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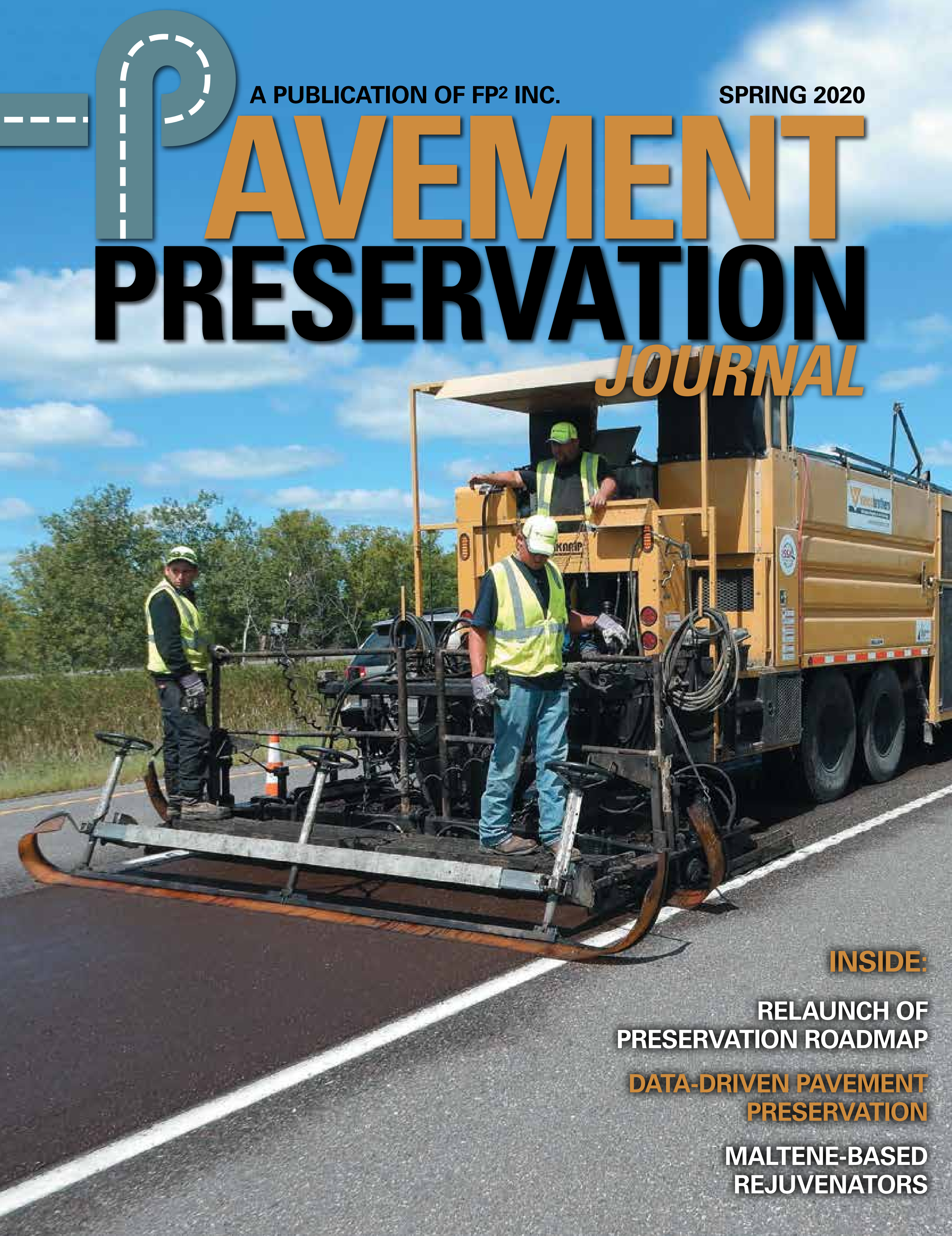


INSIDE:

RELAUNCH OF PRESERVATION ROADMAP

DATA-DRIVEN PAVEMENT PRESERVATION

MALTENE-BASED REJUVENATORS

Maltene-Based Rejuvenators Restore Flexibility, Quell Oxidation Effects

BY MICHAEL P. DURANTE

Asphalt rejuvenators are petroleum-derived additives and modifiers that aim to revitalize, provide sealing, and restore the physical and chemical properties of aged asphalt.

