Section 1 - CHEMISTRY

CHEMCRETE MODIFIER is composed essentially of organo-metallic components dissolved in a softening oil.

CHEMCRETE MODIFIER is a catalyst which, unlike polymer additives, reacts with bitumen and changes the chemistry and the molecular structure of the bitumen under the influence of temperature and oxygen.

This catalytical reaction results in the formation of ketones at the most reactive sites within the bitumen molecules, thereby greatly reducing the bitumen's susceptibility to oxidative ageing, and improving its anti-stripping properties. In a second consecutive phase, the organo-metallic components of the CHEMCRETE MODIFIER will react with the ketones, producing strong irreversible bonds between the bitumen molecules, resulting in a bitumen with highly reduced temperature susceptibility.

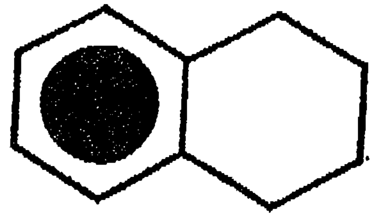


Fig. 1.1. Tetralin

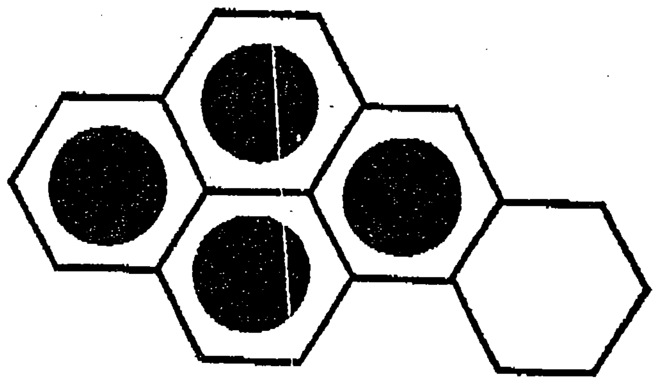


Fig. 1.2. Tetralin like structure in bitumen

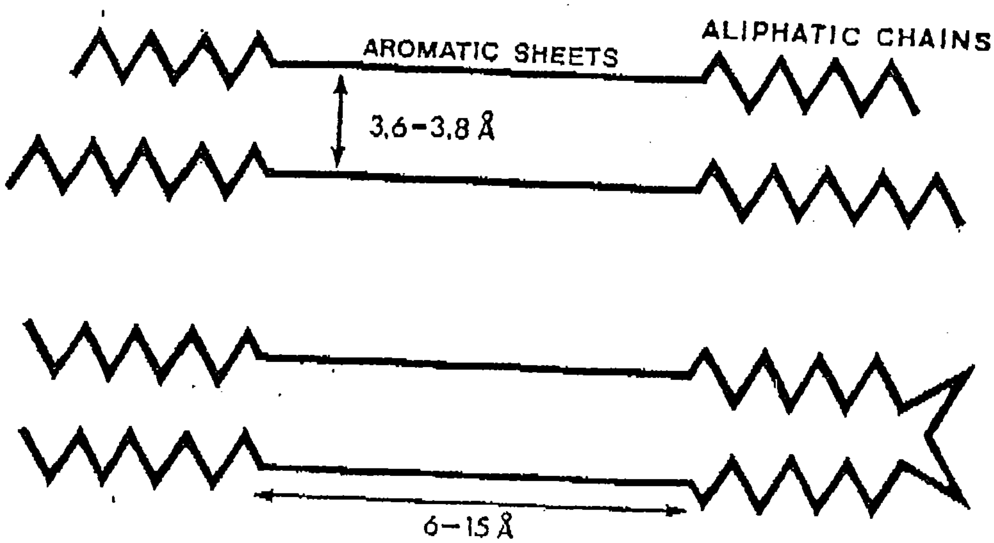


Fig 1.3. PLatelets stacking

1.1. CONVENTIONAL BITUMEN CHEMISTRY

1.1.1. Chemical structure

Bitumen is a very complex mixture of organic molecules which vary widely in composition from non polar saturated hydrocarbons to highly polar, highly condensed aromatic ring systems.

