PAVEMENT MATERIALS

Lecture 16

Pavement Surface Layers

- Bituminous Materials
- Aggregates
- Asphalt-Aggregate Interaction
  - Adhesion
  - Water Sensitivity
- Asphalt-Aggregate Mixtures
  - Weight-Volume Relationships
  - Design (Mix Design Methods)
  - *CRITICAL ISSUES*
- Construction

Bituminous Materials

- Definitions
  - BITUMEN?
  - ASPHALT?
  - TAR?........
- History
- Sources / Manufacture
- Chemical Composition
- Structure
- Properties
  - Chemical, Physical, Rheological

Lecture 14 & 15

Bituminous Materials-*Chemistry*

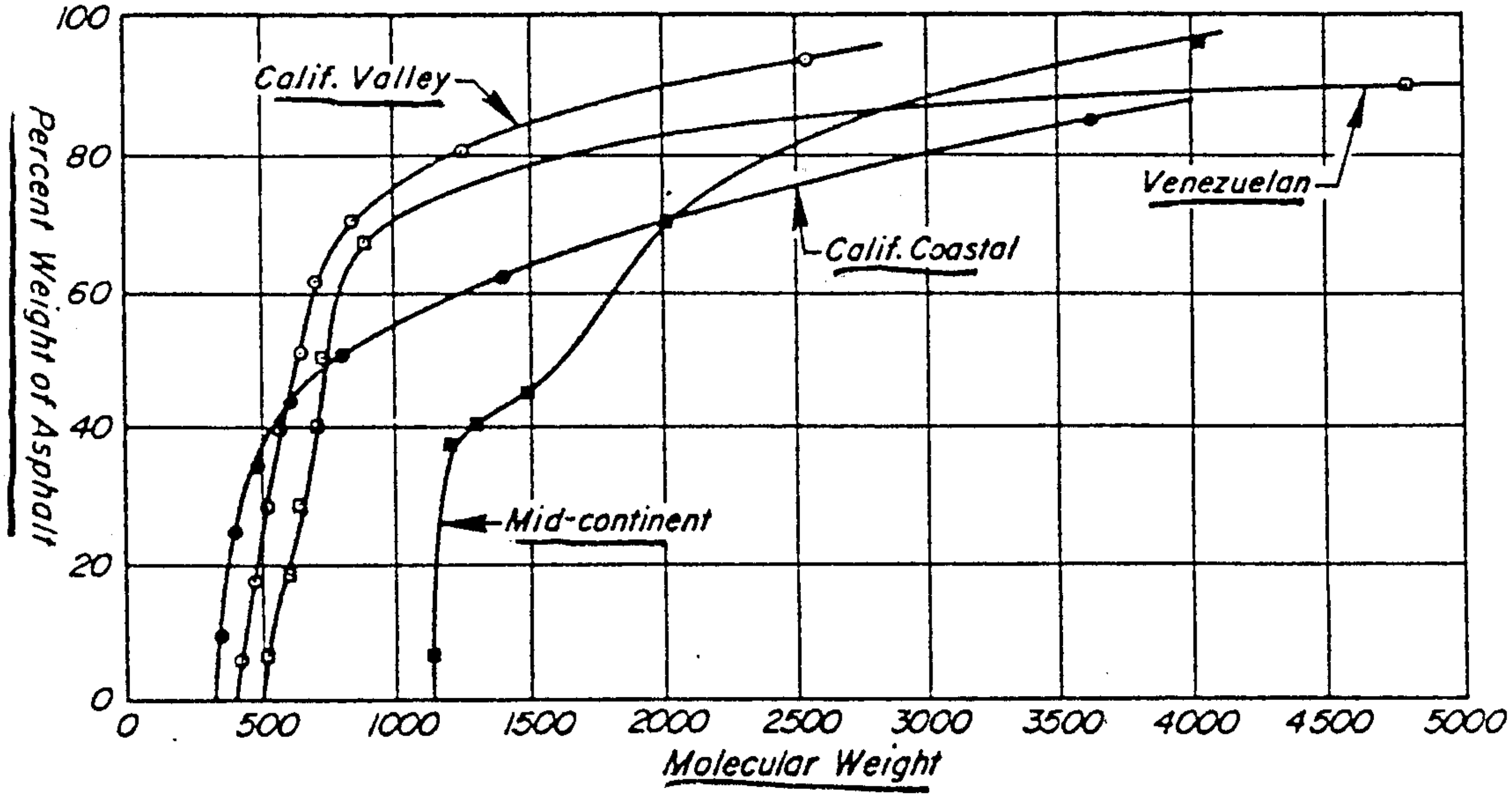
- *Asphalts are Complex Mixtures of Hydrocarbons*
- Hydrocarbons are compounds that contain carbon and hydrogen.

- Organic Chemistry
- In organic chemistry, hydrocarbons are classified on the basis of chemical behavior as saturated or unsaturated.
- Essentially, saturated hydrocarbons have no multiple linkages between carbon atoms.
- Unsaturated hydrocarbons contain one or more double or triple bonds between carbon atoms and, as a consequence, have a great reactivity with other elements.

Bituminous Materials-*Chemistry*

- Asphalt Composition

- Asphalts are a complex mixture of hydrocarbons, varying, in the case of semi-solid asphalt cements, from low molecular weight (approximately 300) materials to very high molecular weight materials (larger than 5000).
- Figure illustrates the molecular weight distribution of four penetration asphalt cements.
- Although these materials have the same consistency at a specific temperature, 77 F (25C), it can be seen that the size distribution is different. It is quite probable that these materials will react differently to changes in temperature and behave differently under load.
- Moreover, the chemical composition of the materials will, in all probability, vary in the different molecular weight ranges, depending upon the crude oil source.
- *Hence, suffice it to say that each material is quite complex unto itself and the materials vary considerably among each other chemically.*



✳ FIGURE 1.14 - MOLECULAR WEIGHT DISTRIBUTION OF FOUR 200 PEN. ASPHALT CEMENTS. (after Griffin, Simpson and Miles)

Bituminous Materials-*Chemistry*

- Asphalt Composition

- Some generalizations can be made, however, with regard to the chemical composition of the semi-solid materials. According to Simpson they generally consist of
- Carbon (70-85%)
- Hydrogen (7-12%)
- Nitrogen (0-1%)
- Sulfur (1-7%)
- Oxygen (0-5%)
- and small amounts of metals either dispersed in the form of oxides and salts or in metal containing organic compounds

