

USE OF A STANTON THERMOBALANCE FOR MICROANALYSIS OF CREOSOTE

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Introduction

In the production of metallurgical coke by modern processes, the gases and tars driven from the coal are condensed to provide the raw material for a wide variety of coal chemicals. These coal chemicals, including millions of gallons of coal-tar creosote, are some of the important products of the United States Steel Corporation. As a major producer of coal-tar creosote, the Corporation has sought to learn more about the properties of creosote as a wood preservative.

One of the best methods for studying the chemistry of creosote as a wood preservative is to extract the residual creosote from wood that has been in service and for which a completely documented history is available. For analytical purposes, however, the amount of creosote that can be extracted from small core borings, sections of small test stakes, and other small specimens is not sufficient. Therefore the Applied Research Laboratory of the United States Steel Corporation initiated a search for a relatively simple method of characterizing very small samples (0.1 - 1.0 gram) to replace the Church-flask distillation, which requires a sample of 100 grams. The Church-flask distillation, which is accepted as the standard method for characterizing the composition of creosote, is fundamentally an evaporation method. Other apparatus that gives refined measurements of evaporation has been proposed by researchers at Allied Chemical Corporation and at Bell Telephone Laboratories.^{1,2}* These methods, however, were not well-adapted to our problem. It was logical to reason that since we were interested in the evaporation pattern of a small amount of volatile materials, a controlled-temperature recording balance would reveal the desired pattern. Such an instrument was available in the form of a thermobalance manufactured by the Stanton Instrument Company of London.

The Stanton Thermobalance

The Stanton thermobalance, Model TR-1 shown in Figure 1, is an analytical, continuously recording balance so constructed that the sample being weighed is supported within a tube furnace. The electrically heated furnace is constructed to operate throughout a range of 1000 centigrade degrees. The temperature is automatically raised during the weighing period by means of a program control motor. Although motors of different speeds are obtainable, the work reported here was done with a motor providing a constant rate of six degrees per minute temperature rise. The tube furnace, which contains baffles to reduce air movement, is two inches in diameter and has a hot zone two inches in depth. A platinum-rhodium thermocouple located near the furnace wall at the center of the hot zone actuates the temperature-recording pen. The furnace can be easily raised and lowered over the sample on the balance platform. The sample, itself, is contained in a small crucible supported on a rod attached to the weighing mechanism of the balance. A system of guide rods and counterweight keeps the furnace symmetrically aligned with the axis of the crucible.

* See References.

The balance mechanism is sensitive to one milligram and can record a weight change as great as 400 milligrams per minute to a maximum total weight change of 50 grams.

Use of the Thermobalance

Because the temperature-recorder thermocouple is located along the wall of the furnace rather than in the crucible, a crucible of high heat-conductivity must be used to minimize the unavoidable lag in temperature of the sample. We used a 10 cc platinum crucible conforming to Standard D-271 of the American Society for Testing Materials. Experimentation with various covers on the crucible revealed that the best correlation with existing standard was obtained when the crucible was used without a cover.

The Church-flask method of distillation that has been adopted as the standard method for creosote characterization by the American Wood-Preservers' Association (AWPA)³ and the American Society for Testing Materials (ASTM)⁴ is basically a vaporization method because there is no attempt at rectifying the vapors. The major difference in the results obtained by these two methods is caused by the difference in methods of measuring the temperature and weighing the distillate. The Church-flask method measures the temperature at a point slightly above the liquid surface, but the distillate is not weighed until it has been collected in a flask at the end of a side-arm condenser, a distance of 52 to 55 centimeters. The weight of the distillate collected at the end of the condenser is, therefore, considerably less than the weight loss of the sample. The discrepancy is the amount of vapor and condensate held up in the flask and in the condenser. The discrepancy is particularly great during the early portion of the distillation. The thermobalance, however, weighs the residue the instant the vapor leaves the surface of the sample in the crucible. The vapor loss, which is the difference in weight between the weight of the original sample and the weight of the residue, is plotted against a continuous record of temperature. The thermobalance results are not retarded and correspond more nearly to a true measure of evaporation. Plateaus or flats that are observed in the distillation pattern obtained by high-reflux distillation are not recorded by the thermobalance because there is no rectification of vapors, and the temperature is driven upward at a constant rate.

