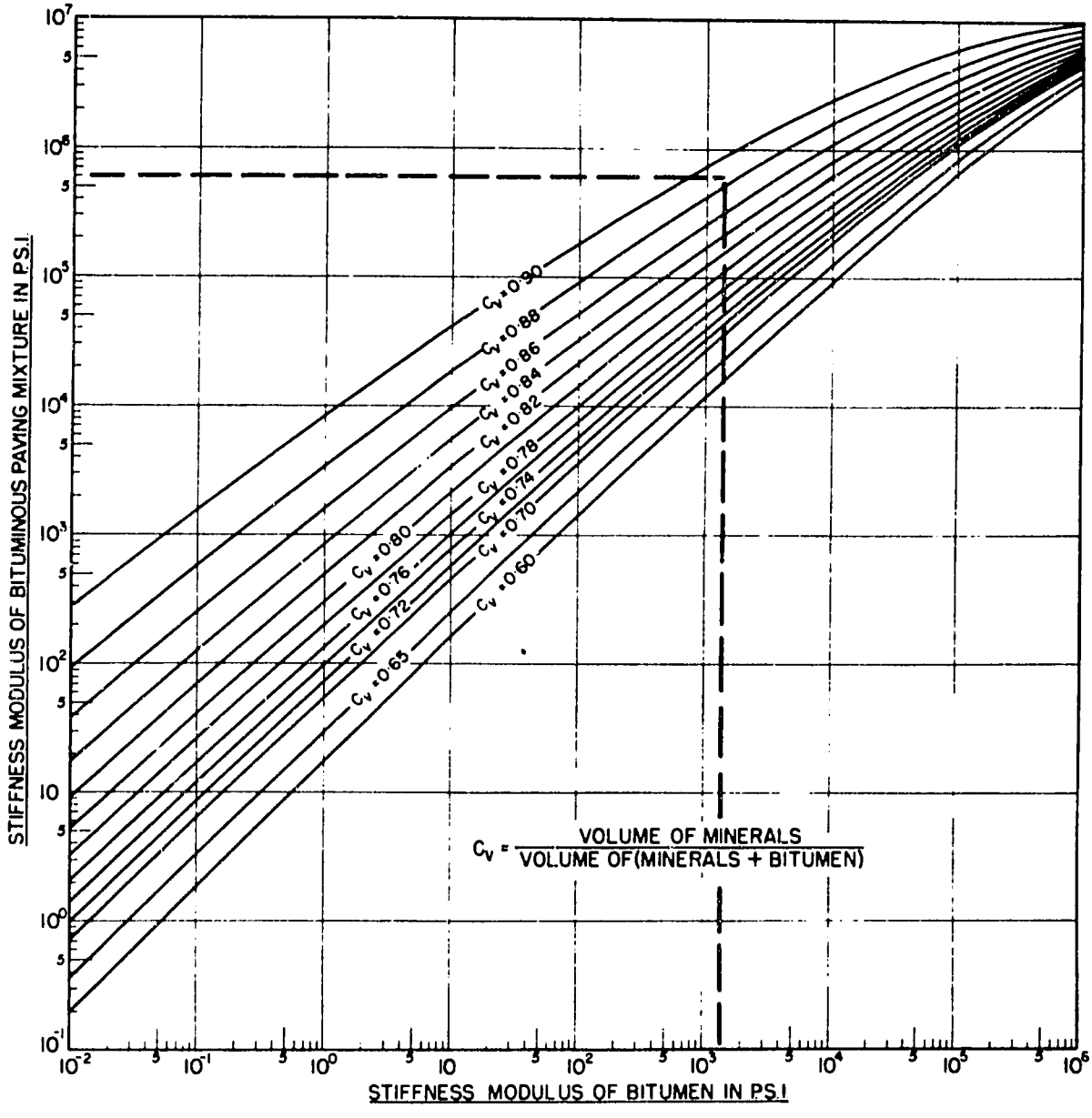


Figure 6.8 Relationships between moduli of stiffness of asphalt cements and of paving mixtures containing the same asphalt cements

CHAPTER 7

EFFECTS OF PARAFFIN WAX IN ASPHALTS

7.1 Physio-Chemical Characteristics of Waxes

Two types of waxes exist in asphalt: Paraffin and microcrystalline waxes. Both types are long chain compounds but microcrystalline waxes have higher molecular weights. The common paraffin wax has a molecular weight of 360 to 420, which means that the average molecule in these hydrocarbons contains 26-30 carbon atoms. The molecular weight of the high-melting point paraffins may reach 600. The molecular weight of the microcrystalline waxes is 580-700, and the average molecule contains 41-50 carbon atoms.

The melting point of paraffin waxes is, in general, much lower than that of the microcrystalline waxes. Paraffin waxes usually melt at 126-134°F, and microcrystalline waxes at 145-195°F. The melting point, however, cannot distinguish between the two types of waxes because paraffin waxes melting at 170°F exist and microcrystalline waxes with a melting point as low as 130°F have been prepared.

Paraffin waxes are brittle, but microcrystalline waxes are tough, resisting fracture. Most grades of microcrystalline waxes are plastic and tend to flow under compression whereas all grades of paraffin wax will shatter under compression.

The saybolt universal viscosity at 210°F for paraffin waxes is usually 1,430-1,433, and for microcrystalline waxes, 1,435-1,445.

Microscopic examination of paraffin and microcrystalline waxes show striking differences. Paraffin wax has large, well-formed crystals both when crystallized from the melted wax and from solvents. Microcrystalline wax forms small irregular crystals from the melted wax, but no well-formed crystals of any size from solvents.

Parrafin wax can be separated from the parafrin wax distillate by a relatively simple process. On the other hand, microcrystalline wax cannot be distilled without decomposition and requires a complex series of solvent separations from the residue (remaining in the still). Paraffin wax has very little affinity to oil and usually contains less than 0.5% oil. The oil content of the microcrystalline waxes varies with the grade of wax but is usually 2 to 12%.

Paraffin wax content of petroleum products can be determined using different standard methods:

(1) Holde's Method - The crude oil sample is distilled to remove light ends boiling below 300°C. The asphaltene is precipitated using petroleum ether 40/60°C boiling range (aromatic and sulfur-free) from the residue at a temperature > 300°C. Maltenes are fractionated into their components, namely oils and resins, using alumina as adsorbent and cyclohexane as eluant for oils and benzene-methanol for resins. Wax is precipitated from the oil using equivolume mixtures of ethyl ether/ethanol at -20°C.

(2) UOP Method 46-64 - This method is used for the determination of paraffin wax of petroleum oils and asphalts. About 2 gm of the sample is clarified using fuller's earth adsorbent and petroleum naphtha boiling range 90-150°F as eluant. The petroleum naphtha is evaporated and the clarified oil is redissolved in an acetone-petroleum naphtha mixture. This solution is then chilled to 0°F and filtered at the same temperature to separate the wax.

(3) SMS 1769-2 Method - This method describes a procedure for the determination of the wax content of waxy distillates. A weighed amount of sample is dissolved in a specific amount of methyl iso butyl ketone. The solution is cooled to -30°C and the precipitated wax is separated by filtration at the above temperature. If the sample contains asphaltenes, it may be treated with activated fuller's earth as adsorbent and toluene as extraction solvent. Wax is precipitated from the extract using methyl iso butyl ketone at -30°C.

(4) DIN Method 3.11 U.11 - About 25 gm sample of the bitumen is distilled in a specific apparatus using a definite procedure to produce distillate and residue. About 3 gm of the distillate are mixed with equivolume of absolute ether-ethanol mixture and cooled at -20°C to precipitate the wax, which is then filtered, washed, dried, and weighted.

(5) RLB-6-1964 Method - Asphaltenes are precipitated from the bitumen sample using petroleum ether. Maltenes are vigorously shaked with mixture of sulfuric acid and oleum (2:1 vol.) several times until the color of the acid is not changed. The hydrocarbon layer is washed with water, 5% sodium hydroxide and finally water until neutralization. Waxes are precipitated from the oil layer by mixing with equivolume of sulfuric ehter and ethanol at -20°C.

7.2 Effects of Wax on Properties and Performance

Problems associated with paraffinic bitumens have been encountered in many parts of the world and appear to become more acute with the increasing demand for petroleum products and the recourse to highly paraffinic crude oils. The properties of asphalt concrete mixtures and the performance of flexible pavements constructed with waxy asphalts are affected by the wax content and the type of wax in the asphalt. However, little conclusive information is available on the effects of wax. A major difficulty is caused by the lack of a uniform method of defining and/or determining the paraffin wax content.