In recent years, there has been increased confusion in defining what it means to "rejuvenate" asphalt pavements. A scientific understanding of asphalt chemistry, especially maltenes and the role they play in rehabilitating and extending the life of asphalt roadways, is critical.

It's known that asphalt pavement deterioration is directly tied to the depletion of asphalt binder content due to the high temperature of manufacturing and subsequent in-service oxidative reduction.

For decades, the natural rehabilitative chemistry commonly described as *Maltene Replacement Technology* (MRT) has been the only proven method for sustainable restoration of both the physical and chemical properties of asphalt pavements. In recent years, alternate methods to chemical restoration have developed that take a different approach from "in-kind" maltene replacement. The goal of this article is to review these different approaches.

WHAT ARE MALTENES?

Regardless of any asphalt's geochemistry, maltenes are one of only two core molecular components common to all asphalts. As the resinous and oily fractions found in asphalt binder, maltenes are the medium that imparts to asphalt pavements their flexibility, fluidity and adhesion properties. The other core component is the colloid or filler known as asphaltene, which imparts to asphalt binder its structure.

Maltenes and asphaltene are separately identifiable phases of the same interdependent molecular structure. They are the principal components of asphalt binder and only differ in their molecular weights, solubility and, hence, vulnerability.

The maltenes are largely responsible for asphalt's ability to withstand the considerable environmental and traffic stresses on today's roadways. But they also are more susceptible than asphaltene to oxidation and the high temperatures of manufacturing. As much as a third of maltene content is lost during hot mix asphalt production. Further, asphalt binder begins to photodegrade at pavement temperatures as low as 120 deg F. It's the loss of maltenes that causes asphalt pavements to become embrittled, raveled and cracked.

Rejuvenation of asphalt binder requires replenishing its depleted maltene content to restore the critical chemical balance between maltenes and asphaltene. Nearly 50 years of science, engineering and commercial applications revolve around techniques to either slow-down the phase separation between maltenes and asphaltene, or to restore the proper chemical equilibrium between the two essential molecular components of asphalt binders.

THE ROSTLER ANALYSIS

By the late 1950s, Dr. Fritz Rostler, working in America's petroleum industry, adopted what became the breakthrough approach to analyzing the molecular structure and aging behavior of asphalt binder.

Specifically, in the 1959 paper *Influence of Chemical Composition of Asphalts on Performance, Particularly Durability,* Rostler and his collaborator R.M. White observed that the balance between the maltene and asphaltene content in asphalt, when exposed to lab-simulated sun and weather, declined with time and exposure. And further, that a loss of maltenes directly correlates with asphalt aging and embrittlement.

Chemical Name	Derived From	Kb value	Chemical Name	Derived From	Kb value
Methyl Linoleate	Linseed Oil	58	Octane	Petroleum	27
Methyl Soyate	Soybean	59	Hexane	Petroleum	31
D-limonene	Citrus	68	Kerosene	Petroleum	33
Corn Ethanol	Corn	68			
Turpentine	Pine Tree	68			

Table 1: Kb Values of Common Petroleum and Agriculture-Derived Diluents

The research of Rostler eventually culminated in the maltene replacement approach to asphalt pavement preservation and life extension. Today, this is "settled science."

ALTERNATIVE METHODS

Though not new chemistries, some non-maltene-based products have been introduced to the pavement preservation marketplace. Almost all of them are agriculturally derived. Historically, agricultural or "bio-based" chemicals have been used to replace certain petroleum products, such as fuels and solvents.

