

THE SCIENCE OF MALTENE REPLACEMENT TECHNOLOGY FOR SUSTAINABLE ASPHALTS

Michael P. Durante

In recent years, there has been no shortage of confusion (and some intentional misdirection) in the asphalt pavement preservation marketplace in relation to the definition and understanding of *maltenes* and the role they play in rehabilitating and extending the life of asphalt roadways. Here, the goal is to revisit the naturally resilient chemistry Pavement Technology refers to as **Maltene Replacement Technology (MRT)**, and its demonstrative benefits in comparison with alternative methodologies for preserving asphalt pavements.

WHAT ARE MALTENES?

As defined by the U.S. Geological Survey (*Definition and World Resources of Natural Bitumens*),¹ maltenes are the n-alkane (that is, pentane or heptane) soluble molecular components of asphalt, where asphalt is the residue remaining after petroleum refiners remove other useful derivatives such as fuels and solvents from crude oil stock. Historically, maltenes have been characterized as the critical cohesive (i.e., bonding agent) and most vulnerable component of “asphalt cement” and in more recent years-- “asphalt binder”.

From a geochemical perspective and dependent upon the base oil source from which an asphalt is derived, any specific asphalt represents a wide array of secondary elements in different concentrations. Yet regardless of an asphalt’s varying geography, maltenes are one of the two core molecular embodiments common to all asphalts; the other being asphaltene.

Maltenes are the “media” that enable asphalt binder to impart flexibility, adhesion and flow properties to asphalts. They are the *resinous* and *oily* fractions found in the binder, where the asphaltene is the “filler” and together maltenes and asphaltene are the unique petroleum colloidal solution needed to create (along with aggregate) an asphalt pavement.

Maltenes and asphaltene are separately identifiable phases of the same interdependent molecular structure. The two components differ, however, in their molecular weights, solubility and critically - their chemical reactivity. The maltenes are largely responsible for the strength or ductility of asphalts to withstand considerable environmental and traffic stresses. But they also are more vulnerable (to oxidative aging) due to their chemical nature. By contrast, asphaltene is not easily soluble and is less reactive and provides asphalt binder its structure.

¹ <https://pubs.usgs.gov/bul/1944/report.pdf>

For a deeper understanding, maltenes can be further broken-down using adsorption chromatography in the presence of a reagent (e.g., acids or solvents) into four distinct subfractions:

- **Polar Compounds (aka nitrogen bases)**, which are highly reactive petroleum resins that act as a colloidal dispersion stabilizer or “peptizer” for the asphaltene substrate ²
- **First Acidaffins (A₁)**, which are aromatic resinous petro-hydrocarbons, with or without O, N and S, and provide a homologous or chemically compatible dispersion agent for the peptized asphaltene
- **Second Acidaffins (A₂)**, which are straight chain or cyclic unsaturated petro-hydrocarbons (olefinic) and are quasi-oily and quasi-resinous
- **Paraffins** ³ **(aka Saturates)**, which are either straight or branch chain saturated hydrocarbons and are the truly *oily* component of asphalt binder, functioning as a gelling agent for the asphalt compounds ⁴

Each of these fractions imparts very specific and necessary performance attributes to asphalt binder critical in evaluating and reconstituting asphalt binder integrity and functionality *in-service* as asphalt pavements age.

HISTORICAL CONTEXT

The earliest evidence of maltene-rich asphalts being used for building roads and waterproofing roofing materials was in the remarkable engineering feats of the Roman Empire. The Romans called their naturally resinous building and waterproofing material *maltha*, and it seems most likely the word maltenes was derived directly from that Latin base.

Over the centuries that followed, common custom was to simply rebuild new roads as old ones failed. However, scientists had long suspected if they could more precisely identify the specific molecular components of asphalts, they could develop asphalt specifications to optimize longevity. What held them back is the overwhelming number of variables involved.

