

tars, contains a proportion of undecomposed paraffin oils and is lacking in tar acids.

Fractional distillation of coal tar creosote and water gas tar oil may give very similar results, but it is generally possible to identify the origin of such oils by a closer examination of the composition and physical properties of the various fractions so obtained. Differences in specific gravity and refractive index are the most reliable of the distinguishing physical characteristics. Fractions distilled from coal tar creosote have higher specific gravity than fractions of water gas tar oil distilled between the same temperature limits, and similarly the indices of refraction of the former are higher than those of the latter fractions. The melting point of the higher boiling fractions—those distilled above  $320^{\circ}\text{C}$ .—is also of value as a means of distinguishing between the two products. Oil tar fractions distilled above  $320^{\circ}\text{C}$ . are liquid at  $60^{\circ}\text{C}$ . while corresponding coal tar fractions are rarely liquid at this temperature. Other characteristic physical properties which may serve as a supplement to the more definite tests noted above are the odor and color of the oil fractions. Water gas tar has a particularly disagreeable characteristic odor which can generally be recognized.

The detection of paraffin oils by sulphonation test is probably the most conclusive chemical test for the distinction between coal tar and oil tar products. Hydrocarbons of the aromatic series are converted into soluble sulphonic acids by treatment with concentrated sulphuric acid, and the undissolved residue—paraffin oils—determined by separation. This test is usually made on the fraction distilling between  $305^{\circ}\text{C}$ . and  $320^{\circ}\text{C}$ . A positive result, i.e., a residue of undissolved oils, indicates oil tar origin. The determination of tar acids by hot alkaline extraction is also of value in identifying a creosote sample. Deficiency in compounds of these series indicates that the oil is an oil tar product. However, this test is, perhaps, not so conclusive as the sulphonation test.

The distinguishing tests above described apply to typical commercial oils, but it should be remembered that low coking temperatures, as in certain types of bituminous gas producers or where bituminous coal is used as a blast furnace fuel, yield tars from which creosotes may be distilled which will be very similar to water gas tar oil. Coal tars of this class are, however, of very limited production in America. It must also be noted that the certain detection of oil tar in mixture with coal tar creosote is not always possible, and in cases where the results of foregoing tests suggest the presence of oil tar products, it may be necessary to investigate the history of the sample for conclusive information.

Detailed methods for the laboratory examination of commercial creosotes are outlined in "Preservation of Structural Timber," H. F. Weiss (McGraw-Hill Book Co.), or in publications of the United States Forest Service as noted below. Complete laboratory examination includes determination of specific gravity of the whole sample, fractional distillation, determination of specific gravities and refractive indices of the fractions distilling between  $235^{\circ}\text{C}$ . and  $305^{\circ}\text{C}$ ., sulphonation test of fraction obtained between  $305^{\circ}\text{C}$ . and  $320^{\circ}\text{C}$ ., and determination of tar acids and water.

In the following quotations, all temperatures refer to Centigrade scale.

**\*Specific gravity of the whole oil.**—The perfectly liquefied oil is poured into a hydrometer cylinder, and, at a temperature of  $60^{\circ}$ , the specific gravity is read with hydrometer standardized against water at  $60^{\circ}$ .

**\*Fractional distillation.**—The Hempel distilling flask of resistance glass is employed. The empty flask is tared, 250

grams of melted, well-shaken oil introduced, the platinum-wire plug and the glass beads put in place, and a second weight taken. The thermometer is then inserted in the flask, so that the first emergent reading is  $200^{\circ}$ . The flask is supported on an asbestos board with a slightly irregular opening of very nearly the largest diameter of the flask. A condensing tube is employed and the fractions are collected in tared flasks. The distillation is run at the rate of 1 drop per second, and fractions collected between the following temperatures: Up to  $170^{\circ}$ ,  $170^{\circ}$ – $205^{\circ}$ ,  $205^{\circ}$ – $225^{\circ}$ ,  $225^{\circ}$ – $235^{\circ}$ ,  $235^{\circ}$ – $245^{\circ}$ ,  $245^{\circ}$ – $255^{\circ}$ ,  $255^{\circ}$ – $285^{\circ}$ ,  $285^{\circ}$ – $295^{\circ}$ ,  $295^{\circ}$ – $305^{\circ}$ ,  $305^{\circ}$ – $320^{\circ}$ , and if feasible  $320^{\circ}$ – $360^{\circ}$ .

