been added. When a sample of the original oil to which 8 per cent of linseed oil had been added was examined, its spectrum showed only a yellow band; 8.5 per cent of linseed oil was then added to the original sample and the observation made; the "turning point" was now reached, shown by the characteristic red band appearing on the upper side of the spectrum. Subtracting the amount added, 8.5 per cent, from the arbitrary figure 15.5 per cent, it is evident that the sample in question contained 7 per cent adulteration.

2—Another sample taken from a rejected shipment, when first observed in the cell, showed a spectrum which was deficient in the red. It was therefore thought to contain about 10 per cent adulteration. When 6 per cent of linseed oil was added to this sample, the spectrum appeared only as a yellow band, and when 6.5 per cent of adulterant was added to the sample in question the red appeared on the upper side of the spectrum. Subtracting 6.5 from 15.5 the adulteration was shown to be 9 per cent.

3—Another sample, taken from a rejected shipment, when examined by this method, showed an adulteration of 7.5 per cent, and a sample marked questionable by the chemist of a large varnish works, showed an adulteration of 4.5 per cent.

The sample of pure Chinese wood oil used by the American Society for Testing Materials, and reported on as an exceptional oil, required an addition of 17.0 per cent linseed oil before the "turning point" occurred; hence in examining the four adulterated samples of this oil, which were used by the society in the work for 1915, it was deemed advisable, for sake of comparison, to use the figure 17.0 as well as the arbitrary figure of 15.5. Table IV gives the results in both cases:

TABLE IV
Per cent adulteration found by using as
"turning point"

SAMPLE NO.	17.0 per cent	15.5 per cent
2.....	5.25	3.75
3.....	10.50	9.00
4.....	5.0	3.5
5.....	10.0	8.5

If these samples had been examined without having the pure oil the last column would have been considered as the percentage to which the Chinese wood oil had been adulterated.

SUMMARY OF RESULTS

If the adulterating oil is known, very accurate results can be obtained by this method, otherwise the accuracy is limited to 1.25 per cent either way from the true value, owing to the fact that the turning point varies between the limits of 14.5 to 17.0 per cent and the arbitrary value of 15.5 is not correct.

If, however, the oil with which the Chinese wood oil is adulterated can be determined, the accuracy is thereby increased. Lewkowitsch,¹ in commenting on tallow seed oil, says: "The most characteristic property of this oil is that it rotates the plane of polarized light to the left, *viz.*, 6° 45' in a 200 mm. tube in a Laurent polarimeter, corresponding to -29.9 saccharimeter degrees. The optical activity is confirmed by Nash." This is being investigated as a means

¹ "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. II, p. 70.

of detection in Chinese wood oil at the present time in this laboratory. If the attempt is successful the accuracy for adulterations with other oils will be increased, since the only other oil which causes the "turning point" to take place as high as 17.0 per cent adulteration is perilla oil, which is used only occasionally as an adulterant of wood oil.

The detection of sesame by the Baudouin test and the detection of cottonseed oil by the various methods as described in Lewkowitsch, would eliminate most of the oils which affect the turning point as low as 14.5 per cent. The remaining oils affect the turning point within such a close range of each other that the arbitrary figure assumed as the turning point would be very close to the true value.

The writer believes that concentration of the adulterating oils by the light break method described by Ware and Schumann¹ may facilitate the detection of those oils readily identified.

Another factor which must be taken into consideration is the fact that the prism itself has a dispersive power and if its dispersion is too large the anomalous dispersion of Chinese wood oil will be counteracted. Also, prisms, though having a dispersion low enough to be used in this method, may vary from each other, so that in using an instrument of this type one must first calibrate his prism before making determinations. This is readily done by finding the "turning points" brought about by the addition of different oils to Chinese wood oil.

The fatty acids of Chinese wood oil also show anomalous dispersion. This fact gives promise of interesting information when studied in connection with other fatty acids.