Heukelom (1973) investigated the effect of wax by comparing the viscosity of a dewaxed asphalt, at different temperatures, with the viscosity of the same asphalt after a 12% extracted wax was added. At low temperatures, no significant effect of the wax could be detected because the wax was in a crystallized form. However, at high temperatures the waxy asphalt had a markedly

reduced viscosity. Wax crystallization makes thermal history an important factor on properties. For example, for the determination of the softening point, specimens are first precooled to 4°C whereas specimens for penetration testing are not precooled; this difference in thermal history causes differences in the condition of the wax and thus in the properties of the asphalt. Furthermore, penetration test results obtained during heating can be different from the ones obtained during cooling of specimens.

Evans et al. (1971) studied the effect of adding paraffinic resins obtained from the distillation of the residue on viscosity. Test results showed that the addition of wax increases the viscosity at low temperatures and decreases the viscosity at high temperatures, i.e., the asphalt becomes more sensitive to temperature changes.

Ewers et al. (1971) investigated the effect of the paraffinic wax content on the cohesion of asphalt as expressed by the number of shocks required to strip the asphalt between plates. Results show that, for a wax contnet in excess of 2%, cohesion decreases rapidly with the increase of wax content.

Marya et al. (1971) describe experiences in India where bitumens produced from paraffinic crudes exhibit low ductility, low stability, and a significant variation in the rate of setting. At low temperatures, the presence of wax up to 2% appears to have no detectable effects. However, at operational temperatures, properties are significantly affected. Laboratory

experiments indicate that waxy crudes can be suitably processed to yield a satisfactory binder but at a much increased cost. Additional laboratory studies on the use of synthetic resins and other materials such as rubber in bituminous mixtures indicate that the addition of 2% rubber increases the softening point from 47°C to 52°C and reduces the stripping of the bitumen from 30-40% to less than 5%. In a national highway, a bitumen with 2% rubber was used. The rubber improved the viscosity of the bitumen and the aging characteristics of the binder and increased the cost by 50%.

Centolani et al. (1971) report on experiences in Italy where paraffinic middle-eastern crudes are imported in increasing volumes. These crudes need more complicated methods of treatment in order to cause significant structural changes. Modern systems of precipitation using selected solvents or partial oxidation lead to hard bitumens from which various penetration grades can be obtained by the addition of fluid oils. In order to improve the performance of bituminous binders, rubber is extensively used in Italy. In 1970, more than a million square meters of pavements were constructed with the addition of synthetic rubber latex to the concrete mix (3 to 6% of the binder). The synthetic rubber considerably reduced the temperature-susceptibility of the asphalt and improved its viscosity.

Niemi (1971) indicates that paving bitumens used in Finland are obtained by combining bitumens derived from equal

quantities of the bitumen derived from parraffinic Russian crudes with bitumen derived from Venezuelan crudes. Tests conducted on the paraffinic mix containing 2% paraffin indicate some superior behavior:

(1) At high temperatures (in excess of 60°C), paraffinic bitumens have a lower viscosity than bitumens with high asphaltene content. Thus they can be more conveniently handled, manipulated, and mixed at lower temperatures.

(2) Paraffinic bitumens have better aging characteristics due to their chemical nature.

(3) Since paraffinic bitumens contain fewer acid elements, the alkaline agents (such as amines) are conserved. This is also true for bitumen solvent and oils used in roads made of paraffinic bitumen.

On the other hand, paraffinic bitumens showed undesirable properties:

(1) The adherence of the bitumen to the aggregates and the resistance of asphaltic mixtures to water are poor.

(2) For temperatures between 60°C and 25°C, the viscosity is low. Pavements constructed with paraffinic bitumens are thus susceptible to deformations and bleeding during summer months.

(3) For temperatures below 25°C, the viscosity is higher

than asphaltic bitumens. (The breaking point and glass transition temperatures are higher.) Pavements are therefore more susceptible to cracking and wear at low temperatures.

Ewers et al. (1971) from the German Democratic Republic (GDR) emphasize the importance of the paraffin type and the bitumen type in addition to the paraffin content on the properties of bitumens. Crystallized paraffin is less desirable than amorphous paraffin because of the perturbations caused by the paraffin crystals to the colloidal structure of the bitumen. Furthermore, the effects of a given type and quantity of paraffin can be very different on various types of bitumens. Ewers et al. present data showing that an increase in wax content from 2 to 4% decreases the dynamic cohesion (expressed by the number of blows in an Ewers/Walter test) by a factor of two or more. They also indicate that at low temperatures, the paraffin can seriously reduce ductility. Finally, they believe that the 2% paraffin limit adopted in many countries is justified. However, they support the increase of this limit to 3% in the GDR provided that the effects on bitumen properties are carefully monitored and controlled by means of reliable mechanical tests.

Lopienska et al. (1971) present a comprehensive study of paraffinic bitumens in Poland where they are successfully and extensively used in road construction (paraffin content 3-3.2% according to the Holde method). Microscopic analyses of the

paraffin extracted from very low, medium (3-4%) and high (more than 5%) paraffin-content bitumens (according to the Holde method) showed that for the three types of bitumens, the method of extracting paraffin had an important effect on its structure. Furthermore, the increase in asphaltic paraffin content in the oils and resins had no effect on the results of microscopic analyses. This appears to indicate that asphaltic paraffins are in a dissolved state rather than visible crystals and hence raises serious questions regarding commonly-held views on the effects of paraffin on bitumen properties. Lopienska et al. conclude that: (1) Cooling of the asphalt does not develop paraffin crystals and paraffin remains in solution for a long time; (2) The reduction in bitumen viscosity at high temperatures cannot be explained by the fusion of paraffin crystals; (3) The poor ductility of paraffinic bitumens cannot be explained by the presence of paraffin crystals; and (4) The wax content per se does not determine the properties of bitumen.

Mikhailov et al. (1971) improved the rheological properties of Russian paraffinic bitumens through dilution after heavy oxidation. The method improved the bitumen properties by: increasing the plastic range, decreasing the deformation modulii at temperatures below 0°C, and increasing the viscosity at high temperatures.

In the XV World Road Congress, 1975, experiences with paraffinic bitumens are described as follows:

(1) A clear definition of the paraffin content is needed. The structural ratio (degree of dispersion) appears to have an ever-increasing importance.

(2) In Australia, bitumens with a high paraffin content, which crystallize at low temperatures, are not currently used. The latter, however, are not excluded from the specifications.

(3) In Bulgaria, no scientific basis for an acceptable paraffin content in bitumens has yet been reached. The possibility of crystallization of paraffins from bitumen increases with a rise in their point of fusion. The composition of the bitumen and the rapidity of the cooling process have a big influence. Studies show that paraffin leads to a reduction in the ductility of bitumens at 25°C and that this decrease continues during storage. Paraffin, on the other hand, exerts no significant influence on the Fraass point of rupture. A reduction in the crystallization of paraffin is observed with a fall in the softening point and an increase in the penetration with a reduction in the amount of oils and the ratios oils/asphaltenes and oils/resins/asphaltenes. This shows that the negative influence of paraffin is associated more with the structure of bitumens than their quantity. No difference is observed after two and a half years' application on roads

between paraffinic bitumens (up to 2.4 per cent), bitumen with 1.7 per cent paraffin, and Albania bitumen to 0.82 per cent.

(4) In the German Federal Republic, the DIN 1995 specifications limit the paraffin content to a maximum of 2 per cent. This limit is based on obvious practical experience, but it does not appear well-founded today.

(5) In the German Democratic Republic it is noted that two paraffins having different hardening points (46°C and 76°C, respectively) produce different effects on the bitumens; the higher their hardening point, the worse the influence they exert, especially on ductility.

(6) In India unrefined bitumens obtained from Assam have a paraffin content of 11 to 14 per cent. To obtain bitumens of the 80/100 type, it is necessary to employ blowing of the residue, which leads to too low values for ductility. In spite of the low ductility of paraffinic bitumens, their low rate of setting and their low Marshall stability, there has been no problem in applications of these bitumens on roads provided the temperature of these zones of application has not been lower than 10°C and has not exceeded 30°C. It is also stated that there was no problem in the plains of Northern India where temperature in summer can reach 45°C.

(7) In Poland, technology of preparation and construction of mixes with paraffinic bitumens is different from that for ordinary bitumens. Paraffinic bitumens (unrefined Russian Romachkine) have, compared with ordinary bitumens, the following properties:

- high susceptibility to temperature
- viscosity lower at high temperatures
- penetration less than 0°C
- less interval of plasticity
- rigidity modulus at low temperatures two to three times higher
- Holmes index about twice higher
- big difference between Ring and Ball temperature and that at which the penetration of the bitumen is equal to 800
- heat resistance in thin layer identical

Because of the difference of viscosity, coated materials must be applied at lower temperatures.