The geographical location and climate conditions of the oil field from which the crude oil is derived, the processes and temperatures ⁵ used by the asphalt manufacturer, and the enormous complexity of the

² Kalichevsky V and Fulton SC, 1931 patent US1926523A.

³ “Heavy Oil Science Center, More About the Chemistry of Asphaltenes and Maltenes,” Foster Learning Inc. (<http://www.lloydminsterheavyoil.com/asphaltenes2.htm>)

⁴ The Asphalt Institute, ES-8, January 1980.

⁵ With mixing temperatures as high as 380°F, the original maltene content of asphalt morphs into asphaltene, as is explained later in this article.

potential molecular compositions of any particular asphalt discouraged researchers from developing a coherent strategy for extending the life of asphalt pavements.

During the first half of the 20th century, in the modern era of civil engineering, surface treatments such as coal tar and petroleum-based asphalt emulsions and fogs were introduced attempting to extend the life of existing asphalt pavements. It was soon discovered that coal tar is incompatible with asphalt and wears off quickly. And although adsorbed asphalt-based treatments provided some surface-based protection, that protection proved to be relatively short-lived.

It wasn't until mid-century the reason for these disappointing outcomes became clear.

THE ROSTLER ANALYSIS ⁶

By 1959, Dr. Fritz Rostler, working in America's petroleum and rubber industry with his associate Richard M. White, had adopted a backdoor approach to solving the dilemma. Instead of attempting to identify variant types of asphalt molecularly, they attempted to isolate and test the chemical reactivity of asphalt's two major components – maltenes and asphaltene. Their goal was to find a way to identify those chemistries most likely to produce more resilient thermoplastic performance. Their previous rubber-related discoveries had implications for asphalt binders due to the similar polymeric characteristics of the two materials. The research of Rostler *et al.* eventually culminated in today's Maltene Replacement Technology for sustainable and resilient asphalt pavement life extension.

By using sulfuric acid to separate-out the soluble components (i.e., maltenes), and then using an n-pentane solvent to separate the insoluble components (i.e., heavier, more stable asphaltene), Rostler et al., observed the asphaltene content in asphalt, when exposed to lab-simulated sun and weather, increased over time, while the asphalt's maltene content diminished. This suggested a continuously interactive molecular structure that would be receptive to maltene replacement treatments penetrating the asphalt matrix, i.e., if the maltene content of asphalts could be replaced, the pavement's flexibility and adhesion properties could be sustainably restored. Thus, genuine, molecular "asphalt rejuvenation" in the form of Maltene Replacement Technology (MRT) was born.

It was the Witco Corporation, the original manufacturer of Reclamite® ⁷ asphalt rejuvenation technology, which undertook the necessary research to identify the most effective method for feeding maltene-rich chemistry to aging pavements, and then to commercialize it.

Today, an asphalt rejuvenating fog seal is best defined as "a type of pavement preservation treatment applied to an existing asphalt pavement surface to preserve its functional and structural integrity and

⁶ Rostler FS and White RM, *Influence of Chemical Composition of Asphalts on Performance, Particularly Durability*, Third Pacific Area Meeting Papers, Symposium on Road and Paving Materials, San Francisco October 1959.

⁷ Reclamite® is a registered trademark of Ergon, Inc.

delay a more costly rehabilitation...”.⁸ Moreover, asphalt rejuvenators are “oils with chemical and physical characteristics selected to restore properties of aged asphalt binder” and “adding a rejuvenator to a fog seal reduces the likelihood of cohesive failure within the asphalt binder.”⁹

In addition to the deleterious effect of extreme heat volatilization of certain fractions during the manufacturing of asphalt, maltenes will continue to be removed in the field due to the damaging effect of solar radiation (i.e., **Heat Island effect**), in a process commonly referred to as oxidation. In combination, manufacturing-induced volatilization and *in-service* oxidation are the primary factors responsible for the common binder-centric (i.e., cohesive) failure of asphalt pavements.