Specific to asphalts, bio-based products are being used as asphalt "cutbacks" or as "asphalt releasers" to clean or reduce undesired asphalt residue. By their nature, bio-based chemicals are dissimilar from asphalt since they are not derived from petroleum. They are generally based on pseudo-aromatic or paraffinic-based "biofuels," which are molecularly very different from petroleum naphthenic-based asphalt binder.

For example, a common bio-based asphalt solvent is d-limonene, which is a citrus-derived powerful dissolver that is chemically similar to turpentine. Vegetable-derived alternates to petroleum-derived products mostly fall into the category of Fatty Acid Methyl Esters or "FAMEs." FAMEs are created through a transesterification (radicalization) process, which simply means by a process in which an alcohol or acid catalyst reacts with vegetable oils (soybean, corn, or linseed etc.) to create biodiesel fuel. Biodiesels are used as alternate fuels and also as strong solvents.

Common names for some biodiesels include corn ethanol and methyl linoleate. The most widely used biodiesel is methyl soyate, which is soy-derived. Collectively, such compounds are frequently referred to as "biosolvents" on product labels and safety data sheets.

These types of structures chemically dissociate asphalt binders, as do similar non-petroleum derivatives such as d-limonene and turpentine. In fact, EPA guidelines recommend the use of biosolvents in oil spills due to their efficiency at dissolving crude oil stocks.

Since such bio-based approaches do not contain maltenes, their asphalt-modifying behavior is typically measured by Kauri-butanol (Kb) value, which is the standardized (ASTM D1133) method for measuring relative hydrocarbon solvency strength.

For instance, a common petroleum diluent such a kerosene (#1 grade diesel or "jet fuel") has a Kb value of 33. FAMEs register closer to a 60 Kb or twice the solvent power of a petrodiesel. Hence,

Maltene Rejuvenator: Sustainable Water-Resistant Performance. Image of Ohio roadway years after a maltene rejuvenator was applied and shortly after a rainfall. The treated section is dry, while the untreated section of pavement remains wet

FAMEs have been used quite successfully to replace traditional petroleum fuels and solvents with solutions promoting significantly stronger solvency power (Table 1). These agriculturally derived solvents naturally can provide an initial softening effect on asphalts. But can high Kb value biosolvents be repurposed as asphalt rejuvenators?

FIELD TESTING TECHNIQUES

Field testing supports the results of Dr. Rostler's analyses. For nearly half a century, maltene replacement has been used on asphalt roadways across the United States. During that time, a significant number of side-by-side (treated vs. untreated) pavement comparison studies have demonstrated the effectiveness of the technique in rehabilitating and promoting more sustainable asphalt pavements.

It is visually apparent that MRT has provided a more durable pavement that is sustainably hydrophobic (i.e., water resistant).

Chart 1 is an abstract from a multi-year sustainability study in Charleston County, S.C., on asphalt pavements treated with *Reclamite*, a maltene-based rejuvenator. The maltene rejuvenator was able to reduce the initial viscosity of the pavement by over 50 percent, and effectively "reset" the oxidation curve for the pavement over the next seven years, while contemporaneously slowing down the oxidation rate. This study demonstrates the critical importance of sustained rheology improvement.

The sustained plasticity benefit (lower poises = higher resiliency) translates into a materially longer life-cycle assessment, with the greatest benefit of the maltene rejuvenator derived beyond year five. This "second curve," as observed in Chart 1, shows how the initial rheology modification to the asphalt continues to perform over multiple years. Maltene replacement clearly rejuvenates aged asphalt binder in the intended (i.e., sustainable) sense.

In contrast, how bio-based chemicals, commonly used as fuel and solvent alternates to petroleum, can be repurposed into an agency's pavement preservation program is unclear given the nature of these chemistries and a lack of long-term field evaluations.

The key in determining the sustained effect these compounds may have on asphalt binders from point-in-time viscosity adjustment is to study the relationship between a given compound's Kb value and a treated binder's rheology over several years.

