

TECHNICAL BASIS FOR EMISSIONS ESTIMATES IN THE WOOD PRESERVATION INDUSTRY

PREPARED FOR:

J.H. Baxter & Co.

PREPARED BY:

Paul J. Marotta, PhD, P.E. (KY, VT, MI, AR, NY), BCEE

John Michael Corn, P.E. (TN, NC, AL, OH)

AquAeTer, Inc.

Brentwood, Tennessee

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BACKGROUND

Wood preservation, also known as the wood treatment manufacturing process, provides wood-based products capable of withstanding decades of environmental exposure and insect attack. Most notably, creosote treated railroad ties have remained in service for as long as 50 years, with additional usage by the public following the end of service life with the railroads. The combination of its long design life, unique structural capacity, durability and reasonable cost make treated wood very competitive with other materials such as steel and concrete. Its ongoing selection as a preferred product and widespread use is evidence of this fact.

The wood treating process involves the impregnation of wood with a treating liquid composed of a mixture of several different chemicals. This process is markedly different than a painted surface coating or sealant as it penetrates beyond the surface and actually displaces a portion of the water naturally available in wood. To accomplish/improve the displacement, the wood is prepared for treatment by air drying or heating/vacuum. Regardless of the specific wood species or treating process, the treating chemicals vary depending on the application.

The treating liquid is typically comprised of a mixture of chemicals which provide the characteristics required for the specific design. For example, creosote mixtures are used to treat a variety of wood species. The type of wood species used may vary regionally and based on the end use. The creosote mixture includes a range of chemicals characteristic to the heavy ends, i.e., leftovers, of the coal distillation processes. Creosote can be a mixture of 100's of chemicals ranging from those that are well known, such as naphthalene (i.e., commonly used in moth balls), to those that are less familiar.

The next section introduces the testing conducted on treated wood which specifically focused on quantification of the naphthalene vapor emissions from creosote treated wood in the storage yard at the Feather River wood treating facility.

Many of the other constituents in creosote are less volatile than naphthalene, making them less likely to migrate through the air. Because creosote and other treating solutions can include a broad range of organic compounds, the final section introduces the application of Raoult's Law which provides a scientific approach to relating the measured emissions of naphthalene to the emissions from the overall mixture.

FEATHER RIVER TESTING

Testing of creosote treated wood was conducted at the Koppers facility located in Feather River, California in 1990. This testing was conducted to quantify naphthalene emissions from creosote-treated utility poles inventoried in a storage yard. The Feather River testing was done

with creosote-treated utility poles that varied in age from 30 days to less than 30 minutes from removal from the treating process. The poles were tested 6 at a time in a stack three poles wide by two high, using 4" spacers between rows and several inches between each pole in each row. The poles were enclosed in a plastic tent and a constant air flow of 5 mph was passed over the poles. The air flow was sampled at regular intervals. Poles were tested in order of oldest treated poles to newest treated poles.

The Feather River testing objective was to measure the naphthalene emissions from treated wood as a function of time in storage, and derive emission factors that could be used to estimate naphthalene emissions from treated wood in the storage yard. The Feather River study demonstrated that the emission rate from treated and stored materials decreases over time. From these results, the rate of decrease was able to be predicted using an exponential mathematical formula. Because of the nature (obstacles identified in the following section) of the emissions testing from compounds with very low volatilities, the results of the Feather River study have continued to be the basis for estimating emissions from creosote treated storage yard materials throughout the industry. The empirically-derived emission factors can be adjusted for different facilities based on the concentration of naphthalene in the fresh treating solution used at each specific facility.

VAPOR PRESSURE

All materials exhibit a vapor pressure due to the natural tendency for evaporation. Obviously, liquid asphalt evaporates much more slowly than a cup of water. In fact, most of the asphalt remains on the road, while water evaporates from the road after a rainstorm. The question asked concerning what, and how much is escaping as vapor into the air can be answered with two approaches.

OPTION 1 - TESTING

One approach is to attempt to measure the constituents emitted to the air similar to the Feather River testing. This approach may appear as the most straightforward to providing the answer to the question, however there are many drawbacks. These drawbacks include, but are not limited to, the following:

- Measurement methods are limited by their inherent detection sensitivity, i.e., the measurement method may not be able to detect small concentrations. Many of the constituents in typical treating solutions have very low vapor pressures, which means they are not likely to be present in large concentrations in the air. The majority of known constituents within creosote are not expected to be detected in the atmosphere around a tie.