The character of the fractions and their weights are recorded and the results plotted as a curve, in which the ordinates are percentages by weight and the abscissae temperatures. When the distillation has reached the  $225^{\circ}$  point, an asbestos-board box should be placed around the distilling flask, to cover the bulb, but leave the Hempel column exposed. Drafts upon the distilling apparatus must be avoided.

**\*Index of Refraction.**—The indices of refraction of the different fractions between  $235^{\circ}$  and  $305^{\circ}$  are determined at  $60^{\circ}$  in a refractometer with light compensation. The results are plotted with temperatures as abscissae and indices of refraction as ordinates.

**\*Specific Gravity.**—The specific gravities of the fractions between  $235^{\circ}$  and  $305^{\circ}$  are determined by means of specific-gravity bottles. These bottles are filled at  $60^{\circ}$  and the weights referred to water at the same temperature. The results are plotted as a curve, in which the ordinates are specific gravities at  $60^{\circ}$ , and the abscissae temperatures.

**\*Tar Acids.**—Fifty cubic centimeters of the creosote under analysis are measured at  $60^{\circ}$  into a small distilling flask by a pipette. The oil is distilled as completely as possible without breaking the distilling bulb, and the distillate is caught in a short-stemmed, 100 cubic centimeter separating funnel. At the end of the distillation 25 cubic centimeters of boiling hot 15 per cent. sodium hydroxide is added to the distillate and the mixture thoroughly shaken. The alkaline extract is then drawn off into a 100 cubic centimeter shaking cylinder and 25 cubic centimeters more of hot sodium hydroxide added. After extracting with this second portion for five minutes, with frequent shaking, the solutions are allowed to separate and the alkaline extract added to the first portion in the cylinder. A third extraction is made with 15 cubic centimeters of alkali. The total alkaline extract is cooled, acidified with sulphuric acid, thoroughly shaken, brought to  $60^{\circ}$ , and the volume of supernatant oil read off.

**\*Water.**—After weighing the first two fractions of a fractional distillation they are united in a small separatory funnel, and any water which is present is separated from the oil and its amount accurately determined. If particular accuracy is required in the estimation of the water it may be done by the Marcusson xylol distillation method.

**†Sulphonation Test.**—Ten cubic centimeters of the fraction of creosote to be tested are measured into a Babcock milk bottle. To this is added 40 cubic centimeters of 37 times normal acid, 10 cubic centimeters at a time. The bottle with its contents is shaken for two minutes after each addition of 10 cubic centimeters of acid. After all the acid has been added the bottle is kept at a constant temperature of from  $98^{\circ}$  to  $100^{\circ}\text{C}$ . for one hour, during which time it is shaken vigorously every 10 minutes. At the end of an hour the bottle is removed, cooled, and filled to the top of the graduation with ordinary sulphuric acid, and then whirled for five minutes in a Babcock separator. The unsulphonated residue is then read off from the graduations. The reading multiplied by 2 gives per cent. by volume directly. (Each graduation equals one two-hundredths of a cubic centimeter.)

\*United States Forest Service Circular 112, "The Analysis and Grading of Creosote," A. L. Dean and Ernest Bateman. Also reproduced in United States Forest Service Circular 206, "Commercial Creosotes," Carlisle P. Winslow; and in "Preservation of Structural Timber," H. F. Weiss (McGraw Hill Book Co.)

†United States Forest Service Circular 191, "Modification of the Sulphonation Test for Creosote," E. Bateman. Also reproduced in "Preservation of Structural Timber," H. F. Weiss.

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