Bituminous Materials-*Chemistry*

- Asphalt Composition

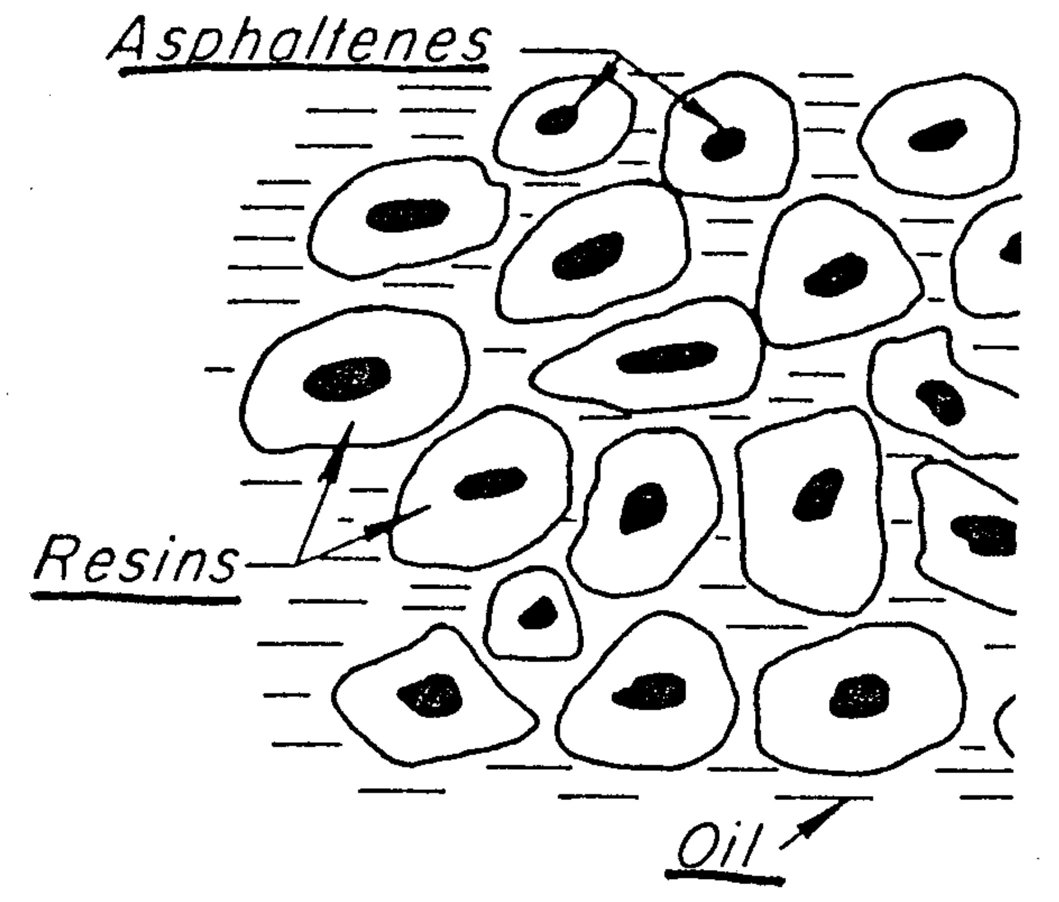
- The lighter molecular weight materials contain a considerable amount of carbon and hydrogen in the form of chain-type or aliphatic organic compounds.
- As the molecular weight increases the tendency toward ring type (naphthenic or aromatic) organic compounds is more apparent with the side chains attached to the ring sections.
- The very high molecular weight compounds consist primarily of the ring type materials with very few side chains of the aliphatic variety present. It is in the higher molecular weight ranges where the other elements mentioned above, i.e., nitrogen, oxygen, sulfur.

Bituminous Materials-*Chemistry*

- Asphalt Composition
- For convenience, the wide spectrum of organic compounds contained in an asphalt are separated into a number of components, one commonly used classifications states that asphalts can be separated into:

- ASPHALTENES
- RESINS
- OILS

MALTENES



Bituminous Materials-*Chemistry*

- Asphalt Composition

- ASPHALTENES are the high molecular weight materials and are primarily of an aromatic nature with very few side chains attached. The hypothetical asphaltene molecule shown in Figure illustrates qualitatively, at least, this composition. It will be noted that sulfur and nitrogen are incorporated in the ring structure in this type of material.
- Asphaltenes have been defined by ASTM as: the components of the bitumen in petroleum, petroleum products, malthas, asphalt cements, and solid native bitumens, which are soluble in carbon disulfide but insoluble in paraffin naphthas.

- RESINS are the intermediate molecular weight materials and contain more side chains than the asphaltenes. Some sulfur and nitrogen is also included in these materials, but to a lesser extent than in the asphaltenes. The resins are polar molecules resulting from their aromaticity and the inclusion of sulfur. This polar nature gives resins the ability to be adsorbed by and to dissolve the asphaltenes.

Bituminous Materials-*Chemistry*

- Asphalt Composition

- OILS are the lightest molecular weight materials in the asphalt and generally have a large number of chains in proportion to the number of rings. A number of the materials in this range are naphthenic-type closed chains.

Bituminous Materials-*Chemistry*

- Asphalt Composition (ASPHALTENE)

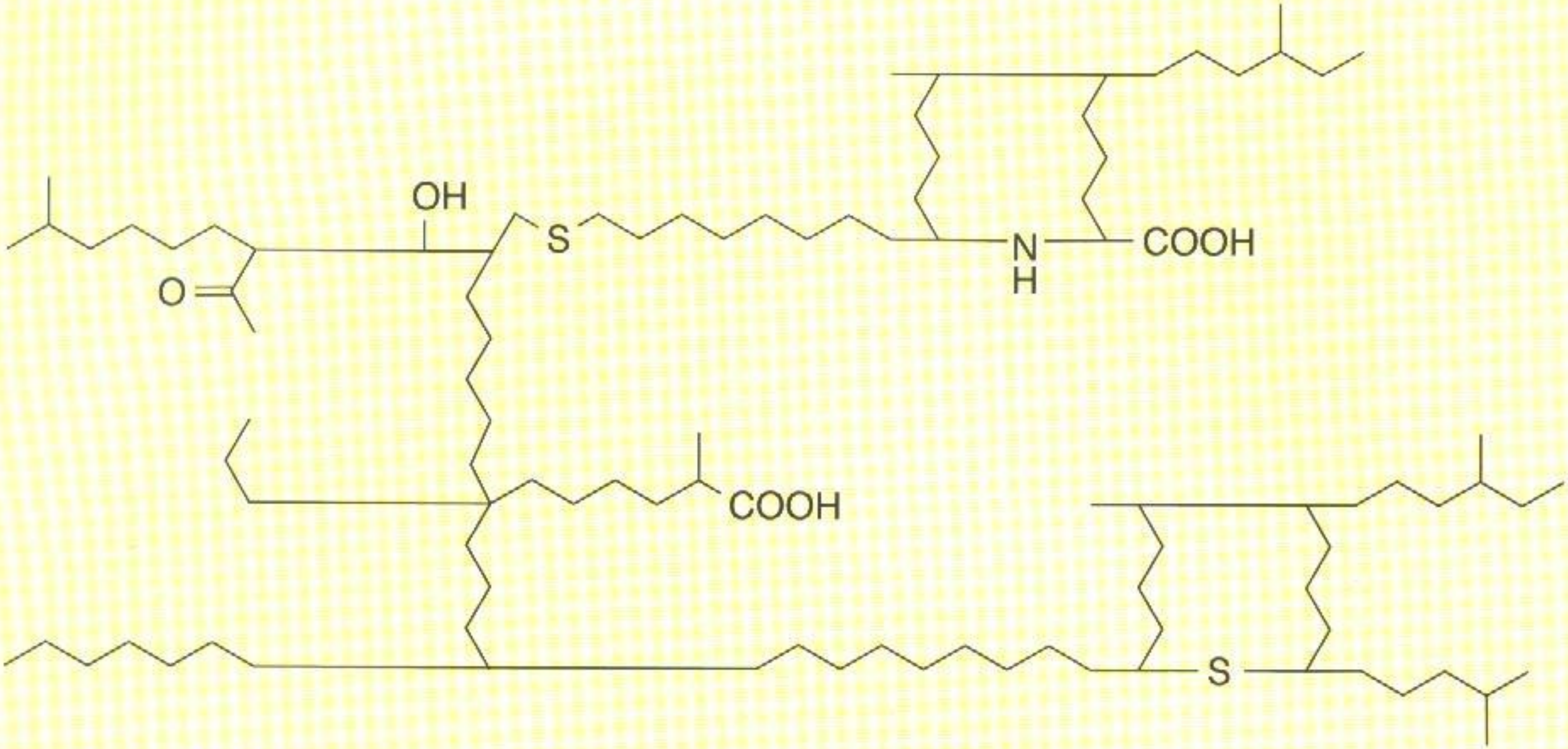


Fig. 3.2 Asphaltene structure

Bituminous Materials-*Chemistry*

- Asphalt Composition
- It should be emphasized at this point that the asphaltenes, resins, and oils are not three distinct compounds. Rather, there exists a range in molecular weights in the oil fraction, the resin fraction, and the asphaltene fraction.
- Moreover, the composition of the materials in each fraction and in each asphalt will vary, depending upon the crude source and method of manufacture.
- In addition to the classification listed above, other terminology has also been used to describe the various components of asphalt. For example, the oils plus resins are at times referred to as maltenes.
- *Actually, there are many methods used to separate asphalts into components for study. Some separation techniques are based on chemical reactivity while others are based on molecular weight or a combination or both.*

