

THESIS

on

THE SOURCE AND CHEMICAL CHARACTERISTICS OF  
COMMERCIAL OIL OF TURPENTINE.

Submitted to the Faculty

of the

O R E G O N A G R I C U L T U R A L C O L L E G E

for the degree of

Bachelor of Science

by

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Redacted for Privacy

APPROVED

Department of Chemistry.

THE SOURCE AND CHEMICAL CHARACTERISTICS OF  
COMMERCIAL OIL OF TURPENTINE.

The earliest inhabitants of the world are thought to have lived in central Asia where they were surrounded by a great variety of plant life. Southern Asia and the islands bordering on its shores were especially rich in spices and aromatic plants which formed the oldest and principal article of exchange. They came into general use, not only on account of their agreeable odor and aromatic taste, but because they were used in their religious rites and in the burial of the dead.

It is probable that at a very early date they learned to distil the volatile oil from the spicy products so that it would be in a more convenient form for use. The earliest record of their scientific accomplishments is the Ayur-Veda which shows that the people of India were acquainted with primitive methods of distillation in very early times, but the exact date of the records is not known. From the legendary history of the Persians, it would seem that they too understood the process of distillation. The ancient Egyptians, whose history is known as far back as 4000 B.B., made and used cedar oil, or as it was called later, turpentine oil, and colophonium, or resin. These older nations and especially the Egyptians were the teachers of the Greeks and Romans, and through them of the modern nations. As early as the fourth century, Greek scholars

had described the distilling apparatus and methods of the Egyptians, and by the ninth century the Arabians are known to have distilled some of the volatile oils.

The early methods used were crude, and the nature of the oils was little understood before the 18th century. After the discovery of oxygen by Scheele and Priestley in 1774, the chemical constituents of substances began to receive attention. Chemists worked first upon the simpler inorganic substances and later upon the organic compounds. Houtton-Labillardiere by an elementary analysis of turpentine oil discovered the ratio of carbon to hydrogen to be five to eight. From 1852 to 1863 Berthelot made investigations concerning the hydrocarbons contained in volatile oils. He studied first the hydrocarbons of turpentine oil and discovered six isomeric hydrocarbons. Much progress has been made in the chemistry of the volatile oils in the last twenty years, yet there is still much to be learned.

The earliest apparatus for distillation that we have any record of was an earthen kettle in which the oleoresin was boiled in water. The oil was either removed from the surface of the liquid, or its vapors were condensed in layers of wool spread over sticks of wood laid across the top of the kettle and wrung by hand when the wool was saturated with oil. The apparatus has been gradually improved until the present methods of distillation which greatly increase the yield

and the quality of the oil.

There are many plants which contain volatile oil. It is obtained from more than 350 different species. The oil is found in the various organs of the plant either in glands or in intercellular receptacles, and is supposed to be an excretion formed during the life processes of the plant but of no further use so far as the growth of the plant is concerned. The trees of the various species of the family Pinaceae contain in ducts under the bark an oleoresin which is a solution of resin in volatile oil. When the ducts are tapped, the oleoresin exudes and when it is distilled, the volatile oil distills as oil of turpentine and the resin remains as a residue.

At the present time the United States, France, and Austria are the principal countries from which the oil of turpentine is obtained. Nine-tenths of the world's supply of naval stores, that is turpentine, resin, pitch and tar come from the United States; the other one-tenth comes from France and Austria.

The pine forests of North America are in the South Atlantic States, in the eastern part of Canada, in British America, and on the western slopes of the Pacific States. The turpentine industry is carried on chiefly in the forests of North and South Carolina, Georgia and Alabama where the species of pines most abundant are: *Pinus palustris*, long-leaved or Southern pitch-

pine; *Pinus taeda*, Loblolly or Rosemary pine; *Pinus heterophylla*, Swamp pine; and *Pinus echinata*, short leaved yellow pine.