Experience has shown that for reliable results the sensitive thermobalance should be placed on an island site, preferably on a concrete floor, away from heat of direct sunlight, dampness, drafts and changes in temperature. There was also an indication that barometric pressure affected the results. Although this influence was not evaluated, it was believed that any adjustment of results would be insignificant relative to the interpretation of the data.

Developing the Procedure

The first step in developing a procedure was to determine the reproducibility of results with the thermobalance. To do this, seven vaporization patterns were made using replicate 0.5 gram samples of one creosote (Figure 2). The range of values show an acceptable level of reproducibility. Vaporization patterns made during any one day agreed more closely than replicate runs made on successive days. We believe that changes in barometric pressure, ambient temperature, and localized drafts account for a large part of the variation encountered.

The next step was to correlate the results obtained by use of the thermobalance with patterns obtained by use of a Church flask and by use of a Snyder 5-ball distillation column. Distillation through a five-ball column was chosen because it is rapid and because it is used by some researchers in the field of wood preservation. The Church-flask method is the accepted standard of the American Wood-Preservers' Association. The similarities and differences between the results of these methods are shown in Figure 3. The thermobalance results are observed to

fall between those of the other two methods. The data show that the differences between the results of the Church-flask method and thermobalance method are due primarily to the lag observed in the use of the Church-flask. Differences between the results of the five-ball column and thermobalance methods are attributed to the rapid rate of temperature rise (6 C per minute), which does not permit enough time for the low-boiling materials within the liquid to diffuse to the surface. It appears that the differences all occur below about 300 C, and all three methods agree reasonably well above this point.

The final step was to determine the ability of the thermobalance to detect differences in creosote composition. This was done by preparing thermobalance vaporization patterns of a fresh creosote and distillation residues from the same creosote after distillates to temperatures of 210, 235, 270, and 315 C had been removed with a five-ball column (Figure 4). This figure clearly shows the effects of removing the low-boiling fractions of creosote. It was reasonable to expect that the effects of any process changing the composition of the creosote could be determined by comparing vaporization patterns. Therefore, the thermobalance vaporization pattern of the chemically changed creosote was superimposed on a similar figure made with a sample of the original creosote. In addition, the thermobalance vaporization pattern provided more information than the Church or five-ball column distillation methods because a higher temperature was obtained with the thermobalance.

Application of the Method

To test the method on actual extracts from creosoted wood, a number of 3/4- by 3/4- by 30-inch stakes were withdrawn from field exposure plots. These stakes had been impregnated with a variety of creosotes and then exposed outdoors for periods of five and ten years, respectively. Each stake was sawn in sections as shown in Figure 5 so that indications of changes in the composition of creosote relative to its position within the stake could be obtained. These sections were shaved individually into fine chips. The residual creosote in each lot of chips was extracted with aromatic solvents. The solvents were then stripped from each extract by distillation under reduced pressure.

These samples of residual creosote were characterized by vaporization on the thermobalance, and the results were graphed. To interpret these graphs, the vaporization patterns were compared with patterns of the original creosotes and with patterns of creosote residues boiling above selected temperatures.

The thermobalance vaporization patterns for the residual creosotes, Figures 6 and 7, from a stake that had been in field test for ten years show that considerable losses of the more volatile compounds have occurred from all sections of the stake. It is noteworthy that the vaporization patterns for all sections fall closely to the vaporization curve obtained from creosote residue boiling above 315 C. The similarity among these curves indicates that much of the creosote boiling up to 315 C has been lost. This loss is known to occur by means of evaporation and migration. If the loss were solely by unhindered evaporation, the curves of the extract and of the control should be very close to each other. If downward migration of residual creosote occurs, then a concentration of high-boiling material can be expected in the lower portion of the stake. Such migration can be expected to appear as a net gain in preservative concentration at the lower end of the stake. This concentration was actually observed. Both below-ground sections retained about 0.08 gram of residual creosote per cubic centimeter of wood. The two sections above ground contained less than 0.05 gram per cubic centimeter.