Bituminous Materials-*Chemistry*

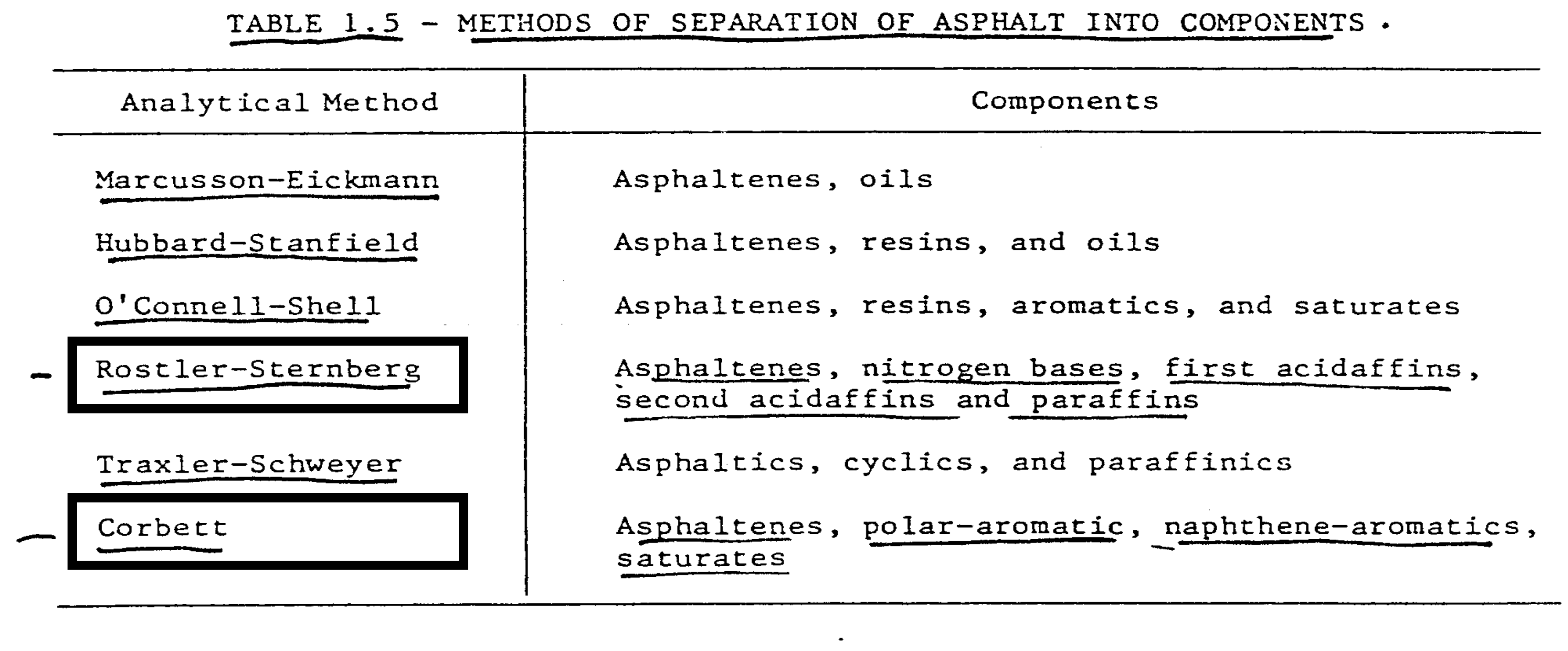


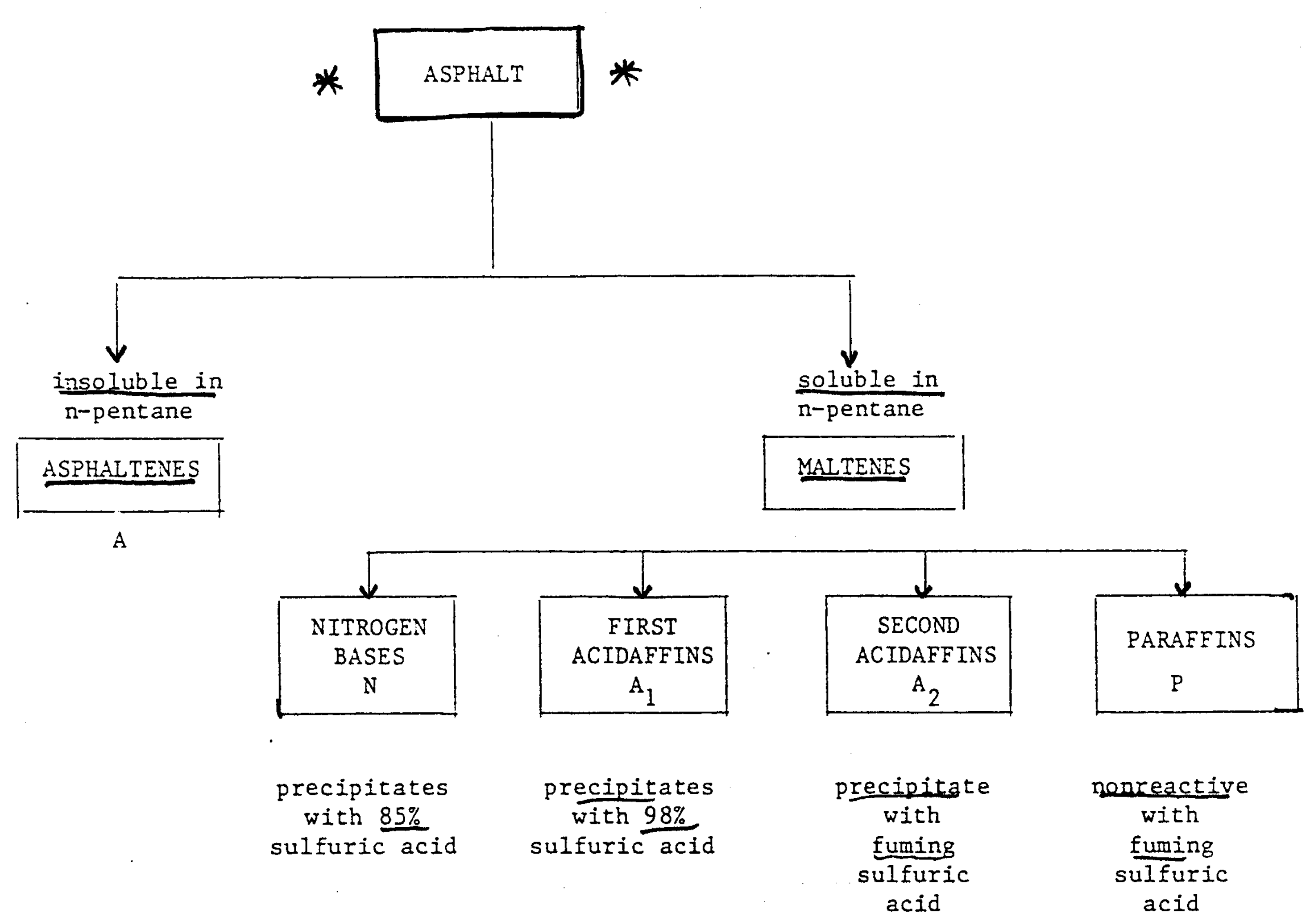
TABLE 1.5 – METHODS OF SEPARATION OF ASPHALT INTO COMPONENTS.