CHAPTER 8

BACKGROUND OF THE PROBLEM IN EGYPT

8.1 Road Construction

8.1.1 Historical Background

Road construction in Egypt began 7000 years ago during the Pharaonic days. These roads were built to transport construction materials to Luxor and Giza where they were used to build the temples and Pyramids. Also, the construction of new roads was necessary to serve the Pharoah's needs for transporting gold and copper from the mines to the capital where tools and arms were manufactured. Most of the roads of those days were earth roads that overlooked the River Nile banks and streams.

The Road Organization was established in 1913 in connection with the Ministry of Irrigation. This connection was necessary for the development of roads in the rural areas and helped in providing the maintenance services on the banks of canals, drains, and streams.

In 1919, the Ministry of Communications was established and was followed afterwards by the Roads and Bridges Organization which was assigned the responsibility of supervising the construction and maintenance of earth roads (850 km long at that time). 300 km of these roads were paved during the period from 1926 to 1936. After the 1936 agreement with Britain, the organization efforts were guided towards paving more roads in the country, and, consequently, the road network increased in length to 1951 km by the year 1947.

The first five-year plan started in 1947, and by 1952, 1727 km of roads were constructed at a cost of 6,771,000 Egyptian pounds. The period of 1952-1973 included paving 8,500 km of roads at a total cost of approximately 84 million Egyptain pounds. During this period, the present network of roads was strengthened and a military roadway network in Sinai was constructed together with some airports. The Nile Valley was connected to the Red Sea by paved roads constructed between Kaft and Al Kusir and Idfo and Mersa Alam.

8.1.2 Egyptian Roadway Network

The Egyptian General Authority of Rural Roads and Bridges classifies the Egyptain roads into the following categories:

1. Expressways; average daily traffic volume $\geq$ 5000 vehicles
2. First class roads; average daily traffic volume between 3000 and 5000 vehicles
3. Second class roads; average daily traffic volume between 1000 and 3000 vehicles
4. Regional roads; average daily traffic volume < 1000 vehicles

The main links of the Egyptian roadway network are shown in Figs. 8.1 and 8.2. Table 8.1 lists these links along with useful information pertinent to these links.

8.2 Petroleum and Asphalt Cement Production

8.2.1 Historical Background

The first crude oil field was discovered in Gemsa by the Anglo-Egyptian Oil Fields Company in 1868. This was followed by the discovery of the Ghardaka oil field in 1931.

Actual exploration activities, however, started in 1935. Special interest was given to Central and Northern Sinai, Eastern and Western Deserts, and Gulf of Suez. By 1938, four major oil companies were working in oil exploration in Egypt: Anglo-Egyptain Oil Fields Company, Socony Vacuum Oil Compnay, South Mediterranean Oil Fields Company, and Standard Oil Company of Egypt. In 1954, the Company Oriental de Petroles d'Egypte started carrying out more exploration and exploitation activities in Sinai. This successfully led to the discovery of Balayim Land, and Balayim Marine oil fields (see Fig. 8.3).

The first oil well to be drilled in the Western Desert was that of Dabaa in 1939. It was followed by the discovery of the Khatatba exploration well, Abu-Rawash-1 and 2 during the period from 1944 to 1947. In 1954, the Sahara Petroleum Company started new exploration activities in the Western Desert. However, the efforts were not successful and the company left its concession in 1958.

The first Egyptian petroleum company, the Gulf Petroleum Company, was established in 1957. The company was very successful in discovering six oil fields in a relatively short period.

These oil fields were Bakr, Kareem, Ras Amer, Shukeir, Um El-Yusr, and El-Eyun (see Fig. 8.3).

Consequently, in 1964 American Oil Company was awarded a concession west of Faghur and Agila. About 24 exploration wells were drilled in this area during the period from 1964 to 1975. Oil and natural gases were discovered in Abu-Gharadig-II in 1969.

The Western Desert again attracted the attention of the Phillips Company which started exploration efforts in 1964. The work of the company was crowned by the discovery of El-Alamein oil fields in 1966. By 1972, the company had discovered Um Baraka and Meliha oil fields.

During the last few years (1975-1979), a number of foreign petroleum companies (Mobil Oil, Shell, Diminix, Conoco, etc.) have performed several exploration operations on the northern coast of the Mediterranean Sea, the Gulf of Suez, and the Western Desert. It is expected that a number of discoveries will be declared in the very near future after the work in these areas has been completed.

8.2.2 Egyptian Crude Oils and their Chemical Nature

Fig. 8.3 shows the major oil producing fields in Egypt. These fields can be divided according to their locations into the following:

1. The eastern oil fields, which comprise the Gulf of Suez and Sinai crude oil fields. This group includes July, Ramadan, Morgan, Ras Gharib, Um El-Yusr, Balayim

Marine, Balayim Land, Bakr, Sedr, Assal, and Aub-Rudis oil fields.

2. The Western Desert oil fields, which include El-Alamein, Abu El-Gharadig I and II, Razzak, Yadama, and Mobarka oil fields.

The main chemical characteristics of the eastern and western curde oils are summarized in Tables 8.2 and 8.3, respectively. Table 8.2 indicates that the eastern crude oils are characterized by their relatively high sulfur, wax, resin, and asphaltene contents. These properties usually suggest that asphalts produced from such crude oils are expected to be suitable for road paving. The eastern crude oils could be classified according to the Carpatica method (see Chapter 3) as of paraffinic-naphthenic-aromatic class of the waxy-asphaltic-sulfurour group (Table 8.4).

Table 8.3 shows that the western crude oils have low sulfur, asphaltene, and resin contents. On the other hand, these crude oils are characterized by their high oil and wax contents. Accordingly, asphalts produced form such crude oils are expected to be of the same nature, unless some precautions are taken during asphalt production. The western crudes could be identified according to the Carpatica method as of paraffinic-napthenic class of the waxy-resinous-sulfurous or non-sulfurous group (Table 8.5).

8.2.3 Asphalt Production

The paving asphalts used in road construction in Egypt were mainly produced from local crude oils obtained from the Gulf of

Suez area. This continued until the June 1967 War. After this war, the Western Desert crude oils were used to produce asphalts and the refineries adopted the policy of mixing the available crudes.

The refining of crude oils takes place in Suez and Alexandria. Straight-run asphalts are produced by the Suez refineries employing the crude oils recovered from the eastern crude oil fields. The crude oil from the Western Desert fields are refined in Alexandria, and asphalts are produced by means of propane-deasphalting and phenol extract processes.

Table 8.6 indicates the total asphalt production rates of the local refineries for the past few years.

8.3 Local Aggregate

The aggregate types most frequently used in Egypt are crushed lime stone, crushed bazalt, and/or siliceous materials. Table 8.7 summarizes the main physical and engineering properties of the local aggregate materials based on information collected from nine quarries located in various regions of Egypt.

8.4 Current Egyptian Specifications

The Egyptian General Authority of Rural Roads and Bridges issued specifications that include:

1. General conditions for roads and bridges construction works
2. Conditions for submitting tenders for roads and bridges construction projects

3. Legal aspects and specifications regarding equipment and machines used in road construction, pavements, and maintenance works
4. Specifications of compacting subgrade, subbase, and base course layers
5. Specifications of constructing asphalt layers, together with specifications of various types and grades of bitumens

These specifications are updated regularly to incorporate and reflect changes and/or progress in the field of roadway construction.

8.4.1 Asphalt Cement Specifications

Table 8.8 summarizes the current Egyptian standard specifications for the asphalt cements.

8.4.2 Aggregate Specifications

The current specifications for mineral aggregates used in asphalt mixtures are shown in Table 8.9.

Also, the gradation requirements for aggregates to be used in constructing hot-mix asphaltic concrete pavements are given in Table 8.10.

8.4.3 Asphalt Concrete Mix Specifications

The Marshall method is commonly used in designing the local asphalt concrete pavement mixtures. The design criteria are shown in Table 8.11.

8.5 Pavement Performance Problems

In the early seventies, the production from the Suez refineries was halted, and the asphalt cements were produced from newly used crude oil fields in the Egyptian Western Desert. However, the new asphalts caused serious performance and construction problems, which can be summarized as follows:

1. The pavement mixtures were very fluid when laid and had very slow setting times.
2. Pavements showed greater flushing tendency under heavy traffic loads. This tendency was greater during hot summer days.
3. Severe creep deformations towards pavement edges and near the median curbs were observed.
4. A remarkable increase in the frequency of transverse cracking was indicated.
5. Most of the previous performance problems started to appear after only 6 to 12 months of construction.
6. Constructed and/or maintained roads showed marked deterioration trends in relatively short time periods which indicated a severe reduction in the pavement service life.

These performance problems were widespread, notably at many locations on the Cairo-Alexandria Expressway (Fig. 8.4) which is one of the most important routes in Egypt. Some of these locations are Kafr El Dawar-Alexandria (km 10.48 to km 19.50),

El Malatia-Abu Korkas, Damanhoor-Abu Hommas, and Toukh-Banha sections.