In all bitumens, a fundamental building block in this complex mixture of aromatic and aliphatic hydrocarbons, is a structure called tetrahydronaphthalene, or more commonly, *tetralin.*

From a structural point of view, tetralin can be thought of as a benzene ring and a cyclohexane ring fused together.

These tetralin structures come together in many various patterns in which the aromatic components form two-dimensional arrays or *platelets.* These platelets will arrange themselves in stacks of layers whenever the bitumen solidifies.

These layers are bound only by the electro-static forces inherent to hydrogen bonds : when the bitumen is subject to low temperatures, the platelets are strongly bound together, making the bitumen stiff ; but whenever the bitumen is heated, these bonds become very weak, and the platelets will slide apart causing critical limitations in cohesive strength. In other words, these hydrogen bonds between the platelets in bitumen are the main reason for conventional bitumen to be highly susceptible to temperature change.

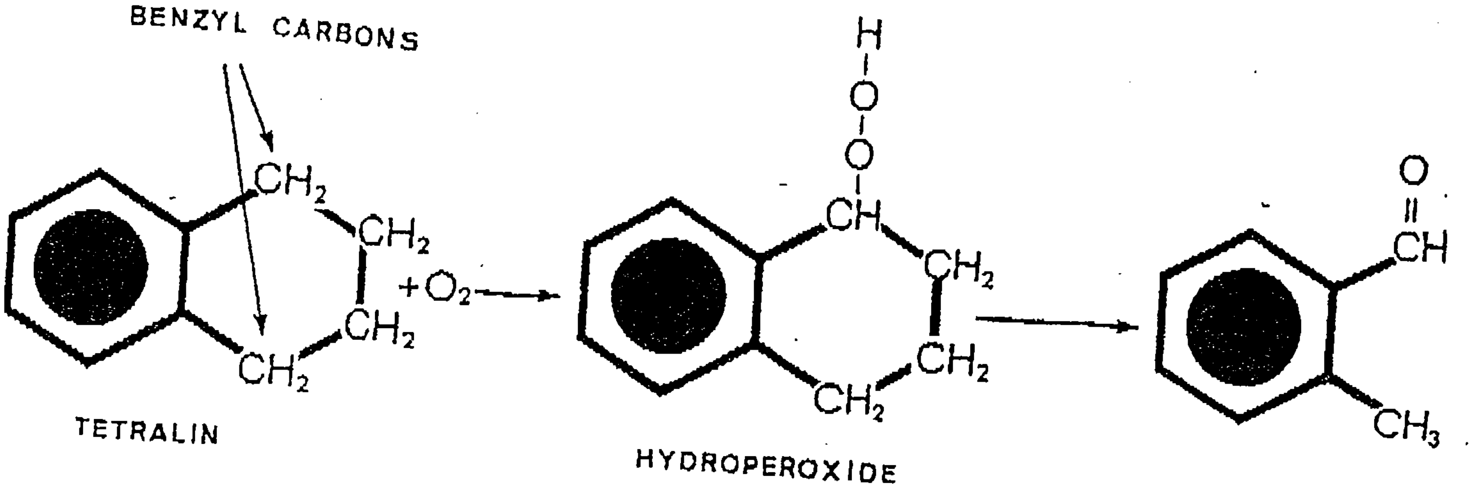


Fig. 1.4. Example of destructive oxidation through hydroperoxide leading to a free radical chain reaction

1.1.2. Ageing of Conventional bitumen

The reaction of bitumen with atmospheric oxygen is the major factor leading to the hardening and embrittlement of bitumen.

The primary mode of oxygen uptake is at those carbons which are immediately adjacent to a benzene ring ; they are the "benzyl carbons" and are far more reactive than any neighbouring carbon atoms.

Atmospheric oxygen attacks the bitumen at these benzylic sites to form a hydroperoxide (fig. 1.4). Naturally the same oxygen uptake will occur at the upper and lower benzylic sites, so that two hydroperoxides will be formed on most tetralin molecules.

The formation of these hydroperoxides is particularly detrimental in bitumen because the bond between the two oxygen atoms is inherently weak and will readily break to form a free radical which in turn may be the cause of :

a. breaking of molecular carbon-to-carbon bonds in the naphtenic ring of tetralin, hence, undermining the structural integrity of the bitumen
   and/or

b. catalyzing the uptake of more atmospheric oxygen to form even more unstable hydroperoxides.