Analytical Method	Components
Marcusson-Eickmann	Asphaltenes, oils
Hubbard-Stanfield	Asphaltenes, resins, and oils
O'Connell-Shell	Asphaltenes, resins, aromatics, and saturates
Rostler-Sternberg	Asphaltenes, nitrogen bases, first acidaffins, second acidaffins and paraffins
Traxler-Schweyer	Asphaltics, cyclics, and paraffinics
Corbett	Asphaltenes, polar-aromatic, naphthene-aromatics, saturates

- The solution and precipitation method developed by Rostler-Sternberg
- The chromatic method advance by Corbett
- *have been the most widely used.*

Bituminous Materials-*Chemistry*

- Rostler-Sternberg



* ASPHALT *

insoluble in n-pentane

ASPHALTENES

A

soluble in n-pentane

MALTENES

NITROGEN BASES N

precipitates with 85% sulfuric acid

FIRST ACIDAFFINS A_1

precipitates with 98% sulfuric acid

SECOND ACIDAFFINS A_2

precipitate with fuming sulfuric acid

PARAFFINS P

nonreactive with fuming sulfuric acid

Bituminous Materials-*Chemistry*

- Rostler-Sternberg

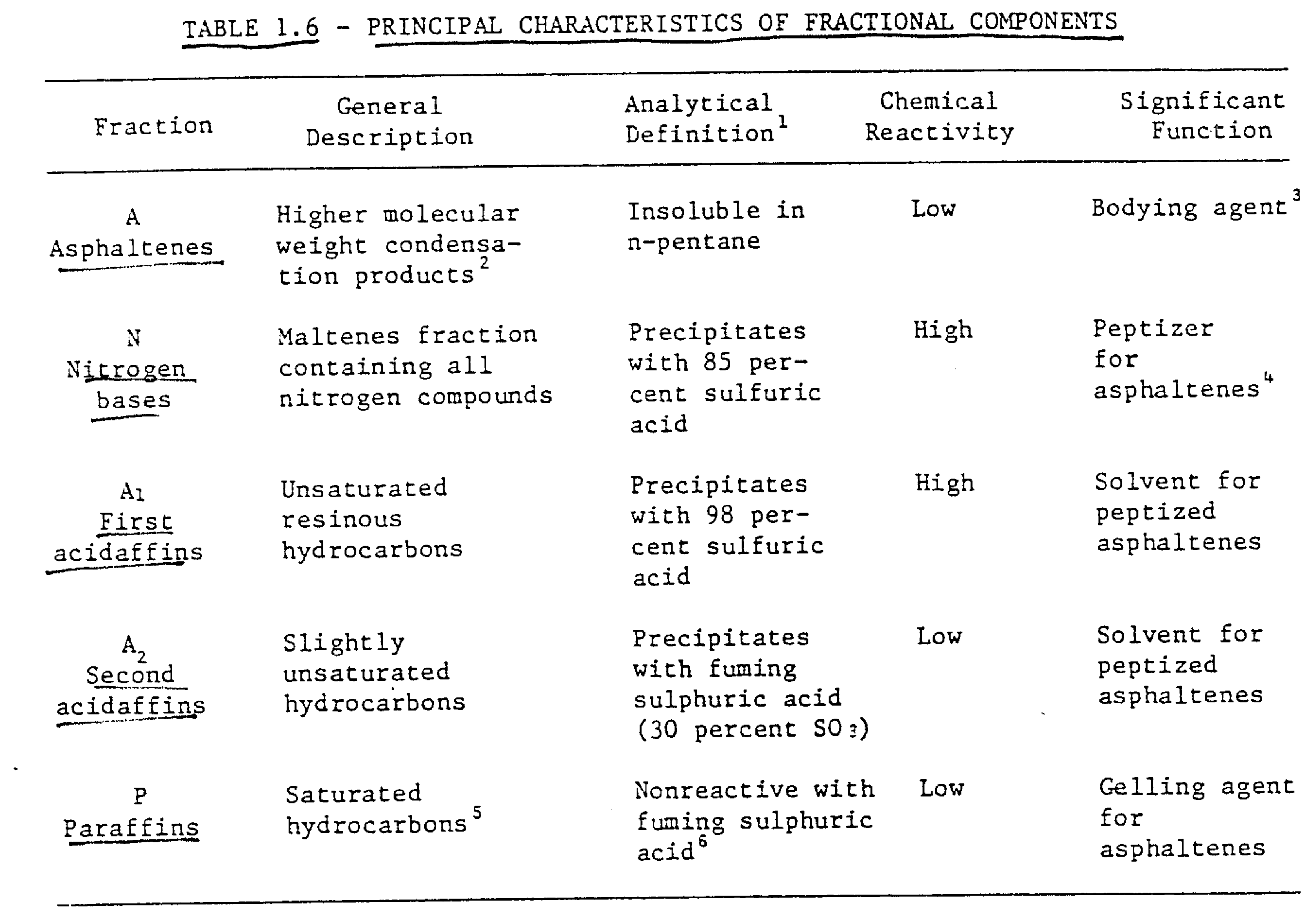
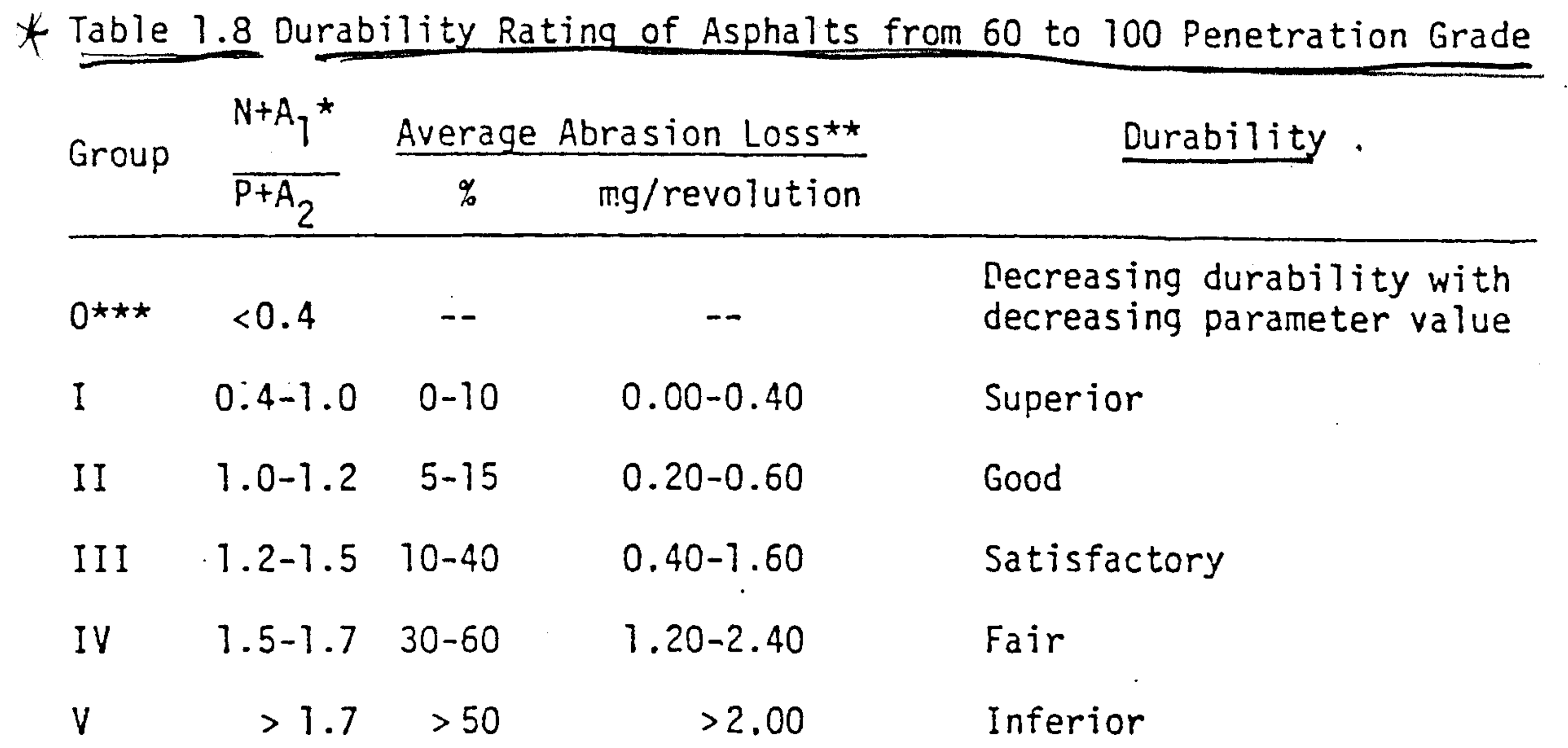