TESTING STANDARD FOR REVITALIZATION TECHNOLOGIES

ASTM TEST D2006-70: MALTENE DISTRIBUTION

Through this break-through examination of the chemical reactivity of asphalt binder sub-components, the research conducted by Rostler *et al.* led to the development¹⁰ of ASTM test D2006-65 T and its successor, ASTM D2006-70,¹¹ which accurately identify the relationships between the various maltene fractions with the goal of determining the optimal maltene content distribution within an asphalt rejuvenating agent for true molecular asphalt binder restoration.

The test rank-orders maltene fractions by their changeability or vulnerability to volatilization and oxidation, consistent with Rostler *et al.*, understanding that the more vulnerable fractions are lost first and more rapidly and thus should be the first and most often replaced under Maltene Replacement Technology.

The formula is as follows: **PC + A₁**

S + A₂

Commonly known as the **Rostler Analysis**, this formula for testing asphalt rejuvenator efficacy was a critical advancement in the development of sustainable asphalts (and, more recently, Life Cycle Assessment (LCA) analysis) for asphalt pavements.

⁸ Moraes R, Evaluation of Rejuvenating Fog Seals, *Asphalt Technology News*, National Center of Asphalt Technology (NCAT) at Auburn University, Spring 2019.

⁹ Ibid.

¹⁰ Rostler FS and Sternberg HW, “Compounding Rubber and Petroleum Products”, *Industrial and Engineering Chemistry*, IECHA, Vol 41, 1949, pp 598-608.

¹¹ https://www.pavementpreservation.org/wpcontent/uploads/2017/03/FPFC335_Aspphalt_Rejuvenation.

The Rostler Analysis should not be confused with ASTM D2007 (SARA), which is a generalized hydrocarbon separation technique for determining the colloidal stability of petroleum extender oils and asphaltic emulsions. It cannot predict the performance of an asphalt rejuvenator.

D2007 does not measure the chemical reactivity of petroleum fractions, but rather, as one of the test's developers explained it, is "a convenient method" for determining "generic fractionation."¹² As such, this so-termed Corbett-Swarbrick fractionation method "separates asphalt into less complex, more homogenous fractions."¹³

The Corbett-Swarbrick method is primarily used to determine proper suspension between asphaltenes and the lighter petrolene componentry to promote application fluidity and workability. Although useful for determining the stability of an asphaltic emulsion or extender oil compound, it is not germane to determining the efficacy of an asphalt pavement rejuvenator.

ALTERNATIVE APPROACHES TO MALTENE-REPLACEMENT TECHNOLOGY

The competitive approaches to maltene-replacement technology can be categorized into three major areas: coal tars, petroleum-based asphaltic emulsions and fogs, and, most recently, bio-based solvents.

PERFORMANCE CHARACTERISTICS OF COAL TAR

Coal tar, as its name implies, is derived from coal conversion to coke as fuel in steel production furnaces. The residue from this process is coal tar.

For centuries, coal tar had been used widely as a waterproofing treatment for many types of exposed surfaces. In the first half of the 20th century, the asphalt pavement industry experimented with coal tar as a possible agent for extending the life of pavements. It was soon discovered, however, that coal tar is chemically incompatible with asphalt and therefore incapable of chemically bonding (fluxing) with an asphalt substrate. As a topcoat, coal tar can temporarily enhance the appearance of the underlying aging, gray asphalt pavement, but it wears off quickly and cannot be considered a rejuvenating agent.

Later, environmental and health scientists became increasingly concerned with the carcinogenic effects of coal tars and their once wide use as a waterproofing material has significantly declined in recent years, including being outlawed in certain jurisdictions.

Coal tars continue to be used in roofing as they are effective for solving challenging flat roof ponding issues; in addition, their fuel retardant properties make them attractive to the aviation industry. However, coal tars are ineffective and unsafe for use on roadways.

¹² Corbett LW, *Composition of Asphalt based on Generic Fractionation, Using Solvent Deasphalting, Elution-Adsorption Chromatography, and Densimetric Characterization*, April 1969.