This oxidation process illustrates the beginning of a chain reaction which is the cause of the classical oxidative degradation of bitumen.

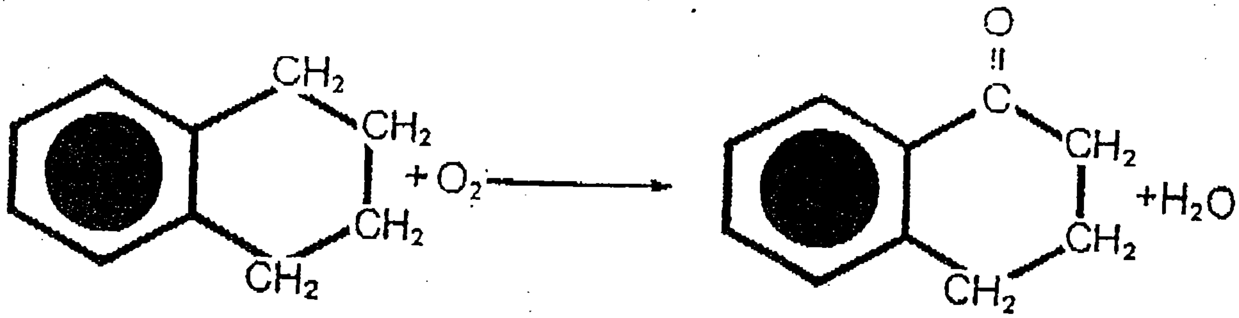
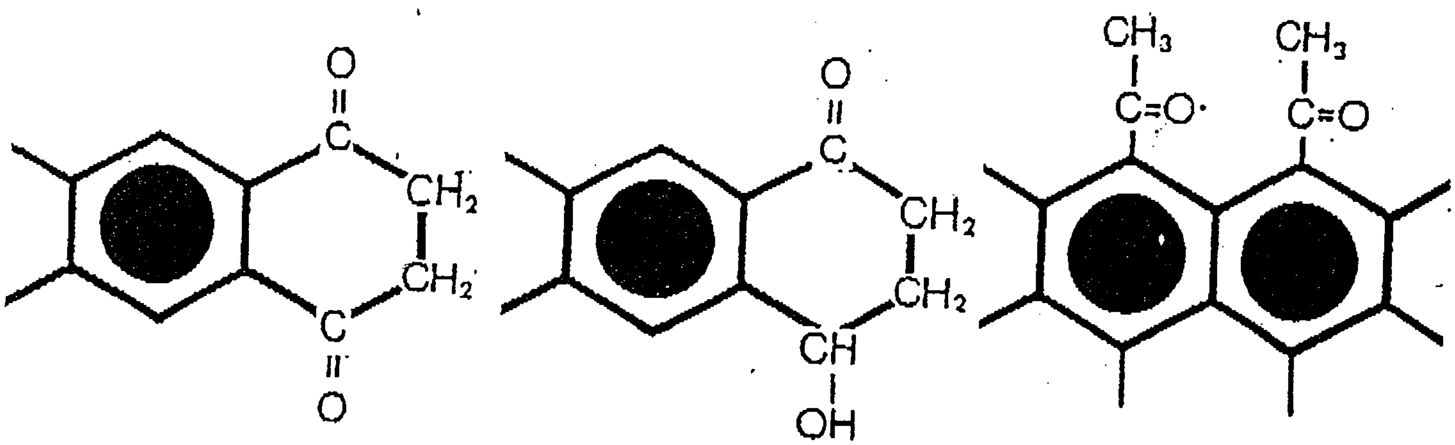


Fig. 1.5. Monoketone formation by the catalyctic action of CHEMCRETE modifier



1,4 DIKETONE

1,4 HYDROXYKETONE

1,8 DIKETONE

fig. 1.6. Example of diketones and hydroxyketones formed by the catalytic action of CHEMCRETE

1.2. CHEMCRETE CHEMISTRY

CHEMCRETE MODIFIER contains a organo-metallic manganese complex which mixed in bitumen causes two separate and sequential chemical reactions, resulting in a permanent change of the chemistry and molecular composition of the bitumen.