RESEARCH LABORATORY
ACME WHITE LEAD AND COLOR WORKS
DETROIT, MICHIGAN

COMPOSITION OF WOOD TURPENTINE²

By MAXWELL ADAMS

Received June 14, 1915

Because of the shortage in the supply of "gum" turpentine, and the enormous wood waste of our lumber mills during the past ten years, many methods for the extraction of turpentine from wood have been proposed. The economics of steam, solvent, alkali digestion, oil bath, destructive distillation, under both increased and diminished pressure processes have been given thorough consideration, but very little attention has been accorded the composition of the turpentine obtained by these different procedures. Although the products obtained by these various methods differ widely as to color, odor and physical constants, without any attempt at standardization, they have all been classed together. The result has been that a strong prejudice has arisen against any product sold under the name of wood turpentine.

The physical properties of wood turpentine obtained, presumably, from long leaf or Cuban pine, have been

¹ This JOURNAL, 6 (1914), 806.

² This work was in part done in Prof. Wallack's laboratory at Göttingen, Germany, and supported by the Adams Fund of the Nevada Agricultural Experiment Station.

worked out by Hawley,¹ F. W. Richardson and J. E. F. Whitaker,² Marcille,³ Parry.⁴ Others have published methods for the analysis of different kinds of turpentine, but for the most part these workers have been concerned with the identification of adulterants, or with physical constants; little attempt has been made to identify or separate the different terpenes present, and in no case observed has wood turpentine obtained from any variety of Western pine been investigated.

The present investigation was undertaken for the purpose of determining the physical properties and identifying the various terpenes present in the wood turpentine prepared from pine growing in the western part of the United States. The "gum" turpentines of the varieties chosen have previously been examined by Schorger.⁵

Samples of wood from Western yellow pine (*Pinus ponderosa*), obtained from trees growing in the neighborhood of Independence Lake, Cal., Jeffrey pine (*Pinus jeffreyi*) from trees growing on the Eastern slope of Mount Rose and near Galena Creek, Nev., and from single leaf nut pine (*Pinus monophylla*) growing on the western slope of the mountains between Steamboat Springs and Virginia City, Nevada, were collected. Each sample was distilled under diminished pressure in a retort, around which circulated hot oil, according to the method described by Adams and Hilton.⁶ The distillate from the wood was separated roughly into three fractions: (1) that which comes over below 160°, (2) the distillate between 160 and 220, and (3) that driven over above 220°. In most of the following experiments only the first fraction was used. The second fraction contained considerable quantities of decomposition products, which could be removed only by alternate treatments with sulfuric acid and caustic soda, together with steam distillation. Since treatment with these chemicals might affect the chemical composition of the oil, the second and third fractions were discarded. This procedure has doubtless slightly increased the percentage of the lower boiling terpenes over that which would be found in ordinary crude wood turpentine.

SINGLE LEAF NUT PINE

A sample of wood turpentine obtained from the distillation of the wood of single leaf nut pine, according to the above method, when redistilled with steam, had the following physical constants: d_{15}° 0.9702, n_{D15}° 1.4771, α_{D20}° +21.15. The oil was colorless and had a very characteristic aromatic odor. A sample of the oil was dried over fused potassium carbonate, distilled at a pressure of 15 mm. and separated into three portions:

I—B. p. 50–60°, consisted of 77.9 per cent of the original oil and had the following properties: d_{15}° 0.8691, n_{D15}° 1.4693, α_{D20}° +29.76

II—B. p. 60–80°, consisted of 7.6 per cent of the original oil and had the following constants: d_{15}° 0.8721, n_{D15}° 1.4777, α_{D20}° +11.78

¹ Eighth Int. Congr. Applied Chem., 1912, and Forest Service, Bull. 105.

² J. Soc. Chem. Ind., 30, 115.

³ Bull. soc. chim., 2, 762.

⁴ Chem. and Drugg., 81, 52.

⁵ THIS JOURNAL, 5 (1913), 971, and U. S. Forest Service, Bull. 119.

⁶ Ibid., 6 (1914), 378.