8.5.1 Chemical and Physical Properties of Egyptian Asphalt Cements

A program of testing was conducted to investigate the properties of the local asphalt cements (Metwally et al., 1975). Table 8.12 shows the chemical composition and physical properties of various asphalt cement samples secured from the Western Desert and eastern regions. The data show that:

1. The wax content for the western and eastern regions is higher than the generally accepted limits (2.0 to 4.0%).
2. The wax content of the western asphalt cements is generally higher and varies in a wider range (from 5.1 to 14.8%).
3. The asphaltene content of the western asphalt cements is generally lower.
4. The kinematic viscosity of the western asphalt cements is generally lower.

These results indicated that the construction and performance problems could be attributed to the considerable wax content and the non-homogeneity of the western Desert asphalt cements.

Table 8.13 presents the test results of three samples taken at different depths of a pavement section. The sampling location was at a relatively bad spot near km 31 on the Cairo-Alexandria agriculture highway. The samples were secured exactly 12 months after reconstruction.

The results in Table 8.13 clearly indicate that oil and wax contents of the flushed asphalt batch were much higher than those of the surface layer samples. In addition, these oil and wax contents gradually decrease towards the bottom of the pavement. This may suggest that at ordinary summer temperatures, waxy asphalt cements separate from the pavement layers and migrate vertically towards the surface and horizontally towards the pavement and median curbs, which leads to successive deflections of the central portion of the highway and severe upheaves near pavement edges.

Marshall stability values of cores secured from finished asphalt concrete layers showed a wide range of variation, with values as low as 39.5 % of that of the design mix (Table 8.14). This indicates that the product is not homogeneous. Although the stability values were high and within the acceptable range, they did not provide an indication of the failure that subsequently occurred in the road.

Road	Length (km)	Pavement Width (m)	No. of Lanes	Pavement Service-ability Index	Average Speed (km/hr)	Type of Shoulder
Cairo-Alexandria (desert road)	224	7.0	2	2.5	73	not paved
Cairo-Alexandria (agriculture road)	213	2×7.5	4	3-4	74	paved (3 m)
Cairo-Ismailia (agriculture road)	133	6.5	2	-	58	not paved
Cairo-Suez	131	2×7.5	4	-	98	paved
Cairo-Ismailia (desert road)	128	2×7.5	4	-	98	paved
Cairo-Fayoum	123	6.5	2	-	55	not paved
Ismailia-Suez	85	7.0	2	-	73	not paved
Zagazik-Ismailia	84	6.0	2	-	61	not paved
Ismailia-Port Said	79	7.5	2	-	56	paved(2.25 m)
Damietta-Port Said	71	6.0	2	-	55	not paved
Benha-Mansoura	70	6.5	2	-	65	not paved
Mansoura-Damietta	64	6.0	2	-	54	not paved
Tanta-Zagazik	59	6.0	2	-	59	not paved
Mansoura-Zagazik	55	6.0	2	-	56	not paved
Tanta-Kafr El Sheikh	37	6.0	2	-	58	not paved
Tanta-Mahalla El Kubra	25	9.5	4	4	78	not paved
Mahalla El Kubra-Talkha	25	6.0	2	-	51	not paved

Table 8.1 - Main Links of Egyptian Roadway Network

Characteristics	July	Ramadan	Morgan	Ras-Gharib	Marine Balayim	Land Balayim	Bakr	Sedr	Um El-Yusr	Ras-Amer
Specific gravity at 60/60°F	0.862	0.861	0.861	0.905	0.882	0.921	0.937	0.919	0.9227	0.929
API gravity	32.7	32.84	32.8	24.8	29.0	22.1			21.85	20.8
Sulfur content, wt.%	1.50	1.00	1.64	3.07	2.0	3.08	5.15	2.50	3.00	3.4
Water content, vol.%	0.5	0.2	Nil	0.3	Nil	0.3	Nil	Nil	0.5	
Engler Viscosity at 20°C	2.5	1.8	2.8	13.4	3.6	33.3				48.4
Pour point, °C	6.5	5.0	18.0	-1.0	10.0	-1.0		8.3	1.0	7
Carbon residue, wt.%	4.6	3.3	4.9	8.5	5.5	10.6		9.6	8.8	10.7
Ash content, wt.%	0.01	0.02	0.05	0.05	0.01	0.05	0.027	0.02	0.04	0.04
Wax content, wt.%	6.5	7.8	9.8	7.3	7.6	7.3			6.5	5.5
Oil content, wt.%	45.5	37.3	40.9		38.3			48.5		39.8
Resin content, wt.%	23.4	21.6	20.7	18.0	23.0	24.4		26.4		20.3
Asphaltenes, wt.%	2.3	2.3	3.4	6.8	4.0	9.4		12.2	5.8	7.3
Salt content		0.006							0.01	0.007
Vanadium content, ppm		10	25	71	38	61	49	55	110	190
Nickel content, ppm			15	43	28	130	86	26		74
Heating value k-cal/kg		10174								
Reid vapour pressure at 37.8 psi	1.0	1.0							2.0	
Flash, pt., °C	51	33							32	
<u>ASTM Distillation</u>										
Initial boiling point °C	60	56	49	68	48	75	78	80	65	61
%vol. recovered at 50°C	2	-	-	-	-	-	-	-	-	-
%vol. " " 75°C	2	3	6	-	4	-	-	-	1.0	2
%vol. " " 100°C	4	5	12	4	7	4	4	2.5	2.5	3
%vol. " " 125°C	8	10	17	7.5	10	7	9	6.0	5.0	6
%vol. " " 150°C	15	14	22	11.5	15	10.5	13	9.0	8.0	9
%vol. " " 175°C	19	19	25	15.0	19	14.0	18	10.5	11.5	12
%vol. " " 200°C	24	24	28	19.0	24	17.0	21	15.5	15.0	15
%vol. " " 225°C	27	28	33	23.0	26	20.0	24	20.5	18.0	18
%vol. " " 250°C	32	33	38	26.0	30	23.5	27	25.0	22.0	23
%vol. " " 275°C	36	38	42	31.0	35	27.5	31	30.5	25.5	26
%vol. " " 300°C	47	45	52	35.0	40	32	38	36.5	31.5	34

Table 8.2 - Chemical Characteristics of Eastern Crude Oils

Characteristcs	El-Alamein	Abu-El Gharadig I	Abu-El Gharadig II	Razzak	Yadama	Mobarka
Specific Gravity 60/60°F	0.863	0.852	0.834	0.835		
API Gravity	31.7	34.2	37.9	38.0		
Sulfur Content, wt %	1.14	0.46	0.36	0.86		
Water Content, Vol.%	Nil	0.25	0.15	0.05		
Engler Viscosity at 20°C						
Pour Point, °C	10			7.2		
Carbon Residue, wt.%	4.7	2.18	2.15	2.74		
Ash Content, wt.%	0.03	0.013	0.005	0.01		
Wax content, wt.%	8.4	4.84	3.72	3.48	6.3	21.1
Oil Content, wt.%	32.3	30.94	29.34	35.34	33.2	40.1
Resin Content, wt.%	19.9	16.97	14.67	3.39	5.2	8.4
Asphaltenes, wt.%	4.5	0.29	0.19	1.89	4.4	0.7
Vanadium Content, ppm				6.3		
Nickel Content, ppm				3.1		
Reid vapour Pressure at 37.8 psi				3.8		
ASTM-Distillation						
Initial boiling point, °C	55	46	41	54		
Vol.% recovered at 50°C	1	3	4	5		
" " " 75°C	5	5	8	10		
" " " 100°C	10	12	14	17		
" " " 125°C	15.5	19	21	25		
" " " 150°C	21.0	25	28	31		
" " " 175°C	27.0	30	34	36		
" " " 200°C	32.0	35	40	42		
" " " 225°C	38.0	40	45	47		
" " " 250°C	42.0	45	50	52		
" " " 275°C	47.0	51	55	58		
" " " 300°C						

Table 8.3 - Chemical Characteristics of Western Crude Oils

Analysis	July	Ramadan	Morgan	Marine Balayim	Ras Amer
Structural indices, wt.%					
$\%C_p$	59.3	63.9	70.5	69.0	66.0
$\%C_N$	27.3	25.7	19.3	20.8	23.8
$\%C_A$	13.4	10.4	10.2	10.2	10.2
Quality indices, wt.%					
Wax	6.5	7.6	9.8	7.6	5.5
Resins & Asphaltene	25.7	22.1	30.0	27.5	27.6
Sulfur	1.5	1.0	1.6	2.0	3.4
Distillate up to 200°C	22.6	22.0	24.8	22.3	14.5
Class	← (Paraffinic-Napthenic-Aromatic) →				
Group	Waxy Asphaltic Sulfurous	Waxy Resinous Sulfurous	← (Waxy-Asphaltic-Sulfurous) →		