- in the first of these reactions the organo-metallic complex acts as a true catalyst forming predominantly ketones.
- in the second reaction the manganese crosslinks the bitumen platelets.

1.2.1. Formation of ketones

In the first reaction, the organo-metallic manganese complex acts as a true catalyst, catalyzing the addition of oxygen to benzylic carbon groups, converting these benzylic carbon groups almost quantitatively to ketone groups. In the fundamental building block - *tetralin* , this initial reaction first forms the tetralin monoketone (fig 1.5). But since both benzylic sites are reactive, the catalytic reaction induced by the CHEMCRETE MODIFIER subsequently forms diketones and hydroxyketones.

In this way the very stable ketones are formed, rather than other oxidation products, and the detrimental free radical chain reaction which otherwise leads to the rapid ageing of conventional unmodified bitumen is broken.

Furthermore, most of the oxidizable sites of the bitumen have been converted to ketones, and ketones cannot be readily oxidized into breakdown products; for this reason, CHEMCRETE MODIFIED BITUMEN will age more slowly than unmodified bitumen, once the initial catalytic curing has stopped.

An additional positive characteristic is that ketones are very effective anti-stripping compounds in asphalt because their polarity gives them the ability to resist water displacement; since a great amount of ketones are formed CHEMCRETE BITUMEN is far less sensitive to water stripping than unmodified asphalt.

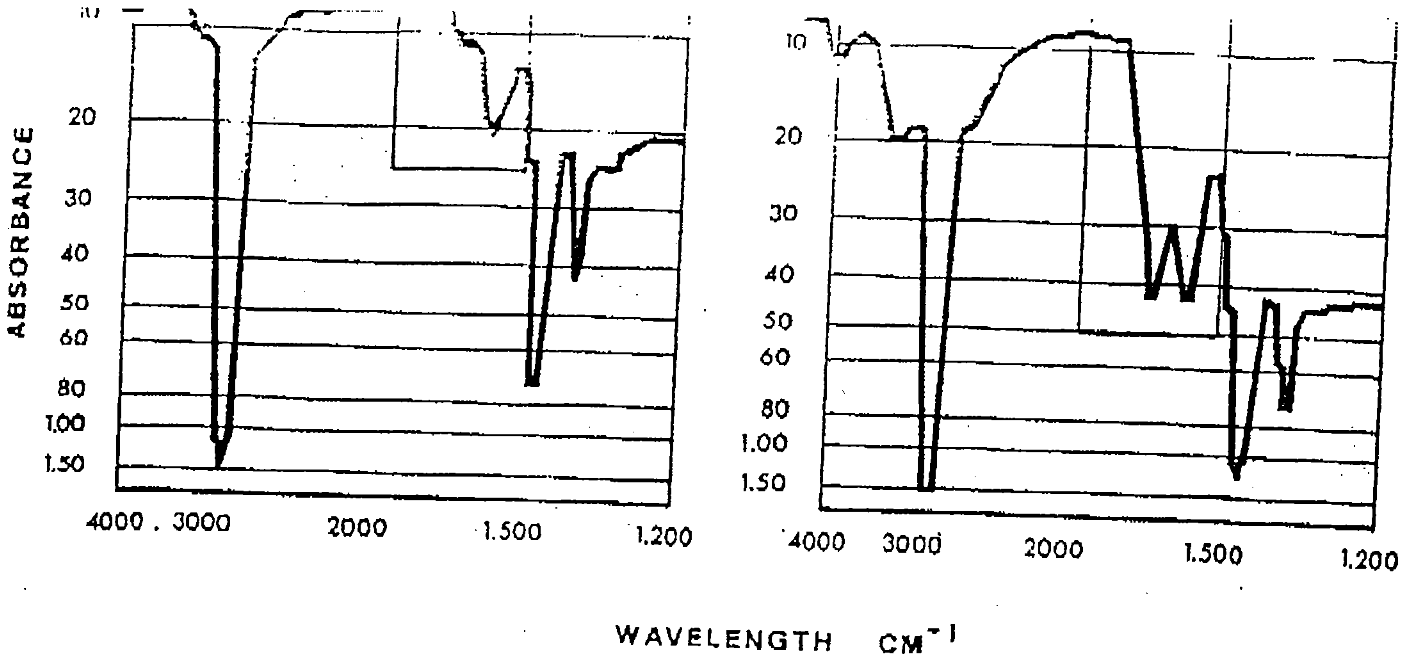


Fig. 1.7. Infrared spectra of unmodified bitumen and CHEMCRETE modified bitumen. (recovered bitumen from test road)