¹³ Thenoux G et al, *Experiences with the Corbett-Swarbrick Procedure for Separation of Asphalt into Four Generic Fractions*, Transportation Research Board 1987.

PERFORMANCE CHARACTERISTICS OF ASPHALTIC EMULSIONS AND FOGS

Asphalt-based emulsions and fogs also provide some temporal, surface-based protection of the underlying asphalt pavement from exposure to the elements and hence delay costly rebuild. Such emulsions share some chemical affinity with a maltene (replacement) asphalt rejuvenator, however the maltene content in an asphaltic compound has super-fluxed with its asphaltene content before being applied to the road. Asphaltic emulsions and fogs are therefore incapable of molecular exchange with the original pavement, hence not used as an asphalt binder rejuvenating agent.

Only "free maltenes" can molecularly revitalize aged asphalts. This is why ASTM D2006-70 requires nearly 100 percent pure maltene fraction content, whereas D2007, not being an asphalt rejuvenator test, does not.

For asphaltic emulsions, D2007 tests for proper suspension between the heavier asphaltene and its lighter, plasticity-promoting components as an indication of the tested material's fluidity and workability. So, it is used for identifying the stability of an asphaltic emulsion or an extender oil compound, albeit ineffectual in determining a material's ability to rejuvenate an existing asphalt pavement.

PERFORMANCE CHARACTERISTICS OF BIO-BASED COMPOUNDS

The jury may or may not be out when it comes to field-validating the benefits of certain bio-based chemistries; but there is adequate research to unequivocally say that – whatever benefits they may yet impart beyond being simple bio-based "cut-backs" for asphalt – those potential benefits will be totally unrelated to any natural asphalt restorative or maltene-related chemical process.

Maltenes, by definition, are petroleum-based. Chemistries derived from oranges, soybeans, corn, flaxseed or other "bio-based" ingredients do not contain maltenes and are therefore incapable of replacing them. A Rostler Analysis e.g., cannot be used to measure the efficacy of bio-based chemistries because they have neither asphaltene nor maltenes to fractionalize.

Some of the confusion in the marketplace over so-called "bio-based rejuvenators" may be attributed to the misappropriation of ASTM D2007 as a substitute for the Rostler Analysis. As previously noted, SARA is highly useful as a generalized hydrocarbon separation technique, applicable to a wide range of emulsion industries such as cosmetics, paints, wood treatments, and asphaltic fogs. It is not, as described, useful as a test for asphalt rejuvenation.

Most significantly, D2007 may produce 'false positive' results on bio-based products and other low-molecular-weight non-petroleum composites, including materials that are asphalt-damaging solvents.

As an example, powerful bio-based solvents will appear to soften treated asphalts when, due to their high Kauri-butanol (Kb) value,¹⁴ they are doing so by chemically separating (dissolving) the asphalt binder

¹⁴ https://en.wikipedia.org/wiki/Kauri-butanol_value

matrix in much the manner that Rostler et al., originally used powerful acids and solvents to test the chemical vulnerability of asphalt binder componentry in order to establish restorative technology. So, if one desires to avoid using asphalt damaging solvents on your roadways, always inquire into the Kb value of the materials you are considering by requiring full and detailed Chemical Abstracts Services (CAS) reports on all products to be considered.

Historically, such bio-based materials were marketed as “asphalt releaser” agents because they promote dissolution of a petroleum suspension phase or the maltenes. Because elevated Kb value bio-based reagents destroy asphalt pavement through chemically induced separation of the asphalt binder’s components, the damage may be irreversible and future maltene-replacing rejuvenation infeasible.

Although claiming to be *environmentally friendly*, some bio-based reagents are substantially composed of ecologically damaging volatile organic compounds or VOCs (e.g., citrus-based d-limonene) and semi-volatile organic compounds or SVOCs (e.g., soy and linseed-based biodiesel fuels), which climate scientists believe to be ozone (i.e., “smog”) precursors toxic to humans.

