



Pacific Southwest Forest and Range
Experiment Station - Berkeley, California
Forest Service - U. S. Department of Agriculture

U. S. FOREST SERVICE RESEARCH NOTE PSW-N13 1963

VOLATILITY AND VAPOR SATURATION OF PINE RESINS

By

Richard H. Smith, Entomologist

ABSTRACT: Volatility and vapor saturation were obtained for closed-faced collected resin of 10 pine species and 4 hybrids in California. Volatility ranged from 2 to 32 percent at 25°C., and from 14 to 36 percent at 100°C. Hybrids were usually less volatile than either parent. Vapor saturation ranged widely between species, from 2 to 20 mg. per 150 cc., but only slightly within a species; hybrids were usually intermediate between the two parents.

Considerable speculation exists about the role of pine resins in the success of bark beetle attacks and, therefore, in the resistance of pines to these insects. In investigating part of this problem, studies were conducted to determine the toxicity of pine resin vapors to adult *Dendroctonus*.^{1/} This research yielded considerable data on the percent volatility and vapor saturation of the pine resins investigated. Mirov^{2/} and Williams and Bannister^{3/} have published data on volatility at high temperatures used to obtain gum turpentine for analytical and industrial purposes. Apparently no data are available for volatility at low temperatures, or for vapor saturation. These are properties of resin which could cause a pine to be susceptible or resistant to bark beetles.

^{1/} Smith, R. H. Toxicity of pine resins to adult *Dendroctonus* (Coleoptera: Scolytidae). Unpub. Ph.D. thesis, Univ. Calif., Berkeley, Calif. 125 pp., illus. 1961.

^{2/} Mirov, N. T. Composition of gum turpentine of pines. U.S. Dept. Agr. Forest Serv. Tech. Bul. 1239, 158 pp., illus. 1961.

^{3/} Williams, A. L. and Bannister, M. H. Composition of gum turpentine from 22 species of pines grown in New Zealand. Jour. Pharm. Sci. 51:970-75. 1962.

PROCEDURE

Resin was collected with a closed microtapping device^{4/} from trees growing at the Institute of Forest Genetics, Placerville, California. These trees ranged in age from 20 to 40 years and in diameter breast height from 10 to 20 inches. Pines which served as the source of fresh resin were:

Hard pines

- Pinus ponderosa Laws.--ponderosa pine from California and from Washington.
- P. ponderosa var. arizonita (Engelm.) Shaw--Arizona variety of ponderosa pine.
- P. ponderosa var. scopulorum Engelm.--ponderosa pine from northern Arizona, from Colorado, and from Montana.
- P. jeffreyi Grev. & Balf.--Jeffrey pine.
- P. coulteri D. Don--Coulter pine.
- P. sabiniana Dougl.--Digger pine.
- P. radiata D. Don--Monterey pine.
- P. attenuata Lemm.--knobcone pine.
- P. jeffreyi x ponderosa--Jeffrey x ponderosa pine hybrid.
- P. jeffreyi x coulteri--Jeffrey x Coulter pine hybrid.
- P. jeffreyi x (jeffreyi x coulteri)--Jeffrey x Jeffrey x Coulter pine hybrid
- P. attenuradiata Stockwell & Righter--knobcone x Monterey pine hybrid.

Soft pines

- P. lambertiana Dougl.--sugar pine.
- P. monticola Dougl.--western white pine.

All resin for a given species or hybrid was extracted from one tree. Trees were tapped 1 to 2 days before a test, and the resin collected in the vial was taken directly into the laboratory for use. There a volume was apportioned with a 10 cc. pipette into 3 cc. vials to give 200 to 300 mg. This amount was enough to saturate the atmosphere of a closed fumigation chamber (a 150-cc. glass container with a screwcap lid) within 24 hours at $73^{\circ} \pm 2^{\circ}\text{F}$. The resin was apportioned so that all samples had equal evaporative areas. The samples were kept in the chamber for 3 to 7 days to fulfill the requirements of the toxicity tests. A teflon gasket in the screwcap lid insured a tight, inert seal of the chamber. Earlier work had shown that vapor conditions changed only slightly in the 150-cc. chamber after the first 24 hours. Each sample was weighed to the nearest 0.1 mg. to determine its loss of weight for the period within the jar. The loss of weight was considered the amount of vapor which had developed in the 150-cc. chamber; this amount is defined as the vapor saturation weight of a resin.

At the end of a test the resin samples were allowed to vaporize in an open atmosphere at $75^{\circ} \pm 3^{\circ}\text{F}$. for 5 to 7 days. The loss of weight, or the vaporization, was very rapid for the first 2 days, but tapered off after the third day. Little change in weight occurred after

^{4/} Smith, R. H. op. cit.

the fifth day. The 5- to 7-day period was considered adequate for determining the volatility of resin at this temperature.