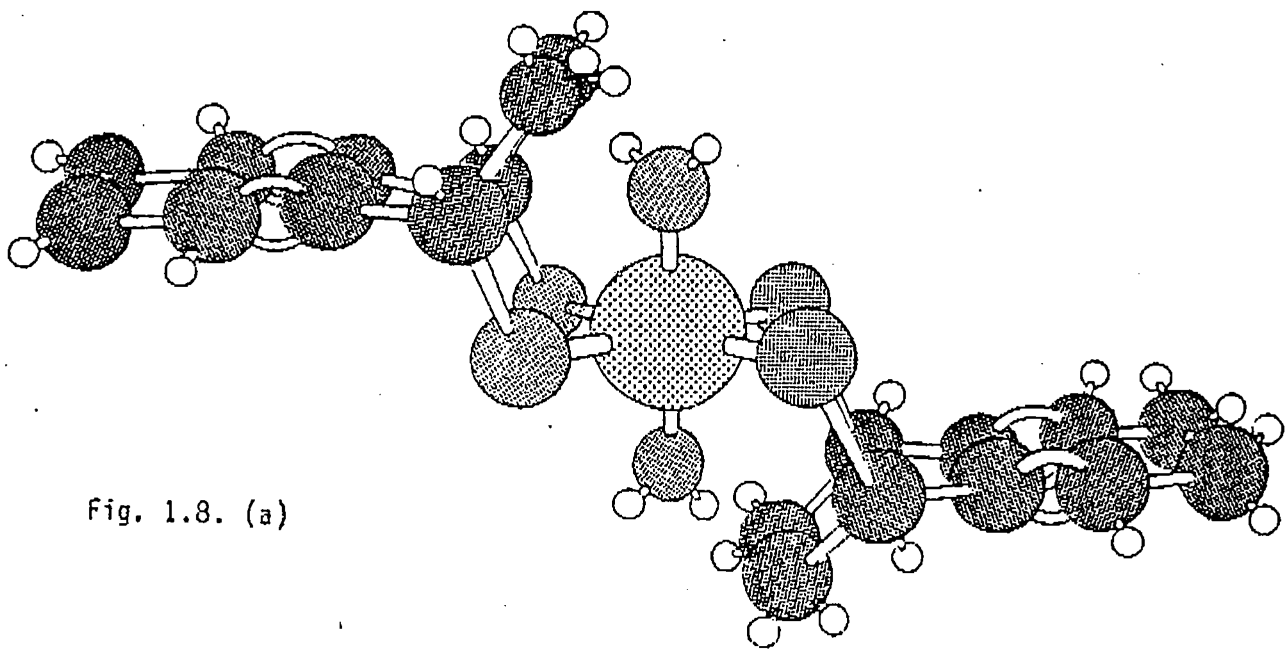


Fig. 1.8. (a)

The formation of ketones can be demonstrated by infrared spectroscopy. The ketones found in bitumen characteristically absorb light in the spectral region defined by wavenumbers around 1690 cm^{-1} (fig. 1.7.).

The comparison of the relative levels of absorbance for conventional bitumen and CHEMCRETE MODIFIED BITUMEN in this spectral region confirms that a very significant amount of ketones is formed in the CHEMCRETE bitumen, while only a small amount of ketones is evident in the unmodified bitumen.

1.2.2. Bitumen Crosslinking

In the second reaction caused by the CHEMCRETE MODIFIER, the manganese is irreversibly complexed with the diketones formed in the first reaction : the result is a link between the diketones on vertically adjacent molecules of bitumen platelets.