- Testing results would also be specific to the specific chemical mixture. Relying on only testing data would not provide a way to correlate air emissions with treating solution formulation changes. This includes variations as the treating solutions are recycled, which happens after every batch.
- The varied age distribution of treated wood in storage would require multiple tests to be completed over a period of several months in order to accurately represent how treated wood emissions naturally decay over time.
- Local ambient temperatures and weather conditions will fluctuate, requiring multiple tests over a period of several months in order to accurately reflect how treated wood in storage is impacted by seasonality.
- Testing emissions from treated wood that is still hot is complicated since the enclosure required for testing reduces the wood's natural cooling cycle. In other words, the testing system will keep the ties hotter for a longer period of time, which would increase emissions and result in potentially significant overpredictions.

Going the testing route would not only require extensive testing for all sources and formulations, but most importantly, the testing could be inconclusive due to the low concentration of constituents in the vapor emissions. It is quite impractical and cost prohibitive for an individual facility to implement a testing campaign that may lead to inconclusive results.

It is also important to note that the J.H. Baxter & Co. facility is a treating service only facility, and does not own the wood products they treat. As a result, the facility does not store large volumes of treated wood in their yard as inventory. This would further complicate testing and make the overall costs even more prohibitive.

OPTION 2 – SCIENTIFIC PRINCIPLES

The second approach is to apply Raoult's Law, which has been the methodology relied on by regulatory agencies including ODEQ since the 1990's for emissions estimates, toxic release inventory (TRI) reporting, and permitting for the industry. Raoult's Law states that the vapor emitted from a liquid is directly related to the composition of constituents in the liquid and the pure vapor pressure of each of the constituents. Raoult's Law assumes the mixture behaves as an ideal solution. There are known mixtures which deviate from Raoult's law due to interactions between the compounds, however, the principle provides a reasonable estimation of the make-up of constituents in the air around a mixture. The USEPA has recommended the use of Raoult's Law to characterize hydrocarbon mixture in previous versions of AP-42 Chapter 7.1 and it is common practice in industry. Numerous references indicate the assumption of ideal behavior, and thus the applicability of Raoult's Law, is reasonable for hydrocarbon mixtures (e.g., Chemistry & Chemical Reactivity, Kotz and Treichel, Saunders College Publishing, Fourth Edition, 1999, page 658.). The USEPA has recently incorporated this method into AP-42 for emissions estimates.

In practice, the approach outlined below is scientifically based, and provides the capability to calculate the vapor emissions from any hydrocarbon based liquid treating mixture with known constituents.

- 1) Samples of the treating solutions and/or process solutions are sent to a laboratory for chemical analysis. This determines the relative concentrations of the chemicals in the liquid.
- 2) The liquid mass fractions for each measured component is computed by dividing the measured concentration by the assumed total density for the sample solution.
- 3) Molecular weights are utilized to calculate the liquid mole fraction in the mixture for each component.
- 4) The pure vapor pressure for each component at the specified temperature is estimated using available chemical data from various literature and online database references.
- 5) The partial pressure of each component is derived by multiplying the liquid mole fraction from step (3) by the pure vapor pressure from step (4). The ratio of the partial pressure of each component to the sum total of the partial pressures derives the vapor mole fraction of each component in the vapor phase.
- 6) The mole fractions in the vapor phase are multiplied by the molecular weights to determine the relative vapor mass for each component. The ratio of the vapor mass of each component to the sum total of the vapor masses yields the vapor mass fraction.
- 7) Note for mixtures containing creosote and slurry oil, the vapor mass fraction of components that occur in both liquids are added to determine the total vapor mass fraction of each component in the final mixture.
- 8) The calculated vapor mass fractions can then be applied to estimate emissions from applicable emission units at the facility. This is achieved by multiplying the total volatile organic compound emissions rate, obtained from AP-42 or calculated following industry-specific methodologies, for the process by the quantified vapor mass fraction.

Using the outlined Raoult's Law approach provides reasonable engineering basis for air emissions estimates for hydrocarbon treating solutions including: creosote, creosoted/oil blends, diesel oil blends (including pentachlorophenol).