While some research is ongoing on bio-based materials for appropriate asphalt pavement applications, the National Center for Asphalt Technology (NCAT) at Auburn University recently warned that “consideration should be given to the chemical composition of the rejuvenator rather than just its capacity to reduce the viscosity of the aged binder”. So, raising the obvious questions about the chemical properties of any product one is considering is a good precaution to take before applying bio-based materials to any roadway.

PERFORMANCE CHARACTERISTICS OF RAP

In our work in the field, Pavement Technology is increasingly observing accelerated aging characteristics in newly built asphalt pavements. We suspect societal pressures to use recycled asphalts and bio-based additives on America’s roadways may be contributing to this problem.

Recycled Asphalt Pavement (RAP) is recognized for its environmental and financial advantages. Typically RAP with higher quality aggregates is selected. If the use of RAP proves to be responsible for field problems, the mixing process and/or the additives used during reformulation are the likely culprits.

Specifically, to produce high temperature strength (reduced rutting risk) and low temperature fluidity (reduced cracking risk) during asphalt mixing and repurposing of RAP, the mix additives and recycling agents used appear to be producing detrimental results in the field. If high Kb value solvents are used to affect high temperature / low temperature properties through asphalt binder viscosity reduction, the result may be the material declination of maltene phase content.

SUMMATION OF ALTERNATIVE APPROACHES

Although the term “rejuvenator” is today being used to describe a wide range of materials, from topcoats using some maltene content to alternative and “activated” organic hydrocarbon oils representing a multitude of extracts and derivations, the only definitive test is in the purity of the maltene content of the rejuvenator and long-term pavement performance.

While asphaltic pavement top coats can provide temporary oxidation-resistance, and some organic compounds have shown varying degrees of promise as mix additives, primarily as prospectively

environmentally safer “cut-backs,” no alternative chemistry introduced to date has proven capable of mimicking the field-proven results derived from genuine Maltene Replacement Technology.

FIELD TESTING THE EFFICACY OF REVITALIZATION TECHNOLOGIES

Ultimately, the proof is in the pavement, and real-world testing ¹⁵ further supports the results of Dr. Rostler’s analyses. For nearly 50 years, MRT has been used on asphalt roadways across America.

During that time, a wide number of side-by-side (treated vs. untreated) pavement comparison studies have demonstrated the effectiveness of maltene replacement. Such *true* rejuvenators, which return molecularly exact, depleted chemicals into the asphalt matrix, extend roadway life when new pavements are treated within their first two years of service, then retreated three to five years later.

The initial treatment immediately restores those maltenes lost during the high temperatures used during asphalt mixing (and/or those destroyed by certain types of mix additives). The subsequent retreatments restore those maltenes depleted during exposure to sunlight and weather.

Depending upon road conditions, additional retreatments are sometimes recommended, with the goal of achieving a multi-decade service life before pavement rebuild is required.

SETTLED SCIENCE

The science of asphalt composition and rejuvenation is not as complex as some might fear and others wish to promote.

Mother Nature has left us many tools as brilliant as they are obvious. Maltene replacement is one such application, and the most *natural* and only proven solution available for restorative pavement preservation and sustainability.

Michael P. Durante is Vice President, Finance and Strategic Planning for Pavement Technology, Inc. (PTI). The company, founded by the author’s grandfather, Michael G. Durante, and father, Colin M. Durante, in 1972, helped bring to public works professionals America’s first maltene-replacement asphalt rejuvenation technology. Today, PTI is applying its pavement preservation experience and knowledge of sustainable technologies to life-extending asphalt and concrete preservation solutions, including products to reduce the pollution caused by vehicle exhaust emissions. A frequent author pertaining to economic and environmental sustainability, Durante holds degrees in finance and economics from Vanderbilt University and the University of Oxford.

¹⁵ <https://www.pavetechinc.com/wp-content/uploads/2017/12/Charleston-County-Viscosity-Charts.pptx>