It is interesting to note that the diketones and hydroxyketones shown in fig 1.6. have exactly the correct atomic spacing for the manganese to fit in between the platelets, which means that the complex formed with the manganese ion is very stable.

There is a rule in chemistry which states that metal complexes form in a short time into the most stable form, that means that the manganese organo-metallic complex will quickly convert to the diketones-manganese complex once the diketones are available.

These manganese-diketone complexes are very stable and involve interactions with the d-orbitals of the manganous ion. Therefore, the manganese is completely de-activated and will not act as a catalyst for further oxidation.

A view of the three-dimensional model (fig 1.8) shows the way in which the maganese-ketone complex ties together vertically adjacent bitumen molecules.

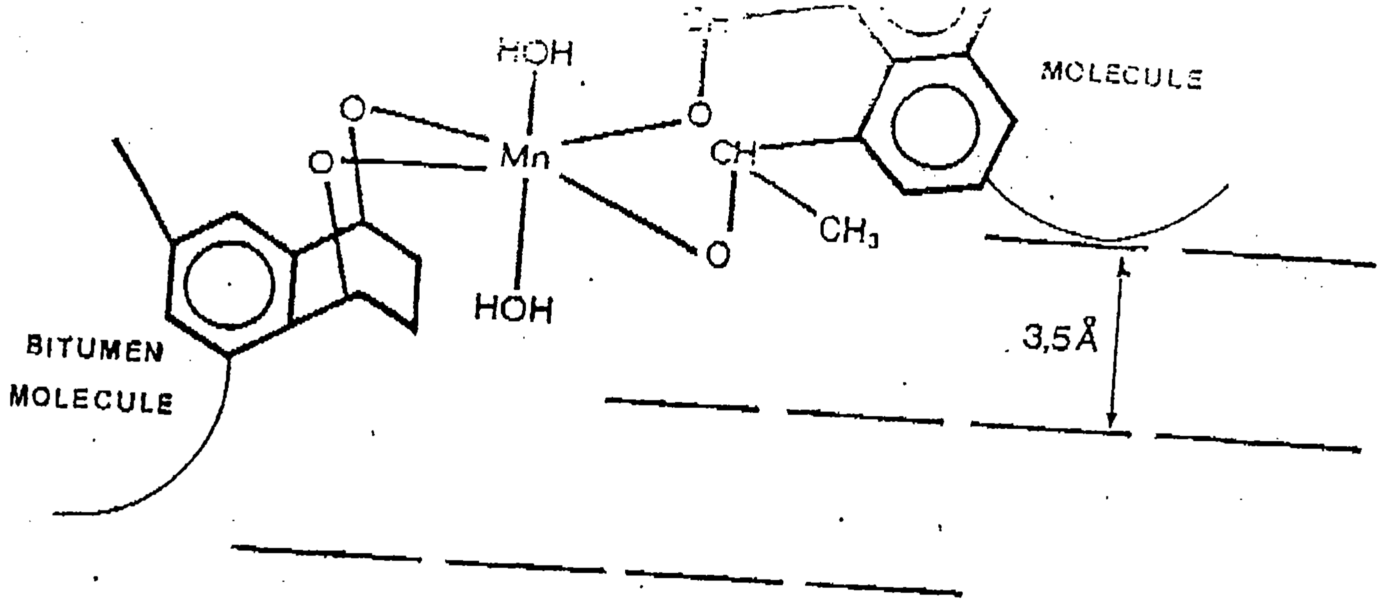


Fig. 1.8. (b) Diketone manganese complex crosslinking of bitumen molecules

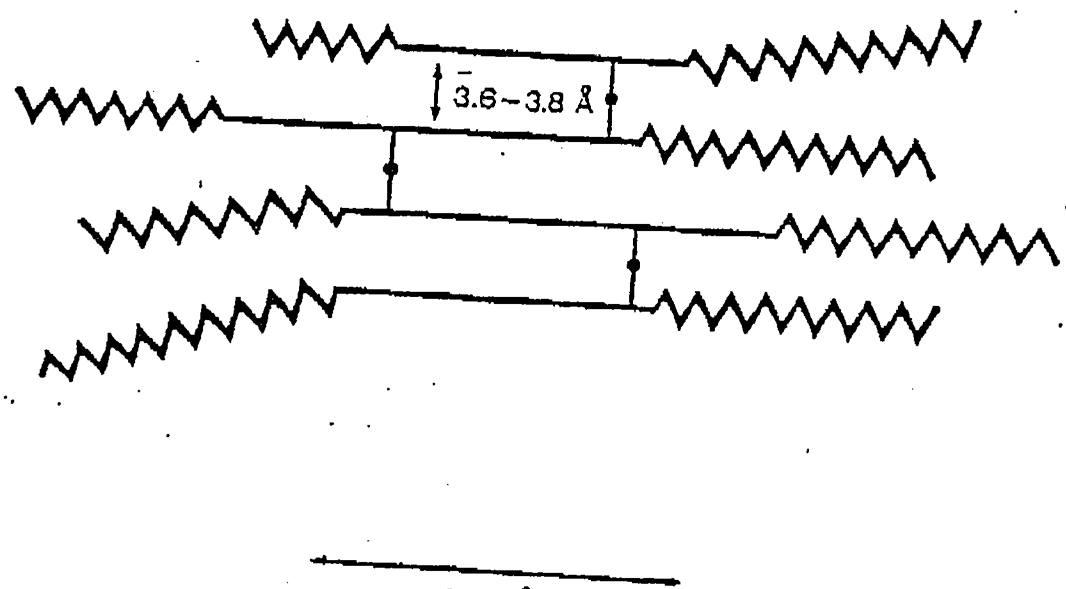


Fig. 1.9. Crosslinking of platelets in CHEMCRETE modified bitumen

This new very strong bond makes the bitumen much stronger because some of the platelike bitumen molecules are prevented from slipping with respect to each other.

The cross-linking is easily visualized in an "edge-on" view, depicting the plate-like structure of the bitumen (fig 1.9), they can be viewed as being like additional crossmembers or struts in a structure. In conventional bitumen (fig 1.3) the platelets are only held together by electrostatic forces which are very weak at higher temperatures, so the platelets will slide apart when under stress at higher temperatures, causing the well-known lack of strength.

In the CHEMCRETE modified bitumen, at higher temperatures , the crosslinking of the bitumen platelets gives the bitumen very high strength; on the other hand, at low temperatures the bond between the platelets in conventional bitumen is sufficiently strong for the crosslinking not to give any additional strength to the bitumen. The result is that a CHEMCRETE MODIFIED BITUMEN will be much less temperature susceptible than the unmodified bitumen . The higher the temperature, the more difference in strength between the CHEMCRETE MODIFIED BITUMEN and the unmodified bitumen.

The formation of this manganese-ketone complex can be verified by noting the shift which occurs in the molecular weight distribution of CHEMCRETE bitumen when compared with unmodified bitumen.

This is illustrated in fig. 1.10 and as would be expected, the crosslinked CHEMCRETE bitumen has an increased average molecular weight.