III—B. p. 80–135°, consisted of 9.2 per cent of the original oil and had the following constants: d_{15}° 0.8982, n_{D15}° 1.4856

There was a residue left in the distilling flask consisting of 5 per cent of the original oil. Each fraction decolorized an alkaline solution of permanganate and absorbed bromine readily, but none gave a test with sodium bisulfite or semicarbazide for aldehydes or ketones.

α -PINENE—From Fraction I, when distilled over sodium, there was obtained a material with a boiling point of 155–156°, which when dissolved in acetic acid and treated with amyl nitrite and hydrochloric acid gave crystals of pinene nitroschloride. After dissolving in chloroform and reprecipitating with methyl alcohol the crystals melted at 103°. The nitrol piperidine, prepared in the usual manner¹ from the nitroschloride melted at 118°. The above results prove the presence of *d*- α -pinene.

β -PINENE—Fraction II, after several redistillations over sodium, yielded 15 per cent, or about one per cent of the original oil, which boiled at 167°; 3.7 grams of this oil were added to 4.9 grams of potassium permanganate, and 1.8 grams of sodium hydroxide dissolved in 11 grams of water and crushed ice. The mixture was agitated on a shaking machine for 6 hours, according to the method of Wallach.¹ As the ice melted the temperature was allowed to rise to that of the room. The hydrocarbons not acted upon were driven off with steam and the solution remaining in the retort was filtered from the oxide of manganese and the filtrate evaporated, while a constant stream of carbon dioxide was conducted through the solution. Crystals of sodium nopinate separated when the solution cooled. The yield, however, was so small that an attempt to prepare the nopinic acid in sufficient quantity for complete identification failed.

CADINENE—The third fraction, which was light yellow in color, when heated at atmospheric pressure began to boil at 170° but turned brown, indicating some decomposition. A second portion was therefore distilled at 15 mm. pressure and separated into two portions. The lower boiling fraction was tested for limonene and phellandrene without positive results. The higher boiling fraction, after distilling over sodium, thereby removing considerable tar, boiled without any apparent decomposition at 205–215°. This fraction, thus purified, was dissolved in four parts of glacial acetic acid, cooled in brine and ice, and saturated with dry hydrogen chloride. A heavy brown liquid separated, which when placed in an open dish evolved considerable gas and quickly solidified. This solid was dissolved in acetic acid and allowed to stand for 12 hours. A good yield of white crystals separated, which melted at 117°, thus establishing the presence of cadinene.

These results, when compared with those of Schorger² on the volatile oil obtained from the oleoresin, indicate that wood turpentine obtained from this species is almost identical in both physical properties and chemical composition with the pure "gum" spirits.

¹ Ann., 356, 288.

² Loc. cit.

JEFFREY PINE

In the following experiments on the volatile oil from Jeffrey pine especial care was taken to identify the wood used, because the differentiation between *Pinus jeffreyi* and *Pinus ponderosa* is very close, and some confusion has arisen on this account. Sadtler¹ reports having obtained heptane from *Pinus ponderosa*. This error probably arose from a confusion of Yellow pine with Jeffrey pine.

Sudwirth² says in writing of Jeffrey pine: "Some specialists consider it a variety of *Pinus ponderosa*, which it resembles so closely in its habits and soil and climate requirements that from the foresters' point of view there appears to be no practical reason for distinguishing the two."

Jepson³ says, "The Jeffrey pine which merges insensibly into the Yellow pine is in its typical form found at high elevations ranging from 6000 to 9000 feet. By some writers this variety is regarded as a species. While the typical form is clearly to be recognized it is to be said, on the contrary, that Jeffrey pine not only passes over into Yellow pine, but that the transition forms in the intermediate region are quite as numerous and occupy as extensive an area as the true Jeffrey pine itself."

In the publications of the United States Forest Service⁴ similar ideas are expressed as follows: "The Jeffrey pine bears very close resemblance to western yellow pine and some authorities regard it simply as a variety."