TABLE 1.6 - PRINCIPAL CHARACTERISTICS OF FRACTIONAL COMPONENTS

Fraction	General Description	Analytical Definition[1]	Chemical Reactivity	Significant Function
A Asphaltenes	Higher molecular weight condensation products[2]	Insoluble in n-pentane	Low	Bodying agent[3]
N Nitrogen bases	Maltenes fraction containing all nitrogen compounds	Precipitates with 85 percent sulfuric acid	High	Peptizer for asphaltenes[4]
A_1 First acidaffins	Unsaturated resinous hydrocarbons	Precipitates with 98 percent sulfuric acid	High	Solvent for peptized asphaltenes
A_2 Second acidaffins	Slightly unsaturated hydrocarbons	Precipitates with fuming sulphuric acid (30 percent SO_3)	Low	Solvent for peptized asphaltenes
P Paraffins	Saturated hydrocarbons[5]	Nonreactive with fuming sulphuric acid[6]	Low	Gelling agent for asphaltenes

Bituminous Materials-*Chemistry*

- Rostler-Sternberg



✱ Table 1.8 Durability Rating of Asphalts from 60 to 100 Penetration Grade

Group	$\frac{N+A_1}{P+A_2}$*	Average Abrasion Loss** %	Average Abrasion Loss** mg/revolution	Durability
0***	<0.4	--	--	Decreasing durability with decreasing parameter value
I	0.4-1.0	0-10	0.00-0.40	Superior
II	1.0-1.2	5-15	0.20-0.60	Good
III	1.2-1.5	10-40	0.40-1.60	Satisfactory
IV	1.5-1.7	30-60	1.20-2.40	Fair
V	> 1.7	> 50	> 2.00	Inferior

Bituminous Materials-*Chemistry*

- Corbett Method

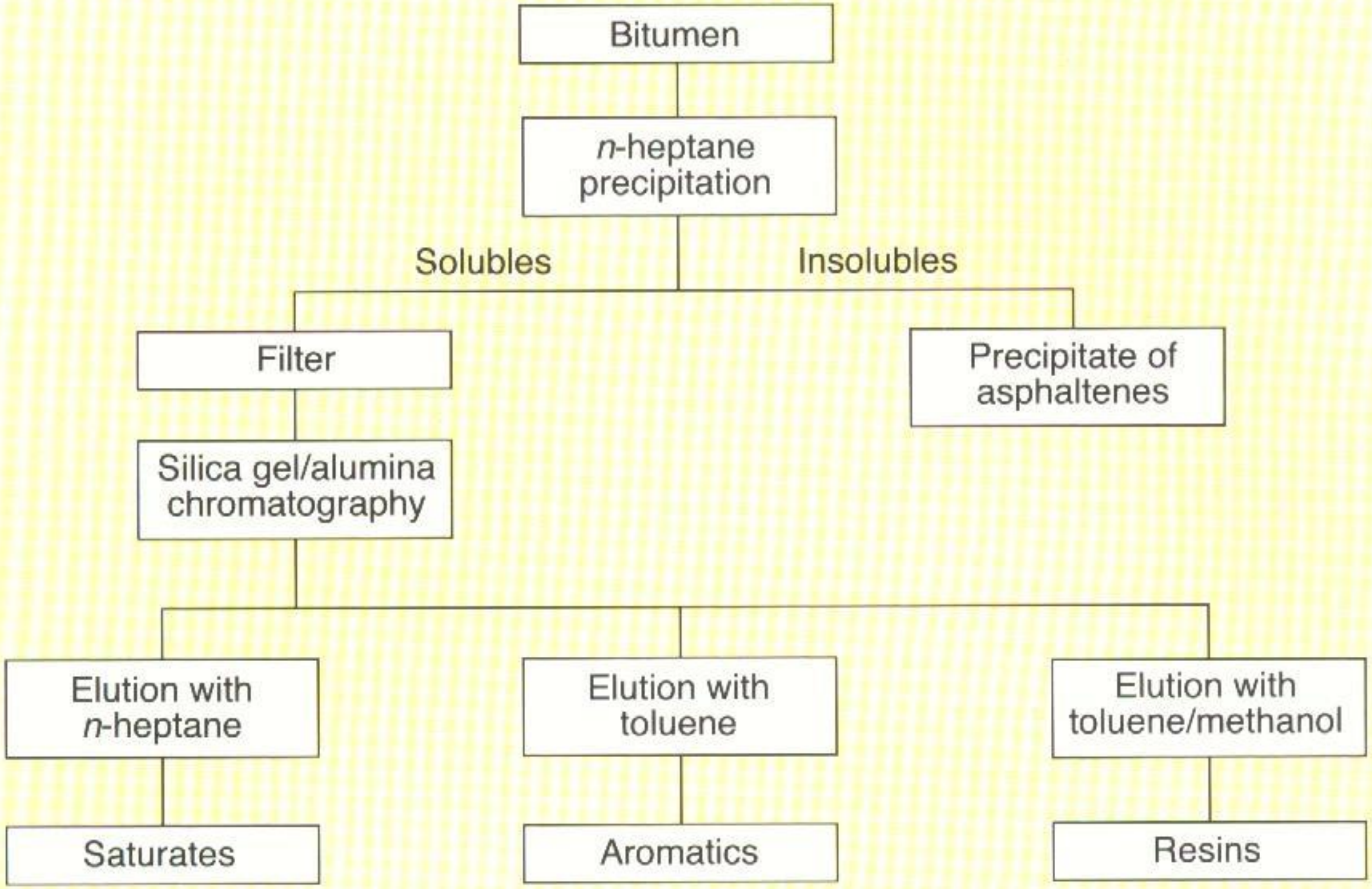


Fig. 3.1 Schematic representation of the analysis for broad chemical composition of bitumen