Table 8.4 Classification of Eastern Crude Oils

Analysis	El-Alamein	Abu-El-Gharadig I	Abu-El-Gharadig II	Razzak
Structural indices wt.%				
% C_P	64.7	66.4	62.7	
% C_N	26.6	23.8	27.4	
% C_A	8.7	9.8	9.9	
Quality indices, wt.%				
Wax	8.4	4.8	3.7	3.5
Resins & Asphaltenes	24.7	17.3	14.9	5.3
Sulfur	1.1	0.46	0.36	0.86
Distillate up to 200°C	26.2	19.4	27.4	33
Class	← (Paraffinic-Naphthenic) →			
Group	← (Waxy-Resinous) →			
	sulfurous	Non - Sulfurous		Sulfurous

Table 8.5 - Classification of Western Crude Oils

Year	1976	1977	1978
Production (ton)	135,000	148,000	193,000

Table 8.6 Asphalt Production Rates

Quarry	Agg. Type	Abrasion %	Absorption %	Disinteg-ration	Bulk sp.gr.	Bulk sp.gr. (SSD basis)*	Apparant Sp. gr.
Abu-Rawash	crushed lime stone	35-42	2-6	0.1-1.0	2.443	2.525	2.662
Alam El-markb	siliceous mat.	22-26	0.8-2	0.1-0.5	2.413	2.481	2.591
Fayed	crushed lime stone	38-42	4-5	0.5-1.2	2.399	2.494	2.650
El-Mokatam	crushed lime stone	30-35	1.5-5	0.9-1.2	2.233	2.366	2.577
Tura	limestone	35-42	3-6	0.5-1	2.117	2.316	2.595
Mersa-Matrouh	crushed lime stone	24-30	2.5-4	0.4-0.6	2.440	2.509	2.621
Abu Simbul	siliceous materials	16-22	0.5-1.5	0.1-1.0	2.859	2.874	2.901
Abu-Soltan (El-Menia)	crushed lime stone	35-40	2-3	0.0-0.5	2.445	2.501	2.598
Abu-Zabal	Bazalt	18-22	0.5-1.5	0.1-0.8	2.789	2.841	2.943

* Saturated surface dry basis

Table 8.7 - Engineering Properties of Local Quarries Materials

Test	Grades							
	6/12(x)	10/20	20/30	30/40	40/50	60/70	80/100	180/200
- Penetration at 25°C, 100 gm-5 sec.	6-12	10-20	20-30	30-40	40-50	60-70	80-100	180-200
- Softening Point (Ring&Ball), °C(xx)	30-90	65-75	58-68	54-64	50-60	45-55	42-52	35-45
- Ductility at 25°C (min)	-	5	25	60	80	90	100	50
- Flash point (Cleveland Open Cup), °C (min)	290	250	250	250	250	250	200	200
- Solubility in carbon tetrachloride(xxx), %wt. (min)	99	99	99	99	99	99	99	99
- Solubility in carbon disulfide %wt.(min)	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5
- Loss on heating at 163°C-5hrs, %wt. (max)	0.1	0.5	0.5	1	1	1	1	1
- % decrease in penetration after loss on heating test (max)	-	25	25	25	25	25	30	35

Notes:

(x) Commercially known as S 80/90 (S refers to Solid)

(xx) Not a basic test but only for guidance.

(xxx) One of the two tests is satisfactory.

Table 8.8 - Egyptain Standard Specifications for Asphalt Cements

Test Property	Bituminous Surface	Bituminous Base
Abrasion of coarse Aggregate (Los Angeles test)	$\not> 40\%$ or $\not> 45\%$ (500 rev.) and $\not> 10\%$ (100 rev.)	$\not> 50\%$
Sand Equivalent Test	≥ 50	≥ 45
Soundness of Aggregates	$\not> 12\%$	$\not> 12\%$
Absorption	$\not> 5\%$	$\not> 10\%$
Plasticity Index	0	$\not> 6$
Swell test (Bit.Agg. mix)	0	$\not> 0.03"$ (A) $\not> 0.062"$ (B)
Stripping (Bit.Agg. mix)	$\not< 95\%$	-

Table 8.9 Quality Standards for Mineral Aggregates

No. and type of mixture	2½"	1½"	1"	3/4"	1/2"	3/8"	#4	#8	#16	#30	#50	#100	#200
Surface treatment Courses													
2a open graded						100	40/85	5/20					0/4
2b open graded					100	70/100	20/40	5/20					0/4
Wearing Surface Courses													
2b open					100	70/100	20/40	5/20					0/4
2c open				100	70/100	45/75	20/40	5/20					0/4
3a coarse					100	75/100	35/55	20/35		10/22	6/16	4/12	2/8
3b coarse				100	75/100	60/85	35/55	20/35		10/22	6/16	4/12	2/8
4a dense					100	80/100	55/75	30/50		18/29	13/23	8/16	4/10
4b dense				100	80/100	70/90	50/70	30/50		18/29	13/23	8/16	4/10
4c dense			100	80/100		60/80	48/65	35/50		19/30	13/23	7/15	3/8
Binder Courses													
2c				100	70/100	45/75	20/40	5/20					0/4
2d			100	70/100		35/65	15/35	5/20					0/4
3b				100	75/100	60/85	35/55	20/35		10/22	6/16	4/12	2/8
3c				100	75/100	60/85	30/50	20/35		5/20	3/12	2/8	0/4
3d			100	75/100		45/70	30/50	20/35		5/20	3/12	2/8	0/4
4c			100	80/100		60/80	48/65	35/50		19/30	13/23	7/15	0/8
Leveling Courses													
3b		100		100	75/100	60/85	35/55	20/35		10/22	6/16	4/12	2/8
5b				100	85/100		65/80	50/65	37/52	25/40	18/30	10/20	3/10
5c				100		85/100		65/80	47/68	30/55	20/40	10/25	3/8

Table 8.10 - Gradation Requirements for Hot-Mix Asphaltic Concrete Pavements

Traffic Category	Heavy		Medium		Light	
No. of Compaction Blows (each end of specimen)	75		50		35	
Test Property	Min	Max	Min	Max	Min	Max
Stability, (lbs.)	750	-	500	-	500	-
Flow, (0.01 in)	8	16	8	18	8	20
% air voids						
Surfacing	3	5	3	5	3	5
Sand mix	5	8	5	8	5	8
Base	3	8	3	8	3	8

Table 8.11 - Marshall Design Criteria

Source of crude Oil	Chemical Composition				Physical Properties							
					For Original A.C.				For the A.C. after TFOT			
	Wax % (1)	Oils %	Resin %	Asphaltene %	pen. (2) (1/10 mm)	duct. (cm)	R.&B. °C	Kin.vis. (3) (C.Stokes)	pen. (2) (1/10 mm)	duct. (cm)	R.&B. °C	Kin.vis (3) (C.Stokes)
Western region	7.9	28.3	53.4	18.3	52	>100	49.5	243	44	>100	50	333
	9.5	36.6	44.5	18.9	55	>100	50.0	274	44	>100	51	321
	6.9	35.6	51.8	12.6	58	>100	51	267	43	>100	51	369
	10.5	33.8	53.0	12.2	61	>100	46.5	309	38	>100	49	332
	7.9	30.7	57.2	12.1	57	>100	47.5	281	42	>100	50.5	337
	6.2	26	61.9	12.1	57	>100	47.5	312	43	>100	50.5	368
	6.5	20.6	66.3	13.1	-	-	-	-	-	-	-	-
	9.1	29.4	58.4	12.2	120	45	44	134	91	75	44.5	458
	6.4	22.8	64.0	13.1	51	53	48	295	46	>100	49.5	334
	9.4	22.6	64.7	12.7	54	>100	48.5	277	45	>100	49.5	345
	14.8	28.3	59.5	12.0	64	>100	45	257	45	>100	50	329
	11.4	32.0	53.3	14.6	65	>100	46	263	42	>100	51	332
	8.2	27.1	57.7	15.0	54	>100	47	298	36	>100	51	389
	8.4	30.1	55.7	14.1	55	>100	45.5	260	40	>100	53	292
	10.1	32.4	57.2	10.3	57	>100	46.5	264	44	>100	54.5	305
	6.1	27	54.5	18.4	57	>100	46	259	42	>100	54.5	389
	5.1	24.7	61.6	13.6	54	>100	49	273	37	>100	50.5	367
	6.5	23.7	62.1	14.1	57	>100	51	422	42	>100	53	491
	9.9	24.5	55.5	14.9	60	>100	50	359	34	>100	53	531
	5.5	20.4	63.2	16.3	62	>100	49	265	-	-	-	-
	6.4	22.1	63.4	14.4	85	>100	47	351	-	-	-	-
	10.8	32.1	54.4	13.7	75	>100	46	368	-	-	-	-
Eastern region	5.74	26.29	52.51	21.19	67	>100	53	340	53	>100	53.5	411
	6.5	29.77	50.11	20.11	63	>100	52	327	57	>100	52.5	487
	5.05	22.15	58.87	18.97	75	>100	51	383	36	>100	53.3	404
	5.29	29.01	48.96	22.03	61	>100	53	392	44	>100	54.5	822

