A GUIDE TO TURPENTINE TEST METHODS

Introduction

A number of years ago the Pine Chemicals Association, then the Pulp Chemicals Association prepared a collection of the analytical methods used by the tall oil industry. This collection covered methods used for the analysis of tall oil and its precursors such as black liquor soap. It did not include the analysis of the other major product of pine chemicals industry, namely turpentine as that topic was covered in a chapter of the book Sulfate Turpentine Recovery published in 1971. This current guide is designed to update that chapter and bring together the methods now in use in the turpentine industry and in particular in the turpentine fractionation industry. It also includes the method for measuring the turpentine content of pine wood described in the 1971 book.

This guide was assembled by a small subcommittee of the PCA's Testing Committee and chaired by James Russell. Other members of the subcommittee were Henri Jobard of DRT, Donald Scott of Arizona Chemical Company and John Bailey of Rennessenz The aim of the subcommittee was to bring together the test methods of the industry so that these would be readily available to PCA members, their customers and their suppliers.

As the work of the committee proceeded it was realized that emphasis should be on purpose and scope of the test methods rather than the laboratory details. The details of the test methods were readily available in the publications of various standards organizations such as ASTM International, ISO, and the PCA and so it was considered unnecessary to reproduce them as they are all available for purchase. This present guide therefore summarizes the methods in use by the industry, their significance and scope and references where a detailed method is published.

Both physical and chemical analyses are used for the characterization of turpentine. When the chief use for turpentine was as a solvent, the physical characteristics were the most important but now that the main use for turpentine is as a raw material for the production of fine chemicals and terpene resins, chemical analysis, especially gas chromatography, has become of far greater importance.

PHYSICAL METHODS

Appearance and odor are important. Refined turpentine is a water white liquid with a mild characteristic odor. The color of crude turpentine can range from various shades of yellow to brown and, in the case of sulfate turpentine a very foul odor due to the presence of volatile sulfur contaminants overwhelms the characteristic smell. Refined turpentine is clear and any haze is most likely due to the presence of water. (The measurement of sulfur and moisture content are described in other parts of this guide.)

Obtaining a test sample is essential in every instance. Details are given in ASTM Test Method D233.

Specific gravity should be measured at 15.6 degrees Centigrade using any available method having a precision of 0.0005. Details on how to correct for specific gravities measured at other temperatures are given in ASTM Test Method D 233.

Refractive index should be measured at 20 degrees Centigrade. Again details for any temperature correction can be found in ASTM Test Method D 233

Optical rotation can be measured by any accurate polarimeter. Optical rotation is a characteristic of many terpenes and is a measure of the purity of these terpenes. With refractive index it is valuable for characterizing the turpentine source. It should be measured at 589nm (sodium) at 20 degrees Centigrade.

CHEMICAL METHODS

Moisture content

Knowledge or water content is important in two phases of turpentine processing. On delivery, turpentine containers may be contain some water and during processing moisture can interfere with the chemical reactions. Usually, the moisture content is determined by the Karl Fischer titration method. This involves the reaction between water and Karl Fischer Reagent, a complex mixture of iodine, sulfur dioxide, pyridine and methanol. This method is very suitable for measuring small amounts of water in a wide variety of turpentine derived products as well as turpentine itself. It is not appropriate for measuring high levels of water such as might occasionally be found in a shipping container as the amount of titrant would be large. In such cases a sample should be drawn from the bottom of the container and then, if water is found it should be drawn from the container and measured gravimetrically

Details of the Karl Fischer method are given in ASTM Standard Test Method D890.

Sulfur Content

Foul smelling sulfur compounds such us dimethyl sulfide, are contaminants in crude sulfate turpentine, a by-product of the kraft wood pulping process. These need to be removed if the turpentine is to be used as a raw material for the production of end products such as flavors, fragrances and polymers.

Determining the sulfur content of turpentine uses the same techniques as the determination of sulfur in any other media such as petroleum, i.e. UV fluorescence or X-ray fluorescence.

In both methods the fluorescence emitted by the test samples is compared to the emission from standard samples containing known amounts of sulfur. Suitable standards can be obtained from the manufacturer of the testing equipment or can be prepared in the laboratory. It is preferable to use a standard similar in composition to the test substance.

Detailed procedures for these standard test methods are described in ASTM D5453 (UV fluorescence) and ASTM D4294 (X Ray fluorescence).

Composition by Capillary Gas Chromatography

Gas chromatography is an extremely important technique for the analysis and characterization of turpentine and related products as all its components are volatile. Knowledge of the composition and purity is critical as many of the fractions are used as intermediates in the production of flavors, fragrances and polymers. Gas chromatography is by far the most widely used technique for determining the individual components of turpentine and their concentrations.

The method involves injecting the test sample into a temperature programmed gas chromatograph fitted with either a polar or non polar column. The relative concentrations of the various components can be calculated from the resulting chromatogram using the area percent method and assuming the response factors are equal. If greater precision is required, especially if a large amount of heavy components is expected, first determine the response factors using known standards or an internal standard and then use those to calculate the concentrations.

Complete details of the methods can be found in ASTM Test Method D6387 (Turpentine), D801 (Dipentene) and D802 (Pine oil)

Peroxide value

The peroxide value of turpentine and related products is a measure of the degree of degradation of the material. When exposed to oxygen the double bonds of the terpene react to form peroxides. The peroxides catalyze other reactions leading to increased color and instability.

The peroxide value is determined by the reaction of the peroxide with potassium iodide solution. The iodine released in the reaction is measured by titrating with sodium thiosulphate solution using a starch indicator. A typical good quality turpentine can be expected to have an active oxygen content of 50 mg per liter.

Details of this determination are given in ASTM Test Method D1832-65 and AOCS Test method 8b-90.

Chirality is sometimes very important in characterizing turpentine. This property, which pertains to stereochemical structure of certain terpenes, differentiates between dextro and levo optical rotations in certain species i.e. alpha pinene + and alpha pinene -. It can be measured by gas chromatographic analysis using a beta cyclodextrin column.

TURPENTINE CONTENT OF PINE WOOD

No standard method has been published describing a procedure for determining the turpentine content of wood although the PCA's book Sulfate Turpentine Recovery describes a method developed by John Drew. That method was later adapted for the determination of crude tall oil in wood chips and published by the PCA as PCTM 25.

In this procedure wood chips are ground and digested in hot caustic soda. During the digestion the turpentine distils off. Details of the method are given in Sulfate Turpentine Recovery. The turpentine content of wood can also be obtained by following the first steps of PCTM 25 but, in step 6, the turpentine should be collected and measured and not discarded. The of composition of the turpentine can be determined by gas chromatography and the other techniques described in this guide.

Information Sources

Sulfate Turpentine Recovery: J. Drew, J. Russell and H. W. Bajak published by the Pine Chemicals Association, 1971.

Copies of ASTM standard test methods can be obtained by contacting ASTM International, 100 Bar Harbor Drive, West Conshohocken, PA 19428 or on their website: www.astm.org

Copies of PCA PCTM standard test methods can be obtained by contacting Pine Chemicals Association, Inc., PO Box 17136, Fernandina Beach, FL 32035 or on their website: www.pinechemicals.org.