Bituminous Materials-*Chemistry*

- Corbett Method

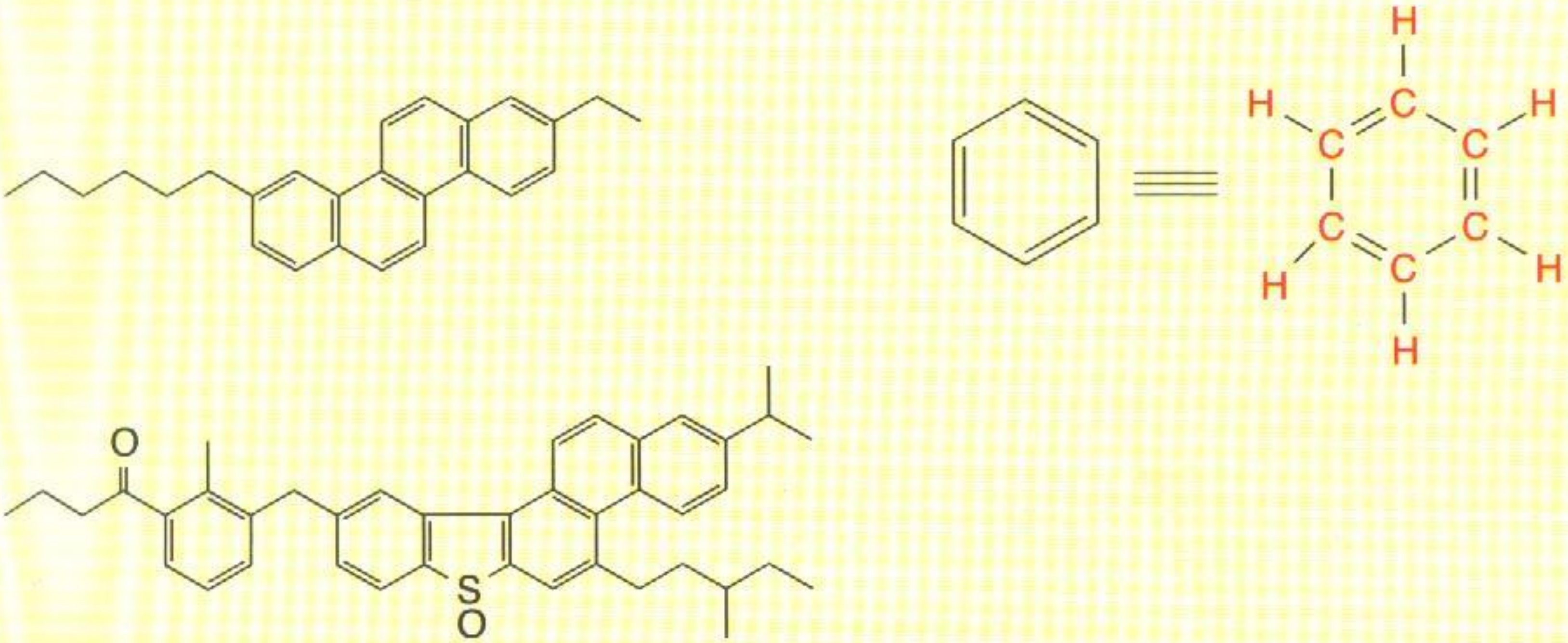


Fig. 3.3 Aromatic structures

Bituminous Materials-*Chemistry*

- Corbett Method

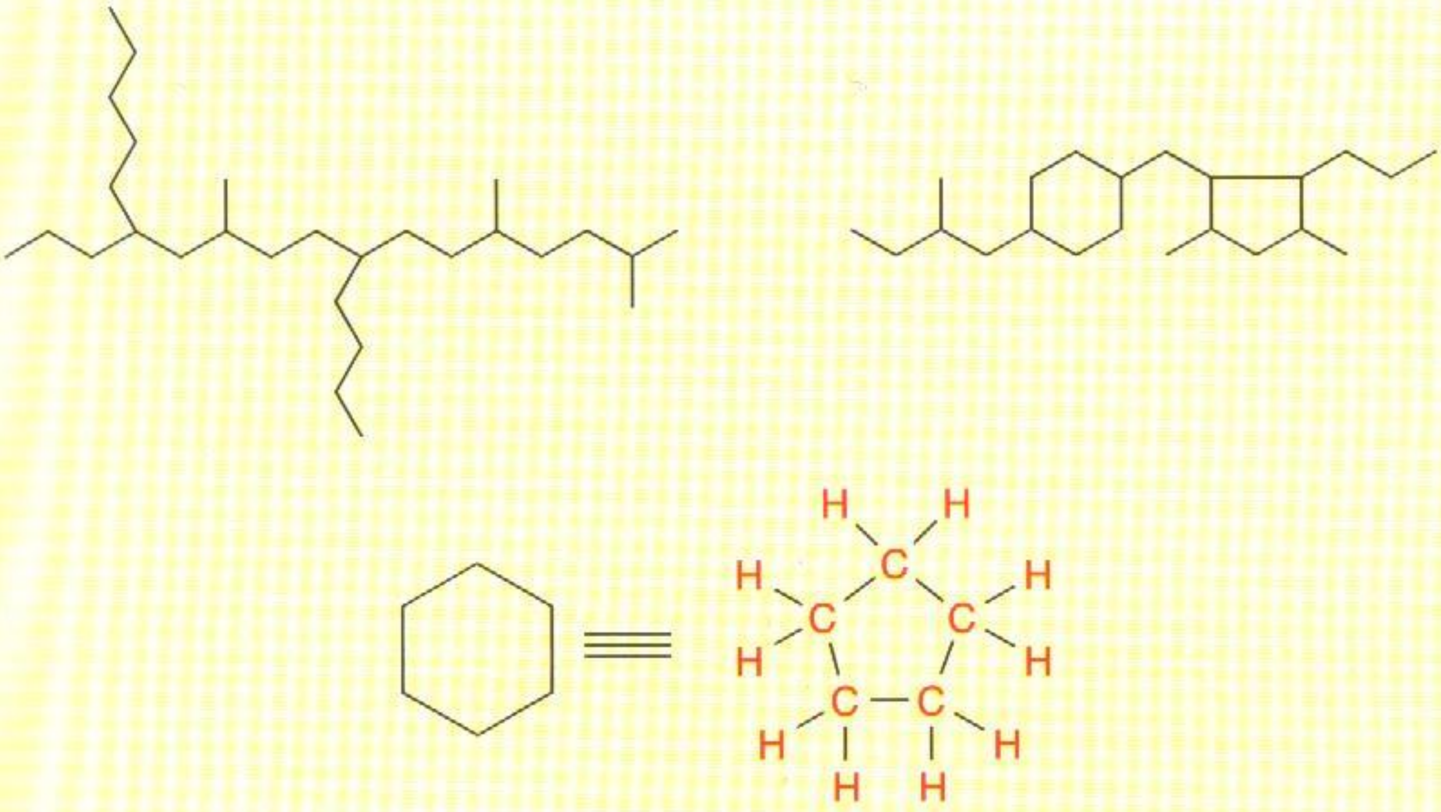


Fig. 3.4 Saturate structures

Bituminous Materials-*Chemistry*

- Corbett Method

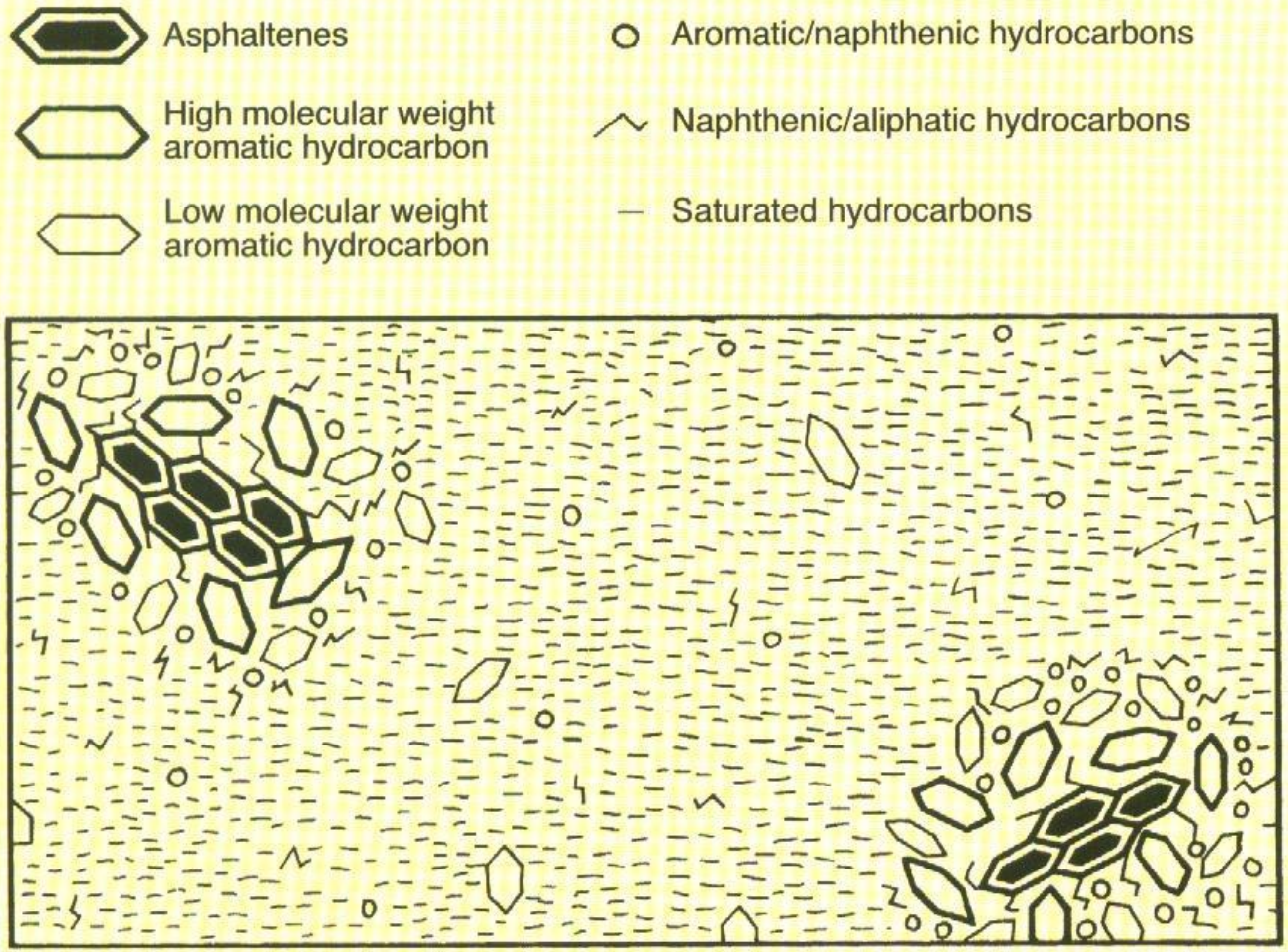


Fig. 3.5 Schematic representation of a SOL type bitumen

Bituminous Materials-*Chemistry*