Figure 6 shows, however, that there is considerable disparity between the vaporization curves of extracts from Section 1 and Section 2, both taken from below the groundline. What then can account for the apparent differences in composition of these extracts? We believe that soon after driving the test stake into the ground, some of the creosote begins to migrate downward through the porous cellular structure

of the wood. As it moves downward, a portion of the low-boiling volatile components are lost by evaporation from the surface of the stake. When the moving creosote approaches the moist groundline section, the downward migration is counteracted by the upward movement of moisture from the soil through the wick-like behavior of the stake. In the section of the stake just below the groundline, the net effect of these counter movements is such as to cause a concentration of creosote. This creosote by now is partially depleted of low-boiling volatile components, and has a high proportion of high-boiling relatively stable components. This concentration of high-boiling material is indicated by the relatively low position of the right end of the vaporization curve for the extract from Section 2.

If we convert the percentages of material boiling above 380 C to absolute amounts of that fraction remaining in the wood, it is found that the quantity of this fraction in Sections 3 and 4 is the same as was impregnated into the wood originally. Below ground, in Sections 1 and 2, the amount of this high-boiling fraction was about twice as great as in the freshly impregnated stake. This increase can result only from chemical changes in the creosote itself. These chemical changes are believed to result primarily from oxidation and polymerization reactions.

Figure 8 shows similar vaporization patterns for Sections 1 and 2 of a stake that had been in field test for only five years. These vaporization patterns lie between the control patterns for residues boiling above 235 and 270 C. Comparison with Figure 6 indicates that evaporation of the creosote has not progressed to the extent observed in the 10-year-old stake. Because the vaporization curves closely parallel the control curves, the chemical change is believed to be relatively small.

Summary

1. The Stanton Thermobalance can quickly and effectively characterize small (0.1 to 1.0 gram) samples of creosote.
2. The continuous vaporization pattern produced by the thermobalance is similar to that of both the Church-flask distillation (adopted by the AWPA and ASTM) and distillation through a five-ball column. The record of weight loss resulting from vaporization on the thermobalance is not retarded, as it is in a Church distillation, and thus is closer to a true measure of evaporation.
3. A method has been developed for estimating the extent of losses of creosote through evaporation.
4. A method has been developed for estimating the relative extent of chemical modifications that have occurred in wood in service during weathering.
5. Natural factors that are conducive to chemical modification of creosote appear to have their greatest effect at the ground line.

References

1. Stasse, H. L., "A Simple Fractional Distillation Test for Creosote," Proceedings, American Society for Testing Materials, 1954.
2. Leutritz, John, Jr., W. McMahon, and G. D. Deeg, "Relationship of Evaporation Pattern and Distillation Characteristics of Coal Tar Creosote," Proceedings, American Wood-Preservers' Association, 1959.
3. American Wood-Preservers' Association "Manual of Recommended Practice," Section A1-58, p 3.
4. American Society for Testing Materials "Standards," Part 4, pp 751-756 (1949).

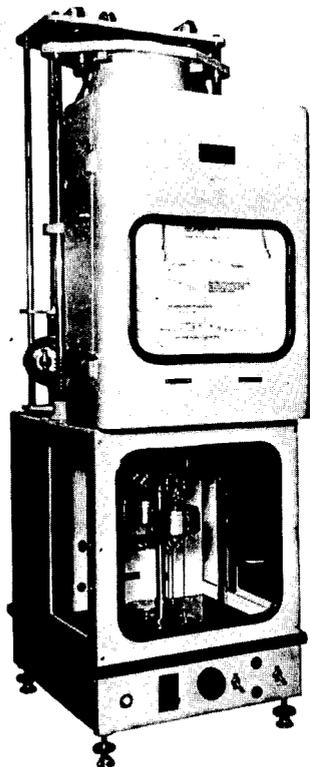


Figure 1. The Stanton Thermobalance.