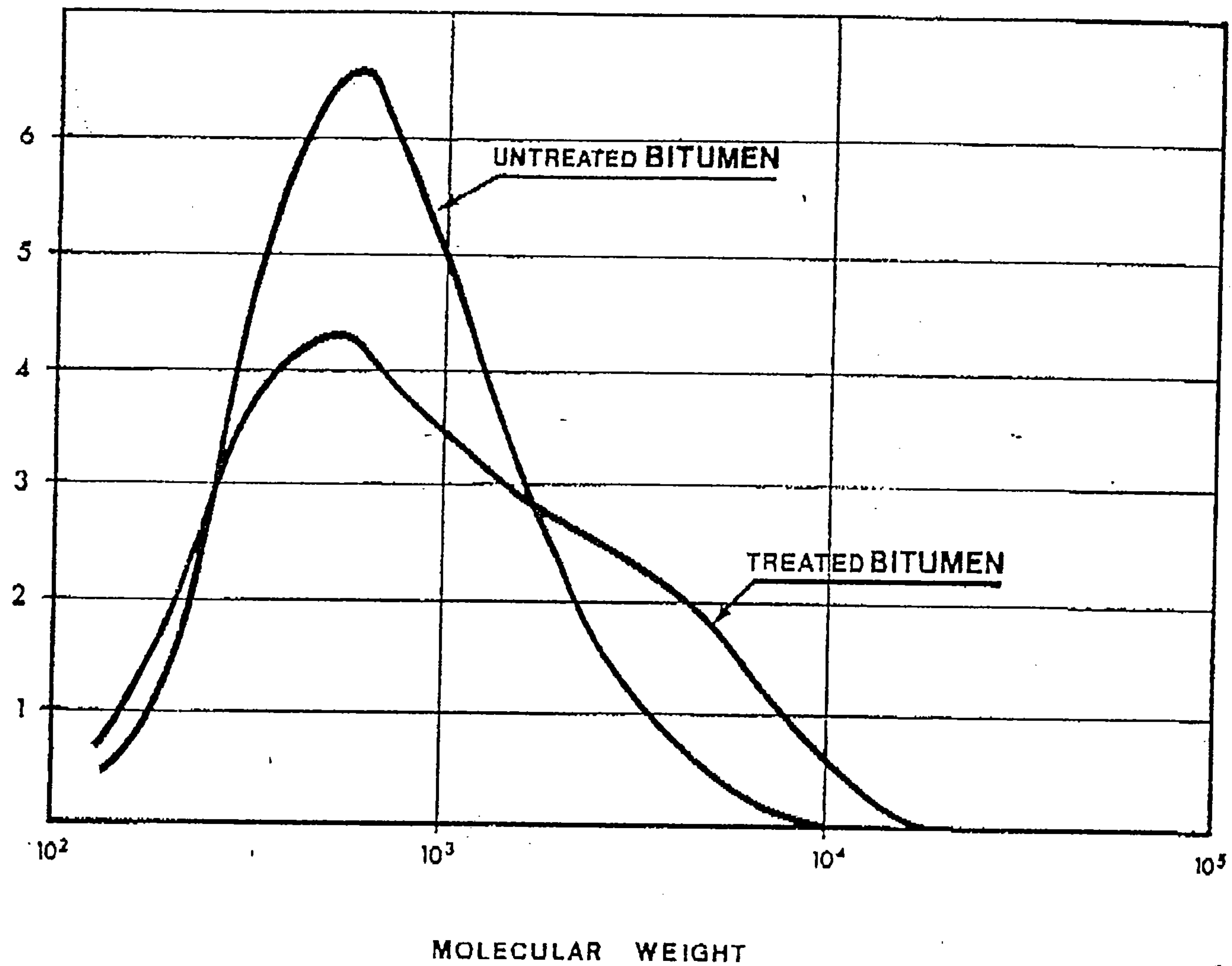


Fig. 1.10. Molecular weight distribution of CHEMCRETE modified bitumen and unmodified bitumen by High Pressure Liquid Chromatography. Vertical axis represents relative absorbance in arbitrary units and horizontal axis molecular weight.

1.3. SUMMATION OF CHEMISTRY

Bitumen is composed of molecules which arrange themselves in platelet structures.

In conventional bitumen, these platelets are bound together by weak electrostatic forces resulting in the high temperature susceptiblity ; also conventional bitumen is very susceptible to age hardening caused by a free radical chain reaction which catalyzes oxygen uptake, breaks molecular bonds and leads to the well known degradation over time.

In CHEMCRETE MODIFIED BITUMEN the chemistry and molecular structure are different.

The detrimental free radical chain reaction is broken and instead of the oxidative breakdown of the bitumen there is a formation of ketones on all reactive sites,and a build up of strong irreversible bonds crosslinking the bitumen platelets.

Ketones are very resistant to degradation and therefore CHEMCRETE MODIFIED BITUMEN will age more slowly than unmodified bitumen, once the initial curing process has stopped and the manganese has been deactivated.

Ketones have very excellent anti-stripping properties which together with the properties inherent to metallic components give to CHEMCRETE BITUMEN outstanding resistance to stripping by wateraction.

The crosslinking of the bitumen platelets makes the CHEMCRETE much less temperature susceptible with great improvement of cohesive strength at higher temperatures.