- Corbett Method

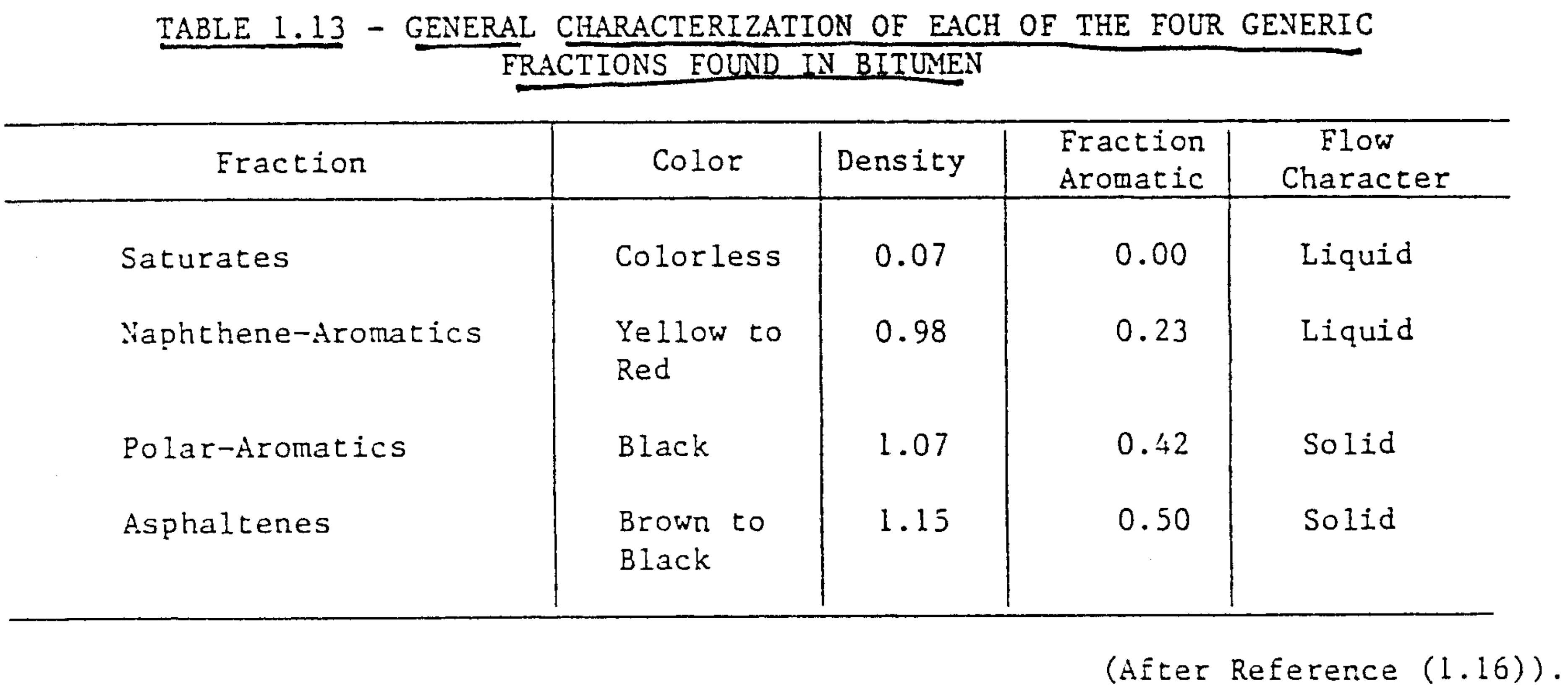


TABLE 1.13 - GENERAL CHARACTERIZATION OF EACH OF THE FOUR GENERIC FRACTIONS FOUND IN BITUMEN

Fraction	Color	Density	Fraction Aromatic	Flow Character
Saturates	Colorless	0.07	0.00	Liquid
Naphthene-Aromatics	Yellow to Red	0.98	0.23	Liquid
Polar-Aromatics	Black	1.07	0.42	Solid
Asphaltenes	Brown to Black	1.15	0.50	Solid

(After Reference (1.16)).