The people of the southern states felt the pine forests were inexhaustible and in collecting the sap they were very heedless of the life of the trees. They would cut a box-like cavity at the base of the tree into which the sap would flow from a cut made above on the trunk. In the spring and during warm weather these boxes, which held about a quart, were filled in from two to four weeks. Later, the sap flowed slower and ceased altogether by the last of October. In 1901 Dr. Charles Herty of the Bureau of Forestry introduced a method of collecting the sap in earthen pails or cups in much the same way that maple sap is collected. This greatly increased the amount of sap collected and helps very much in prolonging the life of the trees. Whichever method is used, men go round and collect the sap and empty it into barrels. It is distilled in copper stills holding usually about fifteen barrels of 280 lb. each. When the still is filled, a gentle heat is applied until the mass is liquified. All the water contained in the crude turpentine is distilled off; then a small stream of cold water is let in so that the heat is kept at or below 316 ° F. The mixture of oil of turpentine and water which distills over is caught in a wooden tub, and the liquid resin is allowed to flow

off through an exit tube at the bottom of the still. It is strained through wire sieves and filled into barrels for shipment. The first year the trees have been tapped, a barrel of crude turpentine will yield about five gallons of oil, and about four gallons to the barrel the second year.

The forests of British America, and the Pacific slope are used mostly for lumber, while trees that are too rich in pitch to be of any value to the lumbering industries are burned or thrown away as worthless. Some attempts have been made to find a way to overcome this waste. The work of studying northern pines and firs was begun several years ago. The red or Norway pine, *Pinus resinosa*, and the Douglas fir or spruce, *Pseudotsuga taxifolia*, on account of their abundance have been taken up first. Both of these species contain considerable pitch, but it must be obtained by other methods than boxing. During the winter months when the lumbering firms fell most of their timber, the pitch is largely in the lower part of the trunk and roots. In the experiments that have been made, this pitch has been recovered from the stumps by extraction, by steam distillation, and by slow destructive distillation. The amount of turpentine present in the wood has been estimated from a large number of determinations from which G.B. Frankforter has given the following results.

Lean wood of Norway pine gave an average of 6.2 % of pitch,

Average wood gave 8.6 % of pitch,

Stumps gave an average of 19.4 % of pitch,

Pitchy wood gave 39.1 % of pitch,

Very pitchy wood gave 42.6 % of pitch,

Specific gravity of Norway pitch at 20° C, 0.8137.

Percentage of turpentine 22.1, of colophonium 77.3, of water 0.6.

Douglas fir varies largely in the amount of pitch.

Very lean wood gave 11.6 % of pitch.

Lean wood, 13.5%.

Medium wood, 19.8 %.

Rich wood, 40.7 %.

Very rich wood, 42.4 %.

Fir pitch as it runs from the trees is a perfectly clear liquid, but on exposure to the air it changes its color and slowly becomes viscous. Its specific gravity at 20° C is 0.9821.

Most of the turpentine oil prepared in Europe is from the Pin maritime, *Pinus pinaster* which grows best in southwestern Europe along the shores of the Mediterranean. The turpentine industry is carried on mostly in western France and in much the same manner as in America. Instead of boxing, they cut a vertical strip near the base of the tree about 10 cm. wide and 30 or 40 cm. long from which the sap exudes and is collected

in a vessel hung below the cut. When it is necessary to increase the flow of sap, the strip is cut farther up the trunk of the tree. The turpentine is distilled over a direct fire and a current of steam is passed into the still.

In Austria the production of turpentine is not carried on very extensively. It is mostly from *Pinus laricio* under the same methods as in America only the trees are not tapped under fifty years of age.

Oil of turpentine consists almost exclusively of pinene,  $C_{10}H_{16}$ . It also contains traces of formic and acetic acids and resin acids.

