



IntegraBase & Nanotechnology: Modifying Asphalt on a Molecular Level

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Introduction

Nanotechnology is defined as fabrication of devices with atomic or molecular scale precision. Devices with minimum feature sizes less than 100 nanometers (nm) are considered to be products of nanotechnology (see Figure-1). A nanometer is one billionth of a meter (10^{-9} m) and is the unit of length that is generally most appropriate for describing the size of single molecules. The nanoscale marks the nebulous boundary between the classical and quantum mechanical worlds; thus, realization of nanotechnology promises to bring revolutionary capabilities. Fabrication of nanomachines,

nanoelectronics and other nanodevices will undoubtedly solve an enormous amount of the problems faced by mankind today.

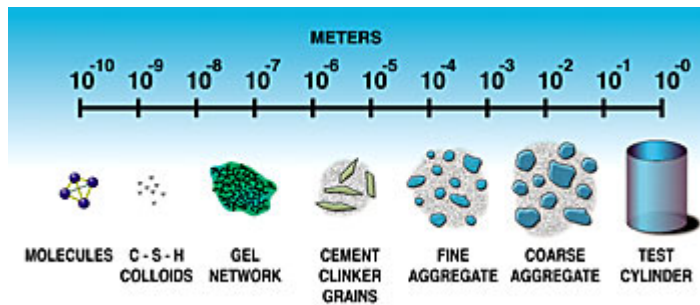


Figure-1 - Nanoscience refers to microstructure of materials on lengths of 0.1 to 100 nm (10^{-10} to 10^{-5} meters) and to the manipulation of that microstructure to produce desired macroscopic properties. Both Portland cement and bituminous concrete are nanostructural materials, with the binder material in both cases consisting of a gel composed of calcium-silicate-hydrate colloidal particles in the 1 to 100 nm range. Nanotechnology refers to devices that have length scales on the order of 1 to 1000 nm.

Nanotechnology is currently in a very infantile stage. However, we now have the ability to organize matter on the atomic scale and there are already numerous products available as a direct result of our rapidly increasing ability to fabricate and characterize feature sizes less than 100 nm. Mirrors that don't fog, biomimetic paint with a contact angle near 180° , gene chips and fat soluble vitamins in aqueous beverages are some of the first manifestations of nanotechnology.

However, imminent breakthroughs in

computer science, medicine and transportation will be where the real potential of nanotechnology will first be achieved.

Nanoscience is an interdisciplinary field that seeks to bring about mature nanotechnology. Focusing on the nanoscale intersection of fields such as physics, biology, engineering, chemistry, computer science and more, nanoscience is rapidly expanding. Nanotechnology centers are popping up around the world as more funding is provided and nanotechnology market share increases. The rapid progress is apparent by the increasing appearance of the prefix "nano" in scientific journals and the news. Traditionally, nanotechnology has been concerned with developments in the fields of microelectronics, medicine and materials sciences. However, the potential for application of many of the developments in the nanotechnology field in the area of transportation engineering is growing.

Nanotechnology and Transportation

After more than a decade of progress in other industrial sectors, the nanotechnology revolution has just begun to impact highway, road, and bridge materials and construction. Right now, under the Federal Highway Administration's Advanced Infrastructure Research program, study is under way on a variety of nanotechnology applications to the highway and bridge industries.

The feasibility of Cyberliths, or Smart Aggregates, as wireless sensors embedded in concrete or soil is being studied. Concrete ills such as alkali-silica reactivity and delayed ettringite formation — the bane of

concrete highways and bridges — are being studied at the molecular level using neutron scattering technology and other processes. In addition, fundamental research into the interactions between fly ash and the nanostructure of portland cement gel is under way, using neutron scattering technology. And nanotechnology is providing a close-up look at the hydration of cement grains and the nanostructure of cement reactivity as hydrated surfaces develop on individual cement grains.

But nanotechnology with application to transportation infrastructure also continues outside the government umbrella. Autonomic (spontaneous) healing research in structural polymers, by Dr. Nancy Sottos at the University of Illinois at Urbana-Champaign, could lead the way to guardrails that heal themselves, or concrete or asphalt that heal their own cracking.

Controlled manufacture of high-performance steel at the nanotechnology level already has led to steels of incredible strength, and more is on the way. Coatings which mimic the surface of the lotus leaf — to which nothing adheres — likely will lead to signage and work zone barricades which shed dirt and grime and never need to be washed, enhancing safety and lowering labor costs.