Bituminous Materials-*Chemistry*

- Corbett Method

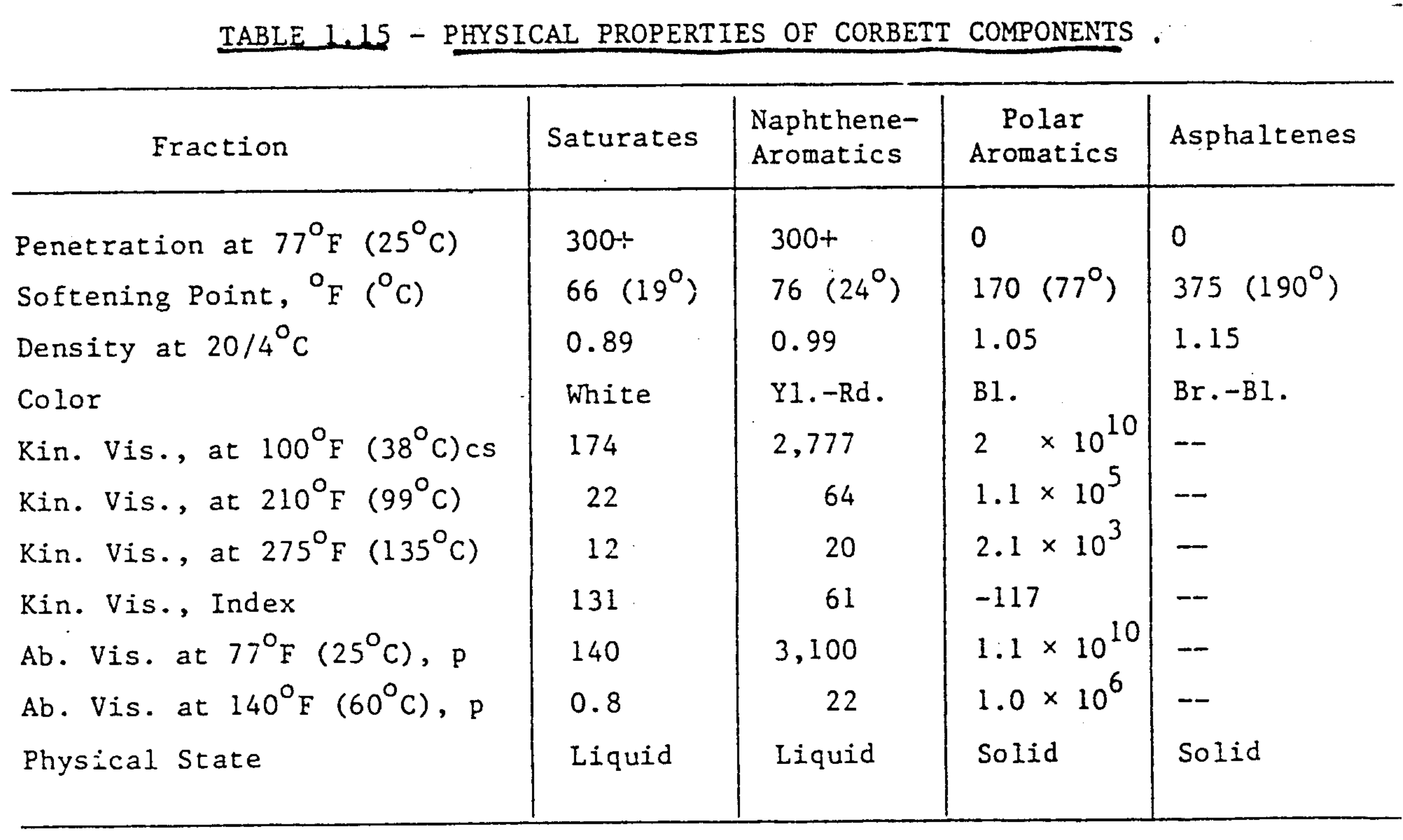


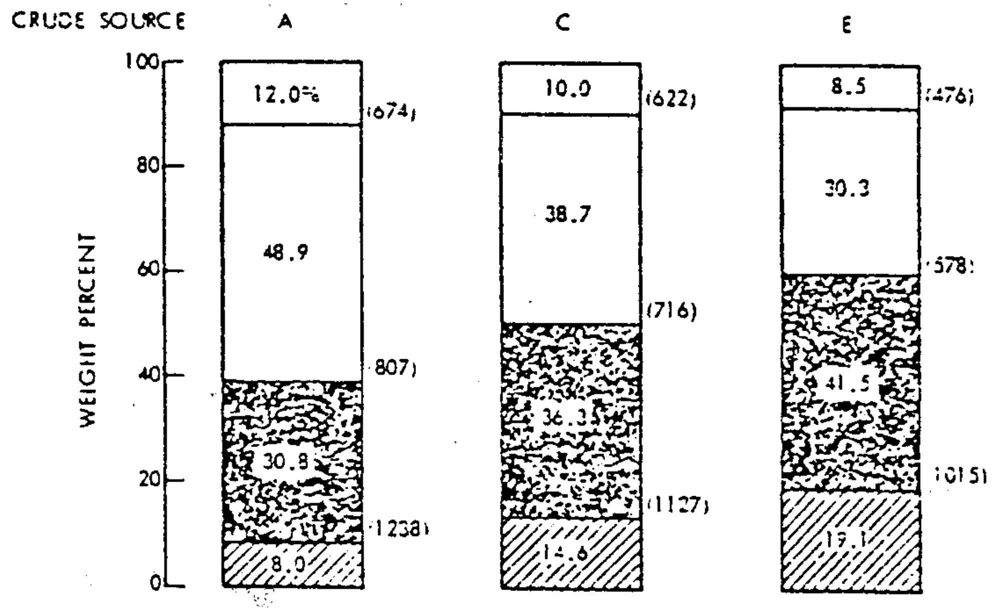
TABLE 1.15 - PHYSICAL PROPERTIES OF CORBETT COMPONENTS .

Fraction	Saturates	Naphthene-Aromatics	Polar Aromatics	Asphaltenes
Penetration at 77°F (25°C)	300+	300+	0	0
Softening Point, °F (°C)	66 (19°)	76 (24°)	170 (77°)	375 (190°)
Density at 20/4°C	0.89	0.99	1.05	1.15
Color	White	Yl.-Rd.	Bl.	Br.-Bl.
Kin. Vis., at 100°F (38°C)cs	174	2,777	2×10^{10}	--
Kin. Vis., at 210°F (99°C)	22	64	1.1×10^{5}	--
Kin. Vis., at 275°F (135°C)	12	20	2.1×10^{3}	--
Kin. Vis., Index	131	61	-117	--
Ab. Vis. at 77°F (25°C), p	140	3,100	1.1×10^{10}	--
Ab. Vis. at 140°F (60°C), p	0.8	22	1.0×10^{6}	--
Physical State	Liquid	Liquid	Solid	Solid

Bituminous Materials-*Chemistry*

- Corbett Method

FIGURE 1.21 - TEMPERATURE SUSCEPTIBILITY OF PETROLENE FRACTIONS
(after Reference 1.16)



VIS 60C/140F	2000	2000	2000
VIS 135C/275F	352	445	540
PEN 25C/77F	50	85	130
PEN RATIO 4/25	24	30	41
RTFO VIS 60C	6100	7700	8650

☐ SATURATES

▨ POLAR-AROMATICS

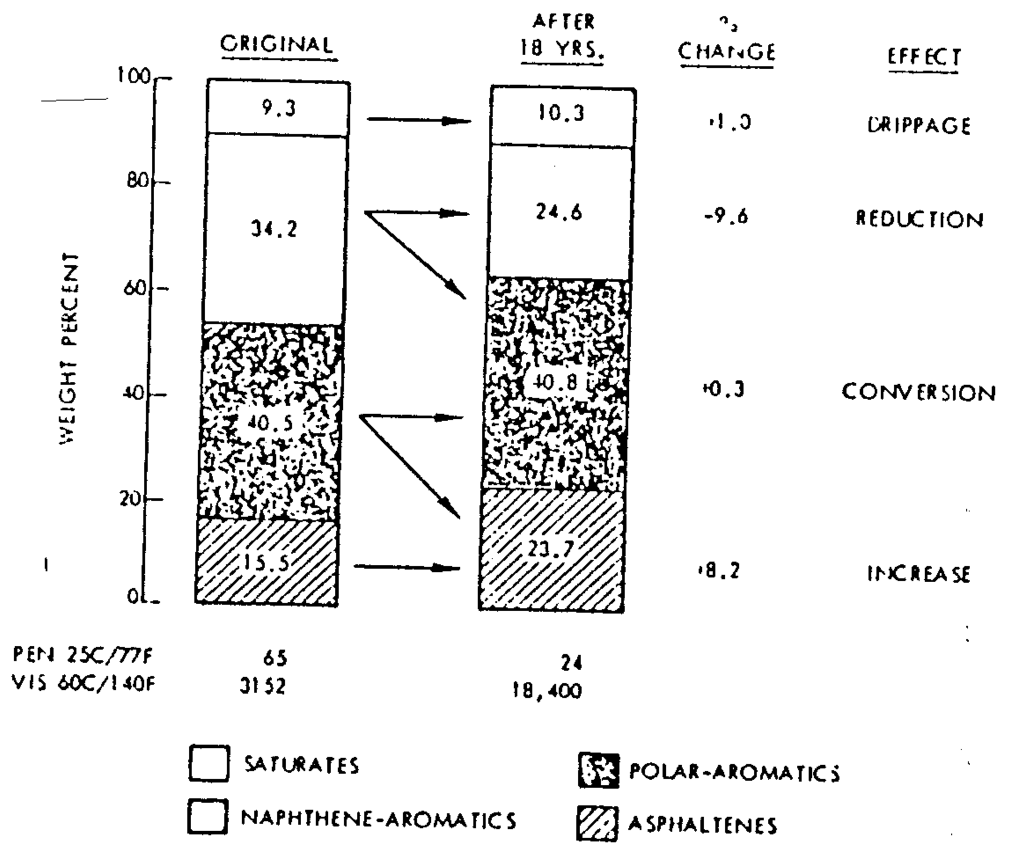
☐ NAPHTHENE-AROMATICS

▨ ASPHALTENES

( ) FRACTION MOLECULAR WEIGHT

Bituminous Materials-*Chemistry*

- Corbett Method



* FIGURE 1.23 – MECHANISM OF COMPOSITIONAL CHANGES DURING AGE HARDENING

(after Reference 1.16)

Bituminous Materials-*Chemistry*

- Corbett Method

- Studies have indicated that

- SATURATES are better plasticizers than NAPHTHENE AROMATICS
- ASPHALTENES are solution thickeners
- SATURATES and ASPHLATENES produce low temperature sensitivity
- POLAR AROMATICS control the ductility of the asphalt

- ………………………………………………………………………

THANK YOU