(1) determined by Holde's method

(2) pen., 1/10 mm (100 gm, 5 sec, 25°C)

(3) kinematic viscosity, at 135°C, centi-stokes

Table 8.12- Chemical Composition and Physical Properties for Different Samples of AC 60/70 (Metwally et al., 1975)

Chemical Composition	Wax[1] Content, %	Oil Content, %	Resins, %	Asphaltene, %
Sample A[2]	12.7	43.8	36.4	19.8
Sample B[3]	6.9	32.1	46.0	22.0
Sample C[4]	6.1	29.6	58.1	12.1

[1]determined by Holde's method

[2]secured from the flushed asphalt batch

[3]secured at a depth of 1 cm from the pavement surface

[4]secured from the rest of the surface layer thickness

Table 8.13 Chemical Analysis of Field Core Samples (km 31, Cairo-Alexandria Agriculture Highway)

Sample No.	Stability (lbs)	% Stability*
1	1,458	75.1
2	1,117	57.5
3	1,346	69.4
4	767	39.5

* Values shown are the % stability of field samples to that of the design mix (1940 lbs.)

Table 8.14 Marshall Stability Values of Field Samples

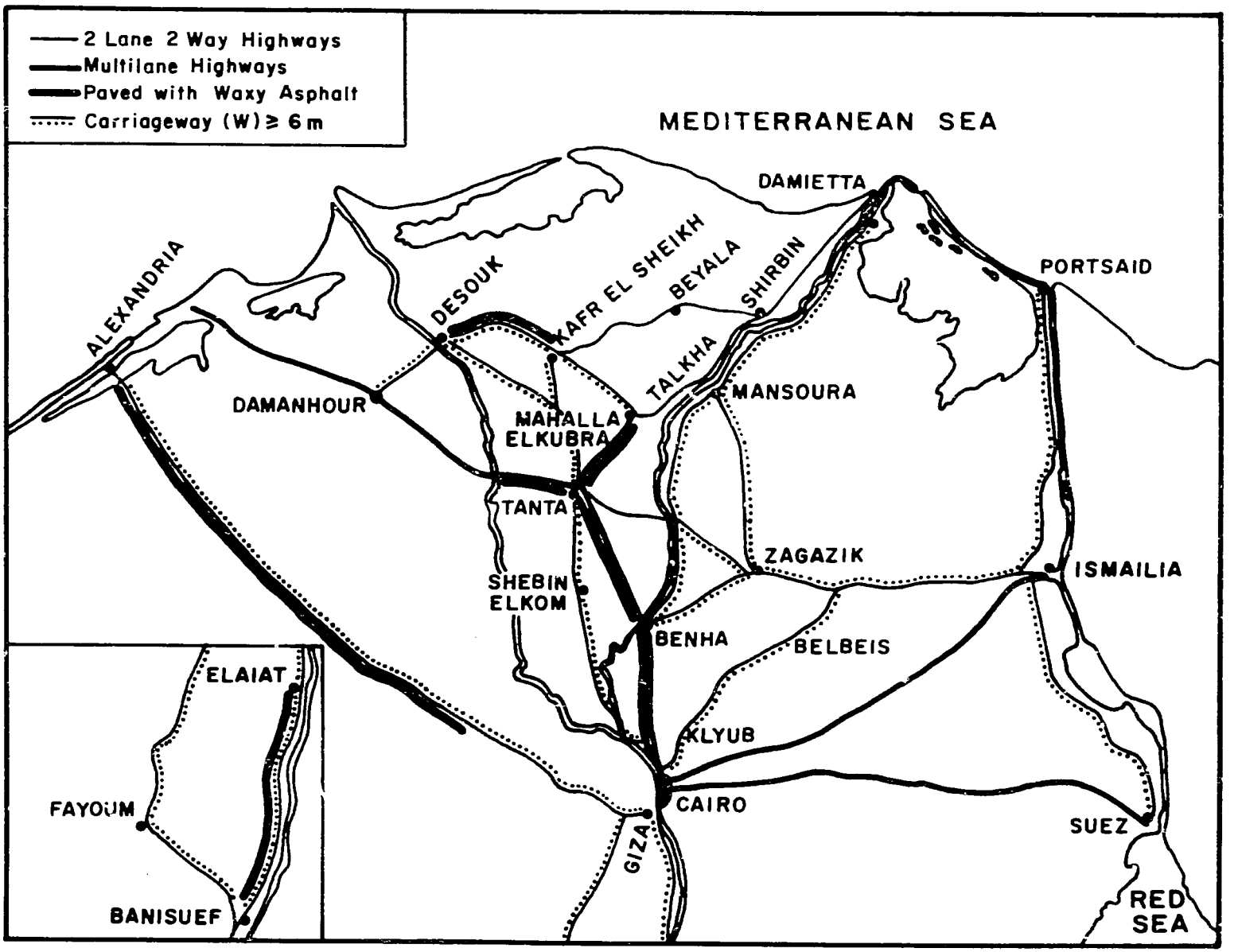


Figure 8.1 - The Main Links of the Egyptian Road Network (Lower Egypt)