Nanotechnology and Asphalt

The term "nanotechnology" in construction can be understood as two different things: (1) Better understanding of organic or inorganic materials by analyzing them at the nanometer scale, and (2) development of micro and nano tools. Since materials designed and manufactured at the nano-scale can change their traditional physical behavior, it is worthwhile to the construction industry to investigate this emerging technology.

The emerging fields of nanoscale science, engineering, and technology – the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new properties and functions – are leading to a new understanding and control over the basic building blocks and properties of all natural and man-made materials, such as asphalt.

Given the composite nature of hot-mix asphalt (HMA), a mixture of aggregate and a binder – the potential for improvements in the engineering properties of HMA through the application of nanotechnology is significant, particularly in the areas of resistance to moisture damage (stripping in HMA), strength and longevity, among others. Nanotechnology-based improvements to pavement performance will result in significant cost savings to pavement agencies around the globe. Ultimately, nanotech improvements to asphalt will result in longer-lasting, more durable pavements for highways, airfields, ports, and other applications.

The mechanical behavior of bituminous materials depends to a great extent on structural elements and phenomena which are effective on a micro- and nano-scale. The basic concept behind nano-modification of materials is that of "bottom-up" engineering, starting with engineered modifications to the molecular structure with an aim to affect the bulk properties of the material. The nano-modification of bituminous materials has the potential to open up whole new uses and classes of bituminous materials, with wide-ranging implications for the transportation infrastructure. The ability to target material modification at the nano-structural level promises to deliver the optimization of material behavior and performance needed to significantly improve mechanical performance, durability, reflectivity and skid resistance, better binding, quicker curing, better maintenance and sustainability.

The IntegraBase Nano-Scale Chemical Reaction

There are currently no other asphalt modifiers on the market that work on a nano-scale. The majority of products that are used with asphalts are simply additives, which don't do anything to the chemistry of the asphalt, rather just improving specific properties such as binding, flexibility, etc. IntegraBase 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 IntegraBase modifier will react with the ketones, producing strong, irreversible bonds between the bitumen molecules, resulting in a bitumen with highly a reduced temperature susceptibility.

Chemistry of Conventional Bitumen

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 known as, 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 the stacks of layers whenever the bitumen solidifies.

These layers are bound only by the electrostatic forces inherent to hydrogen bonds – when the bitumen is subject to low temperatures, the platelets are strongly bound together, making the bitumen stiff; when the bitumen is heated, these bonds become very weak, and the platelets will slide apart, causing critical limitations on cohesive strength. Simply stated, the hydrogen bonds between the platelets in bitumen are the main reason for conventional bitumen to be highly susceptible to temperature change.

IntegraBase Chemistry

The reaction between IntegraBase and bitumen is purely “thin film” chemistry (e.g. 0-30 microns.) Factors which affect the reaction of IntegraBase with bitumen are temperature, oxygen and time. Temperature accelerates the reaction (a doubling of speed with every increase of 10°C.) If oxygen is not present, there will be no reaction – oxygen is the trigger in the reaction. However, the reaction is not standard oxidation, as oxygen becomes part of the final product – an organic-metallic compound. The time for reaction is fairly consistent for all asphalts – most of the reaction occurs in the first 30 minutes, then moves slowly from that point on. Once this reaction takes place, it can never be reversed.

IntegraBase modifier contains an organo-metallic manganese complex which, when mixed with 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 part of the reaction, the organo-metallic complex acts as a true catalyst forming predominantly ketones. In the second part of the reaction, the manganese crosslinks the bitumen platelets.

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, the initial reaction first forms the tetralin monoketone. But since both the benzylic sites are reactive, the catalytic reaction induced by the IntegraBase 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 aging 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, IntegraBase 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, IntegraBase modifier is far less sensitive to water stripping than unmodified asphalt.

The formation of Ketones can be demonstrated by infrared spectroscopy. The ketones found in bitumen characteristically absorb light in the spectral region defined by wave numbers around 1690 cm^{-1} . The comparison of the relative levels of absorbance for conventional bitumen and IntegraBase modified bitumen in this spectral region confirms that a very significant amount of ketones is formed in the IntegraBase bitumen, while only a small amount of ketones is evident in the unmodified bitumen.