NCAT REJUVENATOR EVALUATION

In a recent study by the National Center for Asphalt Technology (NCAT) at Auburn University, NCAT researchers tested several chemical compounds, which are being marketed as asphalt binder rejuvenators and surface sealers, for reactivity with aged asphalt.

NCAT chemist Dr. Raquel Moraes, who led the study, described the maltene-based rejuvenator tested as modifying asphalt binder "…through restoration of the original binder asphaltene to maltenes ratio (i.e., the asphalt chemical fractions)." She determined that the bio-based products evaluated chemically softened the asphalt through "…lowering the viscosity of the continuous solvent phase," referring to the dilution of the remaining maltenes.

So, NCAT identified that the chemical reaction between the bio-based compounds and the asphalt accelerated the separation of maltenes and asphaltene by "diluting" the maltenes, a first stage flocculant reaction consistent with a solvent. The diluting of the maltene phase of an asphalt binder matrix may accelerate the oxidation of the depleted maltenes, accelerating aging and embrittlement.

NCAT qualified their asphalt rejuvenator study with the following warning: "For optimal restoration of the aged asphalt binder, consideration should be given to the chemical composition of the rejuvenator rather than just its capacity to reduce the viscosity of the aged binder."

The NCAT study confirmed that of products currently promoted as asphalt rejuvenators, the maltene replacement products replenish depleted maltene content, while the bio-based compounds dissolve the aged binder's remaining maltenes. Hence, they are two very different chemical outcomes.

Choosing a rejuvenator with proven sustained performance is critical. For an asphalt rejuvenator, sustainability is measured by rheological improvement of the binder over a four-to-six-year period or longer. This life-cycle extension is measured by binder viscosity in comparison to untreated pavement annually over time. Visual inspection in the field should also exhibit reduced surface raveling, less top down surface cracking and reduced water absorption indicated by faster surface drying.

Maltene rejuvenators, with zero KB value chemistry, have proven for decade's sustainable binder rheology improvement with measurable life-cycle extension benefits through maltene replacement technology.

Bio solvents, with tested KB values in the 50 to 70 range, repurposed for asphalt preservation, have no maltene content and soften asphalt binder through maltene dilution. Field evaluation may determine a relation to KB value and performance levels.

In selecting the most effective pavement preservation method, an agency should review products sustainability and the methodology and chemistry employed.

Adapted by Pavement Preservation Journal *from a technical paper. For the full version, including footnotes, please contact the editor at expwys@expresswaysonline.com. Durante is vice president, finance and strategic planning for Pavement Technology, Inc., and managing partner of Blackwall Partners LLC. He holds degrees in finance and economics from Vanderbilt University and the University of Oxford.*