Because of the distinct chemical difference in the volatile oils obtained from the woods of these trees, as shown by the following analyses, there is good evidence for the contention that Yellow and Jeffrey pine are distinct species; at least there is a definite chemical method for distinguishing between them. It would be interesting in this connection to examine chemically the volatile oil from a specimen which the botanist considers a transition form.

A sample of wood turpentine obtained from distilling carefully selected wood from a well identified Jeffrey pine tree, was distilled under diminished pressure. The distillate thus obtained was steam-distilled, the resulting volatile oil dried over potassium carbonate and separated into four fractions by distilling at a pressure of 15 mm.:

Fraction	I	II	III	IV	Residue
Boiling point.....	25-30°	30-35°	35-65°	65-125°	
Per cent obtained.....	74	13	6	4	3

The first three fractions distil without decomposition at ordinary pressure. They were combined and distilled over sodium and a portion, consisting of about 90 per cent of the entire volatile oil, was obtained which distilled between 99 and 100.5°. This distillate gave no test for the double bond with von Beyer's reagent, neither would it absorb bromine. When added to amyl nitrite in acetic hydrochloric acid solution it gave no test for pinene. The physical

properties were d_{15}^0 0.6877, n_{D20}^0 1.3890, optically inactive. These tests prove that the volatile oil from Jeffrey pine wood contains from 90 to 95 per cent of normal heptane.

The fourth fraction was redistilled at diminished pressure and separated into two parts. The lower boiling fraction was distilled over sodium and tested for limonene and dipentene. It absorbed the calculated amount of bromine to form the tetrabromide, but crystals were not obtained from the oil. The higher boiling fraction gave a precipitate with sodium bisulfite, which would indicate the presence of citronellal, but the small amount of the material available prevented making confirmatory tests.

YELLOW PINE

A sample of volatile oil obtained from Yellow pine, according to the method already described, was clear, water-white, and had the odor which is characteristic of Yellow pine wood. Its specific gravity at 15° was 0.8626, index of refraction 1.4727, specific rotation -13.15.

On distilling 500 grams of the oil, using a Norton and Otto distilling tube, and at a barometric pressure of 642 mm., the following results were obtained:

FRACTIONAL DISTILLATION OF THE VOLATILE OIL OBTAINED FROM THE WOOD OF *Pinus ponderosa*

Temp. ° C.	Distillate Observed	Cumulative	Specific gravity, 15°	Index of re- fraction, 15°	Specific ro- tation, 20°
156-158	4.72	4.72	0.8467	1.4621	-15.14
159.9	9.39	14.11	0.8525	1.4710	-14.48
161.2	9.20	23.32	0.8546	1.4731	-14.57
162.1	9.99	33.32	0.8552	1.4732	-13.68
163.0	10.08	43.40	0.8559	1.4738	-12.15
163.9	9.51	52.91	0.8562	1.4740	-11.89
164.9	9.65	62.56	0.8590	1.4744	-11.04
176.7	9.95	72.51	0.8603	1.4745	-10.56
169.8	6.958	79.47	0.8633	1.4752	-10.97
173.4	7.86	87.35	0.8733	1.4913	-14.12
180.3	9.36	97.71	0.9246	1.5038	-17.22
Residue	2.3				

When the above table is compared with a similar one prepared by Schorger¹ on "gum" spirits, it will be noted that the wood turpentine contains more of the low boiling and less of the high boiling fractions than that obtained from the oleoresin of western pine. This difference is perhaps due to the fact that wood turpentine was obtained from the first fraction of the wood distillate and that the barometric pressure was abnormally low.

A second analysis, which was made upon a smaller but a more representative sample of Yellow pine wood distillate, and which contained all the volatile oil given off up to the temperature at which the wood began to decompose, gave the following results:

Fraction	I	II	III	Residue
Distilling temperature.....	156-164°	164-172°	172-180°	
Per cent distillate.....	8.7	72.5	16.4	2.4

Fraction I of the oil when tested for α -pinene readily yielded nitropiperidine which melted at 118°. Fraction II, when oxidized with potassium permanganate according to the method previously described, gave an abundant yield of crystals of nopinic acid, which melted at 125°. Fraction III gave crystals of limonene tetrabromide when treated with bromine.