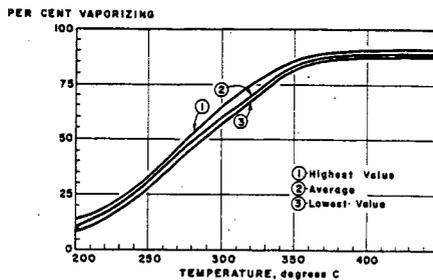


Figure 2. Range of Results From Seven Replicate Runs in Thermobalance.

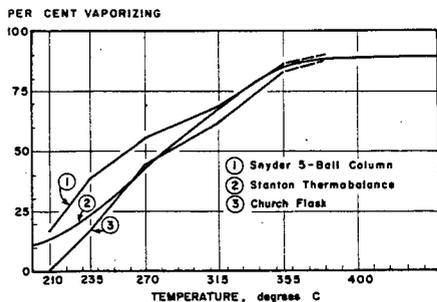


Figure 3. Characteristics of a Creosote Analyzed by Three Different Methods.

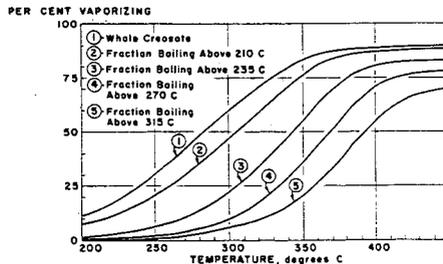


Figure 4. Vaporization Patterns From Whole Creosote and Four of Its Distillation Fractions.

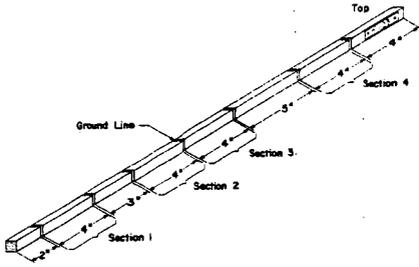


Figure 5. Position of Sections Cut From 3/4-Inch Square Stake for Extraction of Residual Creosote.

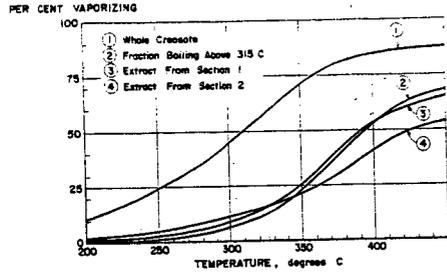


Figure 6. Changes in Creosote Resulting From Ten Years Exposure in Wood Below Ground.

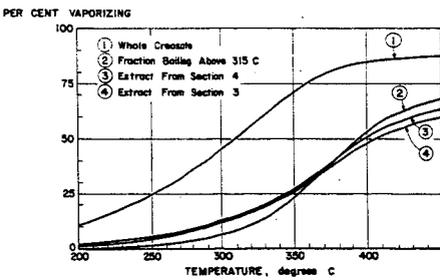


Figure 7. Changes in Creosote Resulting From Ten Years Exposure in Wood Above Ground.

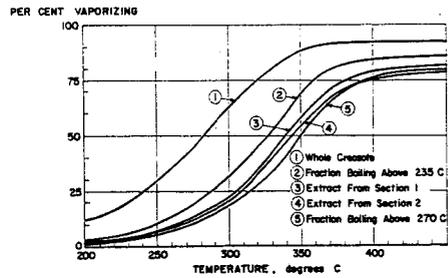


Figure 8. Changes in Creosote Resulting From Five Years Exposure in Wood Below Ground.