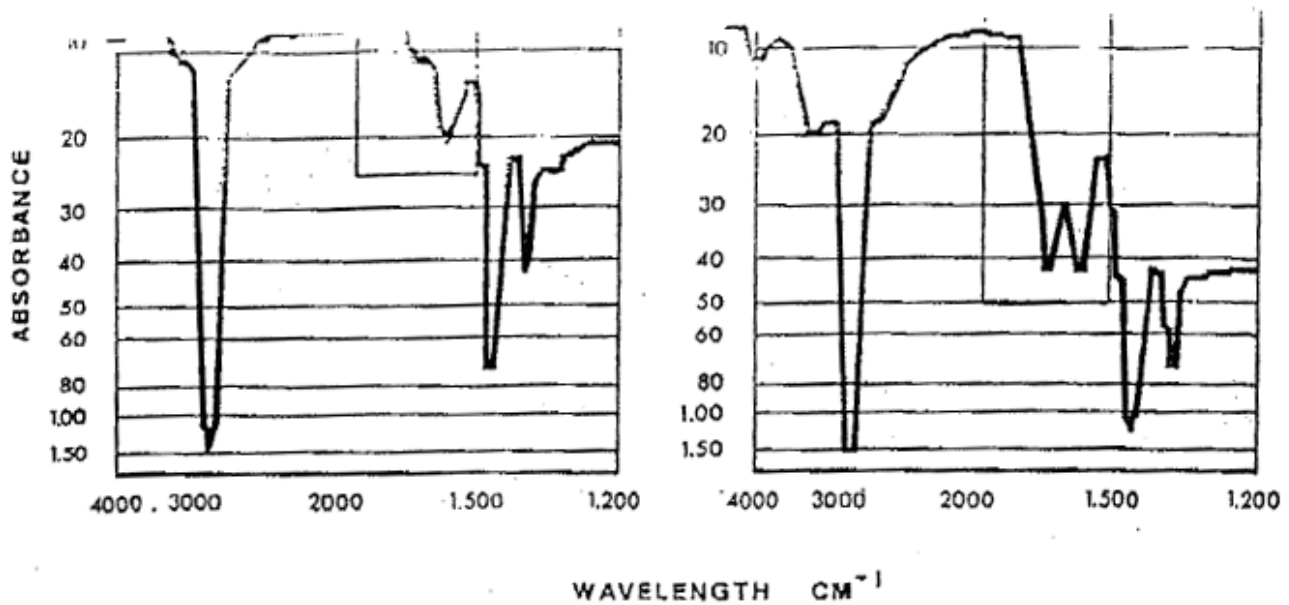


Figure 1.2 – Infrared spectra of unmodified bitumen and IntegraBase modified bitumen. (recovered bitumen from test road)

Bitumen Cross-Linking

In the second reaction caused by the IntegraBase 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 hydroketones 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 quickly transform into the most stable form possible, meaning 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 1.8a) shows the way in which the manganese-ketone complex ties together vertically adjacent bitumen molecules.

This new, very strong bond makes the bitumen much stronger because some of the plate-like 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; they can be viewed as being like additional cross members or struts in a structure. In conventional bitumen, the platelets are only held together by electrostatic forces which are very weak at higher temperatures, causing the platelets to slide apart when under high stress at higher temperatures – resulting in asphalt’s well-known lack of strength.

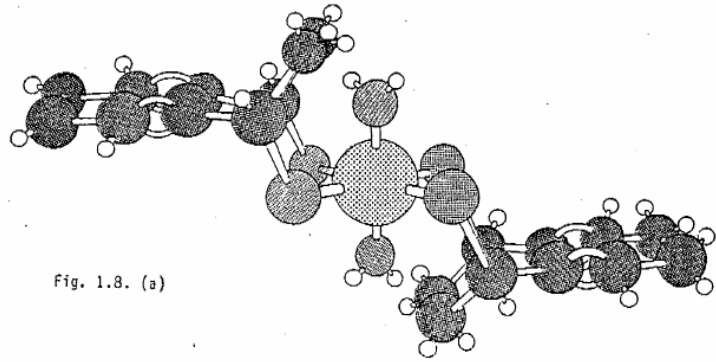


Fig. 1.8. (a)

At higher temperatures in the IntegraBase modified bitumen, the cross-linking 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 cross-linking not to give any additional strength to the bitumen. This results in IntegraBase modified bitumen being less temperature susceptible than the unmodified bitumen. The higher the temperature, the greater the difference in strength between the 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 IntegraBase bitumen when compared with unmodified bitumen. This is illustrated in figure 1.3; as would be expected, the crosslinked IntegraBase bitumen has an increased average molecular weight.