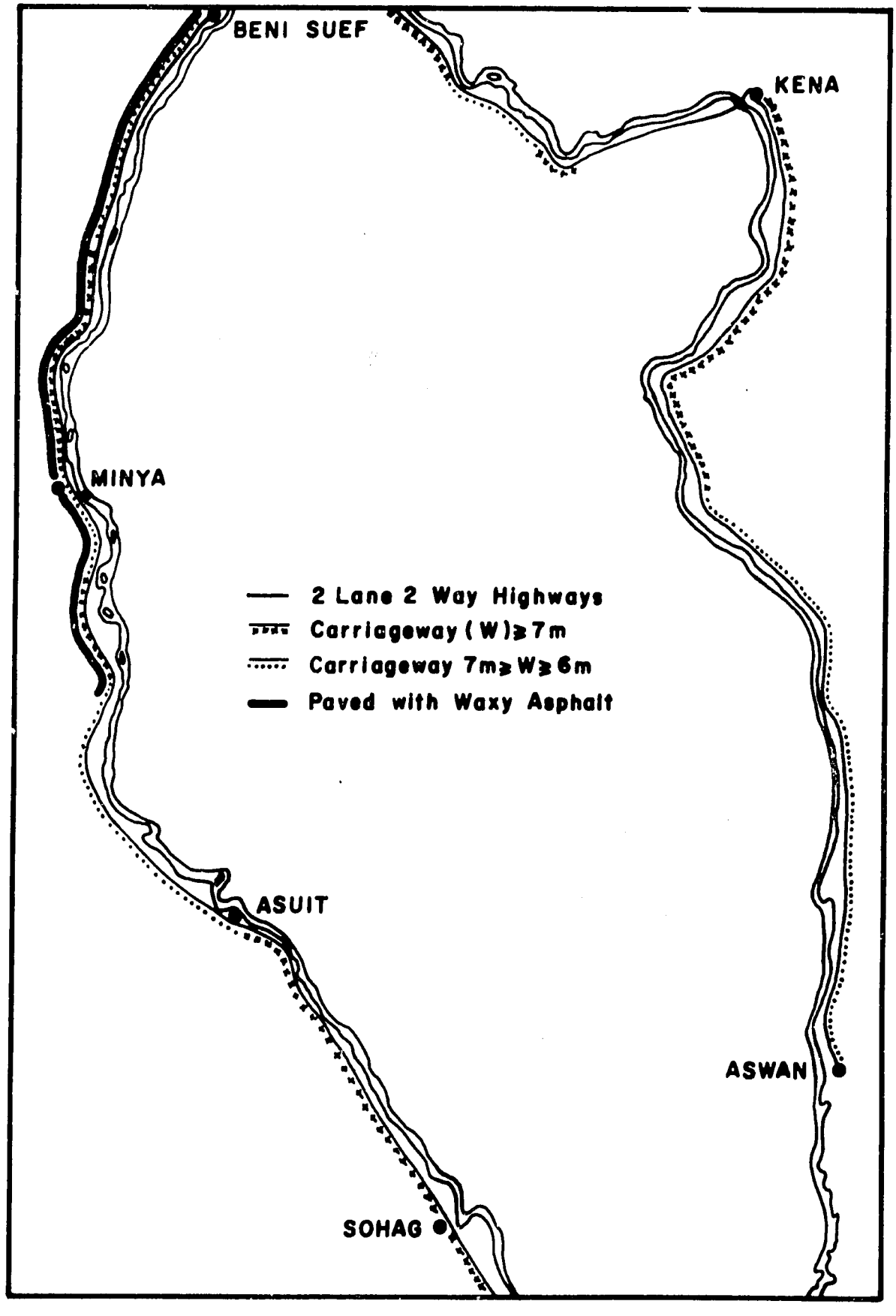
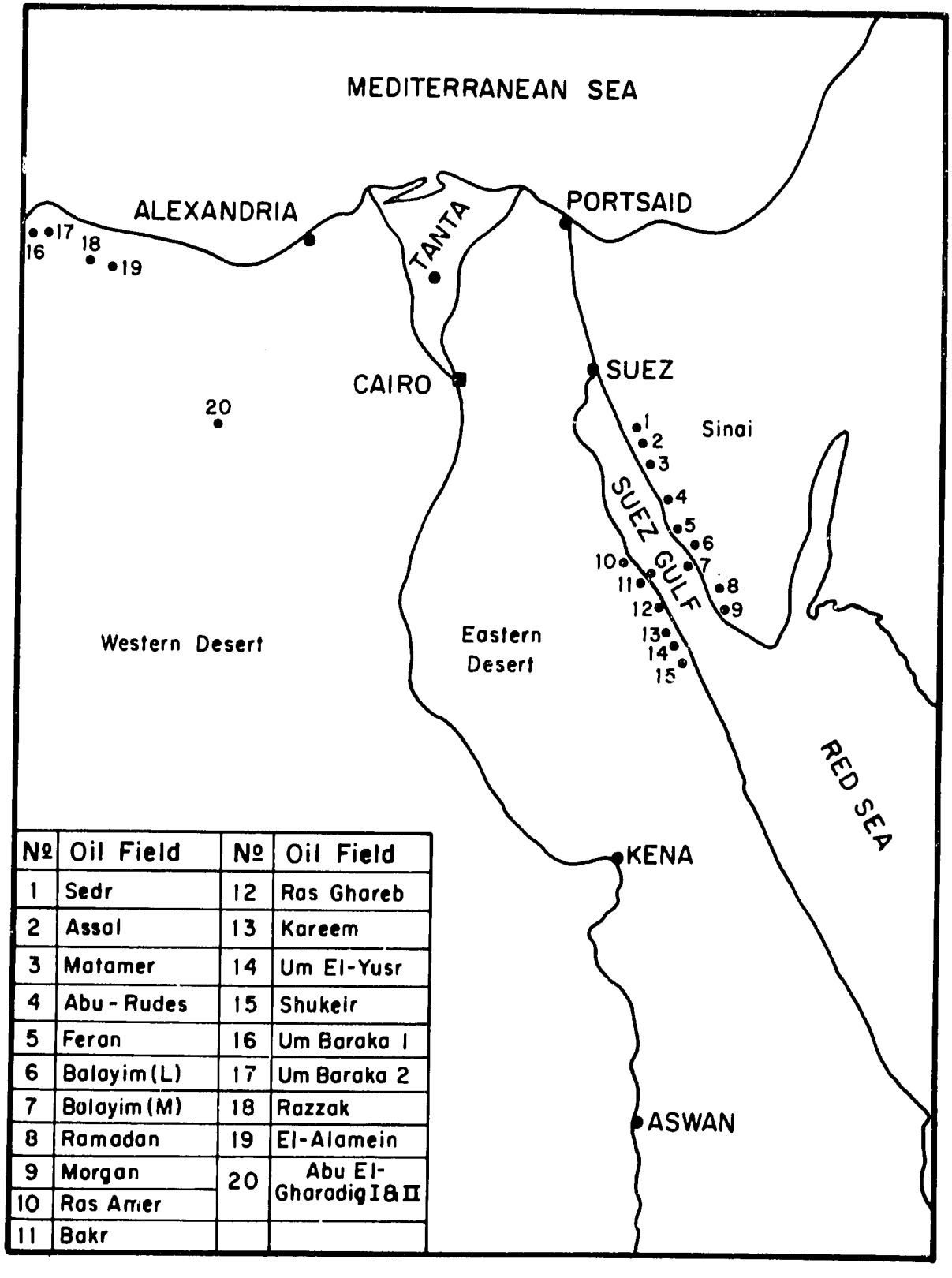
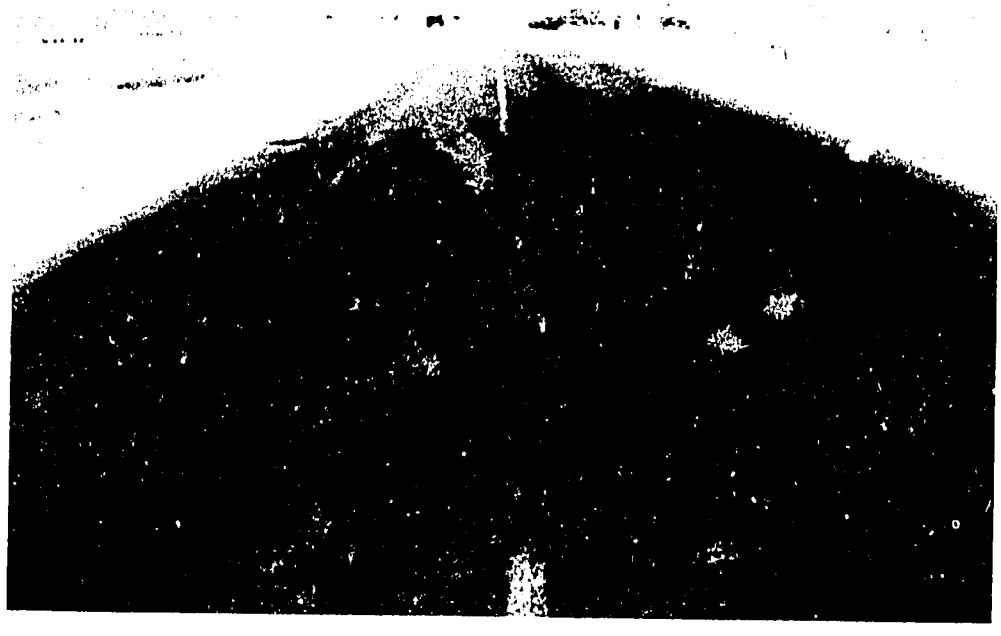


Figure 8.2 - The Main Links of the Egyptian Road Network (Upper Egypt)



№	Oil Field	№	Oil Field
1	Sedr	12	Ras Ghareb
2	Assal	13	Kareem
3	Matamer	14	Um El-Yusr
4	Abu-Rudes	15	Shukeir
5	Feran	16	Um Baraka 1
6	Balayim (L)	17	Um Baraka 2
7	Balayim (M)	18	Razzak
8	Ramadan	19	El-Alamein
9	Morgan	20	Abu El-Gharadig I & II
10	Ras Amer		
11	Bakr		

Figure 8.3 - Major Oil Fields in Egypt.



(a)

(b)

Fig. 3.4 - Pavement Distress (Cairo-Alexandria Highway)

CHAPTER 9

REFERENCES

Asphalt Institute, "Specifications for Paving and Industrial Asphalts," Specification Series, No. 2 (SS-2), 1979.

Bengen, F., German Patent Appl. OZ 12438, Bengen, F., W. Schlenk. Experiments, 5, 200, 1949.

Berridge, S.A., "Finishing Processes," Chapter 11, Modern Petroleum Technology, edited by G.D. Hobson in Collaboration with W. Phol, John Wiley and Sons, New York, 1973, pp. 375-439.

Blott, J.F.T., R.T. Hughes and L.A. Werrett. "The Wetting of Solids by the Process of Direct Contact. Adhesion and Adhesives, Fundamentals and Practice," Society of Chemical Industry, London, 1954.

Buchler, C.C. and G.D. Graves. G.D. Ind. Eng. Chem., 19, 718, 1927.

Centolani, G., et al. Question II, No. II-13, XIV World Road Congress, Prague, 1971.

Clerk, R.J. and M.J. O'Neal, "The Mass Spectrometer Analysis of Asphalt; A Preliminary Investigation," Symposium on Fundamental Nature of Asphalt Sponsored by Div. of Petr. Chem. of the Am. Chem. Soc., N.Y., Sept. 11-16, 1960, Vol. 5, A-5.

Colthup, N.L., Daly and S. Wiberley, "Infrared and Raman Spectroscopy," New York: Academic Press, 1964.

Commins, B., Polycyclic, "Aromatic Hydrocarbons in Carbonaceous Meteorites," Nature 212, 1966, pp. 273-274.