CONCLUSIONS

The presence of practically every constituent of the

¹ U. S. Forest Service, Bull. 119, 12.

¹ Am. Jour. Pharm., 51, 176.

² "Trees of the Pacific Slope."

³ "The Silva of California," p. 80.

⁴ Silvica Leaflet, p. 21.

volatile oil of the oleoresin has been identified in the wood turpentine of the three varieties of wood under examination. The physical properties and the percentage composition do not always agree, yet they coincide as closely as could be reasonably expected, when we consider the inaccuracies of some of the

methods available. The results thus far obtained justify the conclusion that the volatile oil obtained from distilling wood under diminished pressure is similar to that obtained from the oleoresin of the same species of tree.

CHEMICAL LABORATORY, UNIVERSITY OF NEVADA
RENO, NEVADA

LABORATORY AND PLANT

SOME IMPROVED ELECTRICAL LABORATORY APPARATUS

By CHAS. MORRIS JOHNSON
Received July 23, 1915

I—QUICK HEATING ELECTRIC FURNACE FOR THE DETERMINATION OF CARBON IN STEEL, ETC., WITH TRAIN

The train (Fig. 1) consists of: (1) a mercury tube to detect leaks and stoppages; (2) a safety jar containing a 1 : 1 solution of KOH; (3) a tower filled loosely with a plug of glass wool followed with anhydrous calcium chloride, a layer of soda lime and another

placeable heating element, and a supporting stand. The furnace will heat from the cold to 1000° C. in 20 to 25 minutes with a current consumption of 3 to 4 amperes. It can be cooled rapidly, if desired, by lifting off the top half of the split muffle. The writer has supplanted for some time in this laboratory, and in another laboratory under his direction, all of the type introduced by him in 1908¹ with this new type shown in Fig. 1.

This type of electric furnace can be built in any length of heating surface with coils connected in parallel. The type shown in Fig. 1 is 13 inches long by 3⁵/₃₂

FIG. 1

plug of the wool; (4) a jar of short pieces of stick caustic potash with a plug of glass wool at the top and at the bottom; (5) a clay and rubber connector doing away with rubber stoppers at the charging end; (6) the vitrified clay combustion tube with the tapered outlet doing away with the rubber stopper at this point also; (8) is the jar of granulated zinc to stop acid and sulfur; (9) is a jar of phosphoric acid powder and (10) is the bulb for absorbing and weighing the CO₂. This train was designed by the writer, being a simplification of his train described in *J. Am. Chem. Soc.*, May, 1908.

The writer has now used the tapered clay combustion tubes for over two years for the determination of carbon in steel, etc., and has been using them for some months for oxygen determinations also.

The new split muffle type of furnace was designed about a year ago. It is of most simple construction, consisting of a split muffle of kieselguhr, a coil of nichrome wire embedded in alundum cement as a re-

inches O. D. and 1¹⁵/₁₆ I. D. The writer built the same type for organic work 18 inches long. By using three rheostats a long furnace can be made to heat to three different temperatures at once or it can be heated in one part if desired.

The furnace presents a bright neat appearance with its white muffle; new heating elements can be kept in stock and quickly put in place in case of a burn-out as there are no screws or powdered heat insulation to bother with. In case the muffle becomes soiled it can be put in a muffle furnace and heated to a red heat for about 20 minutes when it becomes as white as new. The simple construction makes the furnace a very inexpensive one.

By using a split insulation muffle of 5⁵/₈ inches O. D. and 2⁵/₃₂ I. D., the writer obtained a furnace of this type which is developing 1020° C. with a current consumption of only 2.7 amperes. This furnace has been in daily service in this laboratory for several months.

¹ *J. Am. Chem. Soc.*, 30 (1908), 773.