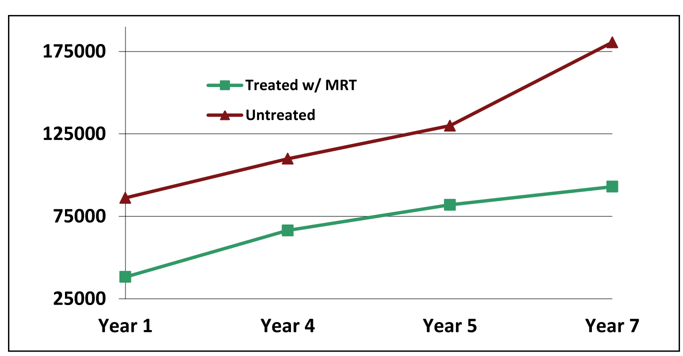
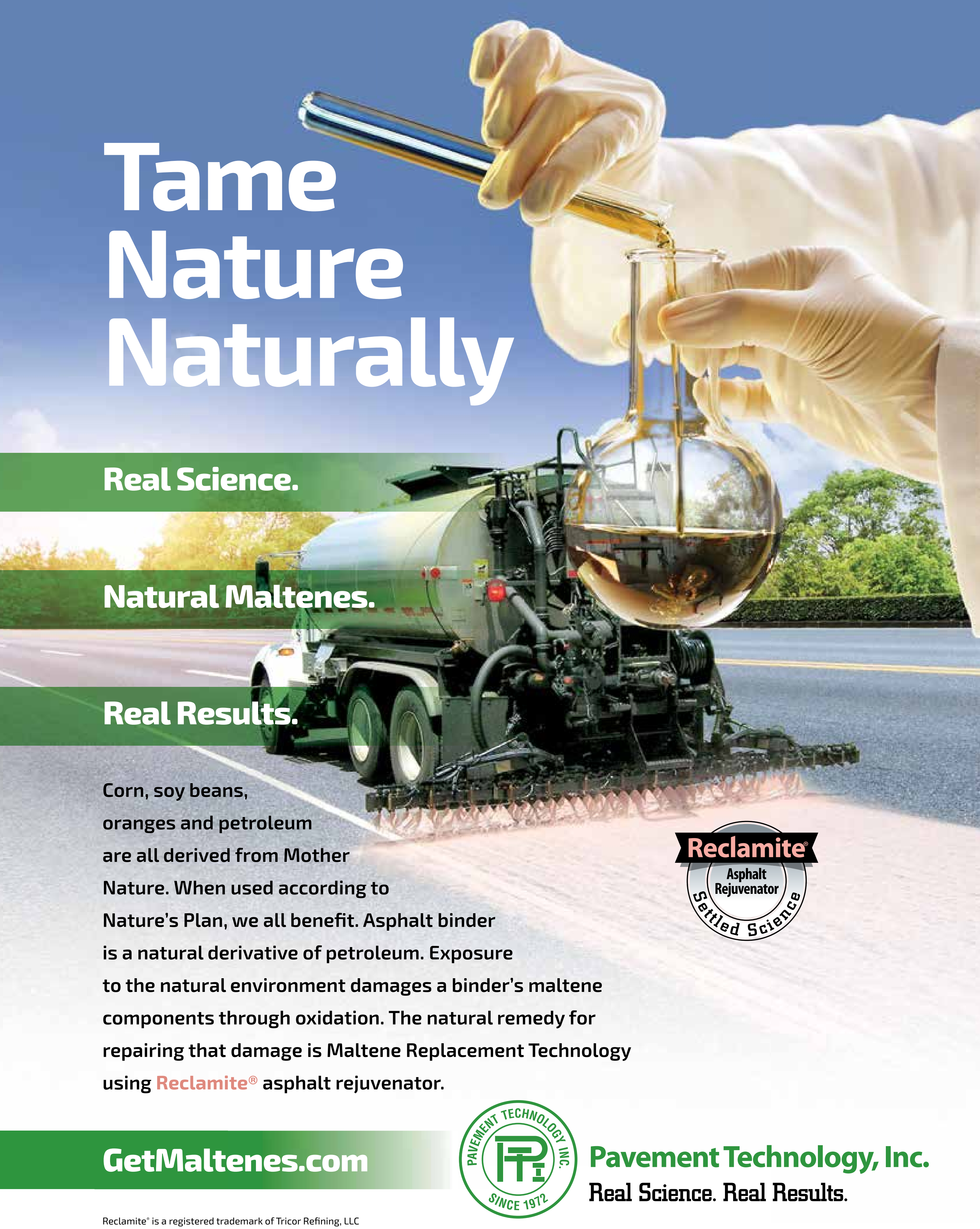


Chart 1: Seven Year Oxidation Rate Curves (in poises) at Charleston County (SC) is an abstract from a multi-year sustainability study in Charleston County, South Carolina on asphalt pavements treated with Reclamite, a maltene-based rejuvenator. The maltene rejuvenator was able to reduce the initial viscosity of the pavement by over 50 percent, and effectively "reset" the oxidation curve for the pavement over the next seven years, while contemporaneously slowing down the oxidation rate.



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