Creanga, C., "Studu Si cercetari de Chimie," Acad. R.P.R. IX, 1, 193, 1961.

Dean, R.A., European Chemical News, Normal Paraffin Supplement, 10, 18, 1966.

Dean, R.A., and E.V. Whitehead, "The Composition of High Boiling Petroleum Distillers and Residues," Sec. V, Paper 9, Proc. 6th World Petr. Congr. Frankfurt/Main 1963.

Deacon, J.A., "Fatigue of Asphalt Concrete," Ph.D. Dissertation, University of California, Berkeley, 1965.

Dickie, J.P., and T.F. Yen. "Electron Microscopic Studies on Petroleum Asphaltenes," Paper presented before the Division of Pet. Chem., Am. Chem. Soc., N.Y. City Meeting, Sept. 11-16, General Paper, Vol. 11, pp. 39-47, 1966.

Erdman, J.G., "The Molecular Complex Comprising Heavy Petroleum Fraction," Hydrocarbon Analysis, ASTM Special Technical Publication, 389, 1965, pp. 259-300.

Evans, J.V., W. Herschel and R.F. Marscher. "Contribution of Components to Asphalt Consistency," Reprint A.S.C., March, 1971, D. 13.

Ewers, N., et al., Question II, No. II-1, XIV, World Road Congress, Prague, 1971.

Ferris, S.W., E.P. Black and J.B. Clelland, "Aromatic Structures in Asphalt Fractions," Preprints, Symposium on Characterization and Processing of Heavy Ends of Petroleum, Am. Chem. Soc.; Pittsburgh, PA. Meeting, March 23-26, 1966, Vol. 11, No. 2, pp. 130-139.

Gray, G.G., J. Inst. Petrol., 29, 226, 1943.

Gregg, S.J. "The Surface Chemistry of Solids." Chapman and Hall, London, 1951.

Hadley, W.O., Hudson, W. and Kennedy, T.W., "Correlation of Tension Properties with Stability and Cohesiometer Values for Asphalt Treated Materials," Center for Highway Research, University of Texas at Austin, Austin, Texas, June, 1970.

Heukelom. W., "A Bitumen Test Data Chart for Showing the Effect of Temperature on the Mechanical Behavior of Asphaltic Bitumen," Journal of the Institute of Petroleum, Vol. 55, 546, 1969.

Heukelom. W., "An Improved Method of Characterizing Asphaltic Bitumens with the Aid of their Mechanical Properties," Proc. AAPT, Vol. 42, 1973.

Heukelom, W., and A.J.G. Klomp, "Road Design and Dynamic Loading," Proceedings of the AAPT, Vol. 33, 1964.

Johnson, J.F., Ind. Eng. Chem., 46, 1046, 1954.

Johgepier, R., and B. Kuilman. "Characteristics of the Rheology of Bitumens," Proc. AAPT, Vol. 38, 1969.

Kallas, B.F., "Dynamic Modulus of Asphalt Concrete in Tension and Tension-Compression," AAPT, 1970.

Kallas, B.F. and J.C. Riley, "Mechanical Properties of Asphalt Pavement Materials," Proceedings, Second International Conference on the Structural Design of Asphalt Pavements, 1967.

King, P.J., F. Morton and A. Sagarra, "Chemistry and Physics of Petroleum," Chapter 6, Modern Petroleum Technology, edited by G.D. Hobson in collaboration with W. Phol, John Wiley and Sons, New York, 1973, pp. 186-219.

Krebs, R.D. and R.D. Walker, "Highway Materials," McGraw-Hill Book Company, New York, 1971, 428 p.

Lane, E. and E. Garton, U.S. Bureau of Mines, Report of Investigations, No. 3279, 1935.

Lewis, R.H. and J.Y. Welborn. "The Properties of the Residues of 50-60 and 85-100 Penetration Asphalts from Oven Tests and Exposures," Public Roads, Vol. 22, No. 2, April, 1941.

Lopienska, H., Question II, No. II-18, XIV World Road Congress, Prague, 1971.

Mair, B., R. Zalman, E. Eisenbraun, and A. Hordoysky, "Terpenoid Precursors of Hydrocarbons from Gasoline Range of Petroleum." Science 154, 1966, pp. 1339-1341.

Mallison, H. Petroleum Z., 33, 1397, 1927.

Martin, J.R. "Simplified Curing Index Determinations for RC-2 Cutbacks," Oklahoma A and M Experimental Station, Bulletin 72, May, 1949.

Martin, J.M., R.W.B. Johnston, J.H. Cannon and M.J. O'Neal, Analy. Chem., 30, 1005, 1958.

Marya, J.S. et al., Question II, No. II-27, XIV, World Road Congress, Prague, 1971.

McLeod, N.W., "The Asphalt Institute's Layer Equivalency Program," Research Series No. 15 (RS-15), The Asphalt Institute, College Park, Maryland, March 1967.

McLeod, N.W., "Prepared Discussion on St. Anne Test Road," CTAA, 1969.

Metwally, S.S., F. Mikhail, A.M. Sadek, and M.T. Mostafa. "Flexible Pavements Paraffinic Asphalt Cements." XI World Road Congress, Mexico, October, 1975.

Mikhailov, V.V. et al. Question II, No. II-25, XIV World Road Congress, Prague, 1971.

Minchin, S.T. J. Inst. Petrol., 34, 448, 1948.

Monismith, C.L. "Asphalt Paving Mixtures," Short Course in Asphalt Paving Technology, University of California, Berkeley, 1961.

Monismith, C.L., R.L. Alexander and K.E. Sector. "Rheologic Behavior of Asphalt Concrete," Proceedings , AAPT, Vol. 35, 1966.

Niemi, A. Question II, No. II-8, XIV World Road Congress, Prague, 1971.

Nijboer, L.W. "Einige Betrachtungen uber das Marshallverfahren zur Untersuchung Bituminoser Massen," Strasse und Autobahn, 8, 1957, p. 210.

Ogilvie, J.L., M.C. Simmons and G.P. Hinds. Anal. Chem., 30, 25, 1958.

O'Neal, M.J., Hydrocarbon Research Group, I.P., London, 1953.

Papazian, H.S. "The Response of Linear Viscoelastic Materials in the Frequency Domain with Emphasis on Asphaltic Concrete," International Conference on the Structural Design of Asphalt Pavements, Michigan, 1962.

Pfiffer, J.P., and P.M. Van Doormal. "The Rheological Properties of Asphaltic Bitumens," Inst. Petrol. Tech. Journal, 1936.

Ridenour, W.P., I.J. Spliners and P.R. Templin, TAPPI, 41, 257, 1958.

Saal, R.H.J., and R.W.A. Labout, "Rheological Properties of Asphalts," Rheology, Vol. II, Chapter 9, edited by F.R. Eirich.

Sayer, W.F., R.F. Patterson and J.L. Keays. J. Am. Chem. Soc., 66, 179, 1944.

Schaerer, A.A., C.J. Busso, A.E. Smith and L.B. Skinner. J. Am. Chem. Soc., 77, 2017, 1955.

Seed, H.B., C.K. Chan, and C.E. Lee. "Resilience Characteristics of Subgrade Soil and their Relation to Fatigue Failure in Asphalt Pavements." Proceedings, First International Conference on the Structural Design of Asphalt Pavements, Ann Arbor, 1962.

Shook, J.F., and B.F. Kallas, Factors Influencing Dynamic Modulus of Asphalt Concrete," Proceedings, Association of Asphalt Paving Technologists, Vol. 38, 1969.

Sugihara, J.M., T. Okada, and J.F. Branthover, "Reductive Desulfurization on Vanadium and Metallo Porphyrin Contents of Fractions from Boscan Asphaltenes," J. Chem. Eng. Data, 11, 190-194, 1965.

Van der Poel, C., "A General System Describing the Viscoelastic Properties of Bitumens and its Relation to Routine Test Data," Journal of Applied Chemistry, May, 1954.

Van Dratt, W.E.F., and P. Sommer. "Ein Gerat Zur Bestimmung der Dynamischen Elastizitatsmoduln von Asphalt," Strasse und Autobahn, Vol. 35, 1966.

Wallace, H.A. and J.R. Martin. "Asphalt Pavement Engineering," McGraw-Hill Book Company, New York, 1967, 351 p.

Watson, K.M., E.F. Nelson, G.B. Murphy. Ind. Eng. Chem., 27, 1460, 1935.

Williams, R.B., and N.F. Chamberlain. Sixth World Petrol. Cengr. Proc., Section V, Paper 17, Frankfurt/Mains, 1963.

Winnifford, R.S. Evidence for the Association of Asphaltenes in Dilute Solutions, J. Inst. Petrol., 49, 1963, pp. 215-221.