It is a colorless, limpid liquid and has a characteristic odor. The sharp odor of old oil is said to be due to an aldehyde,  $C_{10}H_{16}O_3$ , which is supposed to be formed by the exposure of the oil to the oxygen of the air. Turpentine is soluble in from three to six parts of alcohol. The longer it stands the more readily soluble it becomes. Perhaps, on standing, oxygenated compounds are formed which are more readily soluble. It is soluble in almost any proportion in ether, chloroform, carbon disulphide, benzene, petroleum ether, glacial acetic acid, also in fatty oils. It is an excellent solvent for fats, resins, and most varieties of caoutchouc, but will not dissolve salts or mineral substances. It is miscible with alcohol, ether, and glacial acetic acid, but not with water or aqueous solu-

tions. The greater part of the turpentine oil boils between 155° and 162° C. The different turpentine oils have different rotary power. French oil is always strongly laevogyrate; American oil, faintly dextrogyrate. Austrian oils have been found to be dextro- as well as laevogyrate.

According to the United States Pharmacopoeia, oil of turpentine is a thin, colorless liquid, having a characteristic odor and taste, and specific gravity of 0.860 to 0.870 at 25° C. When it is distilled, the larger part should pass over between 155° and 162° C. It is soluble in three times its volume of alcohol, and if 5 cc. of the oil of turpentine be shaken with an equal volume of potassium hydroxide T.S., its color should not become darker than a light straw-yellow upon standing twenty-four hours. If 1 cc. of the oil be evaporated in a small dish on a water-bath, it should leave not more than a very slight residue, showing the absence of petroleum, paraffin oils, or rosin. Three drops of oil of turpentine placed on a sheet of clean white filter paper and exposed to the air should evaporate entirely without leaving a permanent stain, showing the absence of kerosene or rosin oil.

If 5 cc. of oil of turpentine be placed in a small beaker, and 20 cc. of sulphuric acid be gradually added with agitation, while the beaker is cooled by immersion in cold water, and the contents, after cooling and re-

newed agitation, be transferred to a burette, graduated in tenths, the clear layer which forms after the dark mass has settled should not measure more than 0.35 cc, showing the absence of petroleum benzin, kerosene, or similar hydrocarbons.

Eleven samples of oil of turpentine from different drugstores in Oregon were tested with the following results:

Sample. Sp. grav. Boiling. pnt. Distils at H<sub>2</sub>SO<sub>4</sub> test.

Sample	Sp. grav.	Boiling. pnt.	Distils at	H <sub>2</sub> SO <sub>4</sub> test.
1	0.869	100° C.	150° C	0.7 cc.
2	0.875	115	154	0.9
3	0.874	115	150	0.8
4	0.870	115	153	0.7
5	0.869	110	154	0.5
6	0.875	105	154	1.0
7	0.867	112	145	1.0
8	0.868	120	153	0.5
9	0.864	110	152	1.0
10	0.869	95	154	0.4
11	0.869	130	154	0.5

Sample. KOK test 1 cc Evaprt'd 3 drps on fltr ppr left

Sample	KOK test	1 cc Evaprt'd	3 drps on fltr ppr left
1	lght yellow	slght residue	slght stain
2	" brown	" "	Permanent stain
3	yelloish br.	more of "	" "
4	lt straw clr	almost no res	evaporated entirely
5	" "	" "	" "
6	yelloish brn	slght "	permanent stain.
7	lt straw color	" "	evaporated entirely
8	" "	" almost no res.	" "
9	" "	" "	" "
10	yellow	slght residue	" "
11	" "	" "	" "

Of the eleven samples of turpentine tested, eight have the required specific gravity; the specific gravity of the other three is 0.005 too high. All have too low a boiling point which was undoubtedly due to the presence of isomers of terpene. Three samples gave a brown color with potassium hydroxide instead of a light straw color. Only one gave more than a slight residue when evaporated. Three gave a permanent stain on filter paper.

The three samples having the high specific gravity gave a brown color with potassium hydroxide and a permanent stain on filter paper which probably shows the presence of kerosene oil or resin oil. The other eight samples conform to the requirements of the Pharmacopoeia.