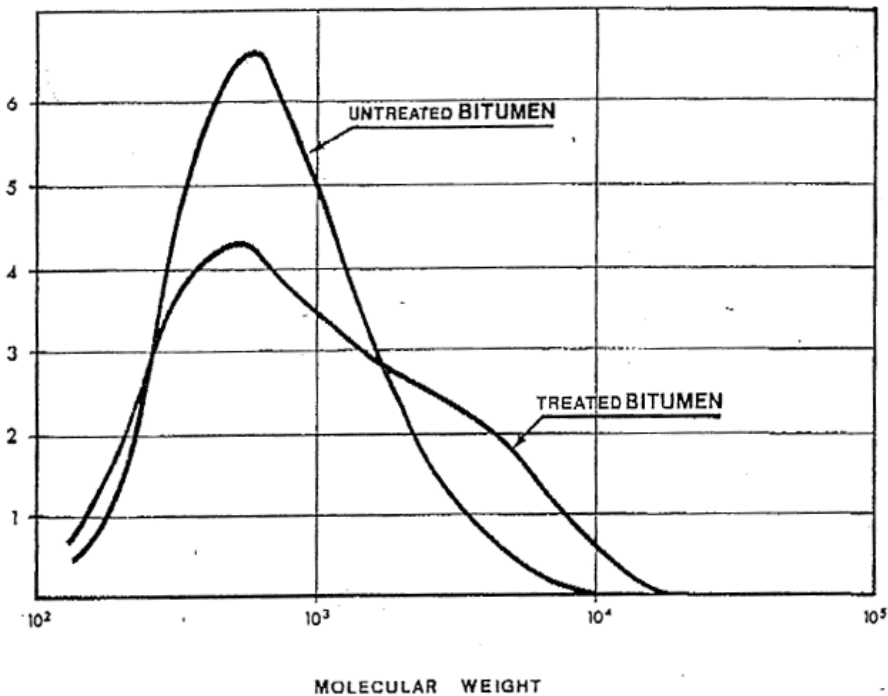


Figure 1.3 – Molecular weight distribution of IntegraBase modified bitumen and unmodified bitumen by High Pressure Liquid Chromatography. Vertical axis represents relative absorbance in arbitrary units and horizontal axis molecular weight.

Summary

Nanotechnology is a rapidly expanding area of research where novel properties of materials manufactured on the nanoscale can be utilized for the benefit of transportation infrastructure, and a number of promising developments exist that can potentially change the service life and life-cycle cost of transport infrastructure.

The requirement for durable asphalt pavements links to both the requirement that the pavement should be able to provide service with a minimum requirement for maintenance, and the requirement that the pavement should be sustainable. For this aspect, the main benefit that nanotechnology can provide to transportation engineering is in terms of the improvement of the materials. This can be provided through the improvement of existing materials or the development of novel materials. The main requirement for these developments is that the material should be able to operate under the applied regime of applied stresses and strains – both internally and externally. In terms of internal stresses and strains the material should provide the required cohesion to keep the internal structure of the material intact, and also provide the required adhesion between the particles and the binder used in the material (i.e. bitumen, cement etc). The focus is thus on those aspects of nanotechnology where the forces and bonds between particles are investigated and the long-term durability of these bonds under a range of cycle stresses and strains are improved.

This improvement in material performance is exactly what IntegraBase accomplishes through its nano-scale alteration of the asphalt's molecular structure. Through nanotechnology, IntegraBase substantially improves all of the key properties of asphalt:

- **Compressive Strength:** The ability to withstand loads in an unconfined state, which is the most critical condition.
- **Tensile Strength:** The ability to withstand flexural loads, which lead to the cracking of pavement.
- **Stability:** The ability to withstand loads at elevated temperature.
- **Fatigue:** The ability to withstand repeated flexural loads, a critical property of a long lasting road.
- **Adhesion:** The strength of the attraction of the asphalt for the aggregate (i.e., stone, sand, etc.) and the ability of is adhesion to withstand replacement by water.
- **Temperature Susceptibility:** The slope of the temperature-strength curve of an asphalt/aggregate mix which signals that the normal unmodified asphalt is changing from hard material to a soft material with a small change in temperature.