After the 5- to 7-day period, the samples were stoppered and held at about 75°F. for 2 to 6 weeks. The samples were then unstoppered and run through a series of temperature-time treatments in a standard laboratory oven. Weights were obtained after each treatment and were converted to percent volatility based on the original weight of the sample of fresh resin and the loss of weight at the end of a given period. The temperature-time treatments were as follows: (a) 50°C. for 40 hours, (b) 60°C. for 120 hours, (c) 80°C. for 72 hours, and (d) 100°C. for 48 hours. The period of time for each temperature was arbitrarily selected and does not represent an end-point in weight loss. The 60°C. treatment was weighed at 48 hours and again at 120 hours; only very slight additional loss of weight occurred during the second period.

The data are limited to individual trees and do not represent a population. In all work the factors of oxidation, decomposition, isomerization and polymerization of resin constituents were not considered, although all such reactions could change volatility and, therefore, could alter the weight changes.

RESULTS AND DISCUSSION

PERCENT VOLATILITY

The data for percent volatility at 24°C. for 5 days (fig. 1) show a wide range of values among the species, from sugar pine at 2 percent to Monterey pine at 26 percent. The soft pine resins--sugar and western white--were less volatile at this temperature than any of the hard pines or hybrids. In general, the percent volatility of hybrid resin was less than that of the resin of either parent species, though the knobcone x Monterey hybrid was an exception, being intermediate to the two parent species. Unfortunately, the hybrids' parents were not the trees used as species trees. The percent volatility of different sources of ponderosa pine resin fall into two groups; the sources from Montana, Colorado, California, and northern Arizona were 19 to 21 percent; the source from Washington and the Arizona variety were 29 to 31 percent (fig. 2). The large standard error for the Washington source can be attributed to both the small sample size and the variation of individual measurements.

The supernatant liquid was obtained by holding fresh resin in a tight container at room temperature for a few days. Under these conditions the resin separates into two fractions; one crystallizes and settles to the bottom of the container; the other--a liquid--collects on the top of the crystals. The two supernatant liquids were about 27 percent volatile and the fresh resin was about 21 percent.

At increased temperatures volatility rose considerably and some shifting resulted in the relative position of the various resins (fig. 3).

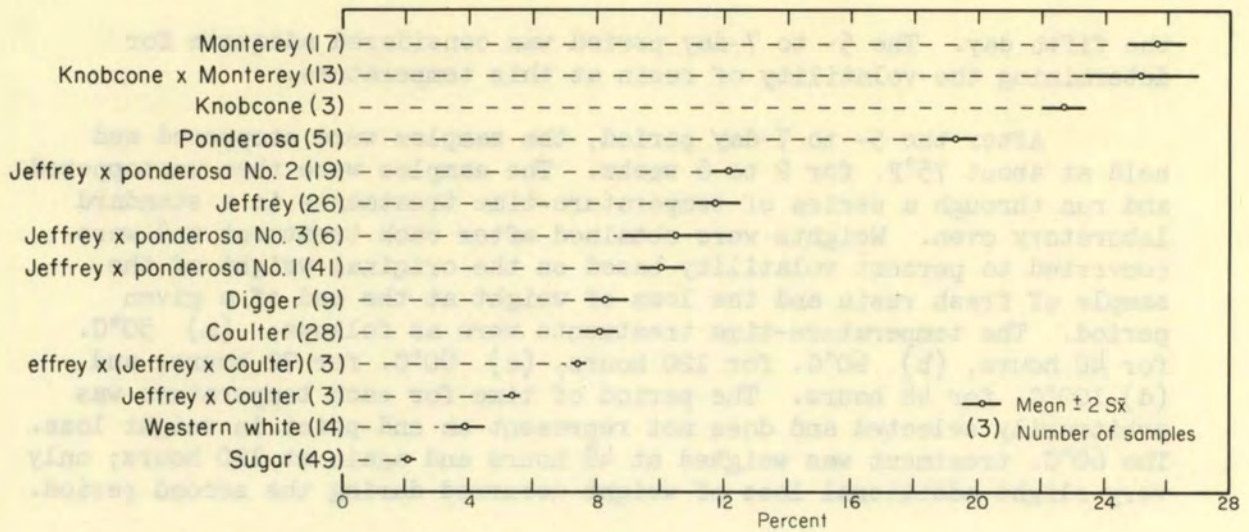


Figure 1.--Percent volatility of pine resins at $75^{\circ} \pm 3^{\circ}\text{F}$. for 5 days, all samples for one species from a single tree.

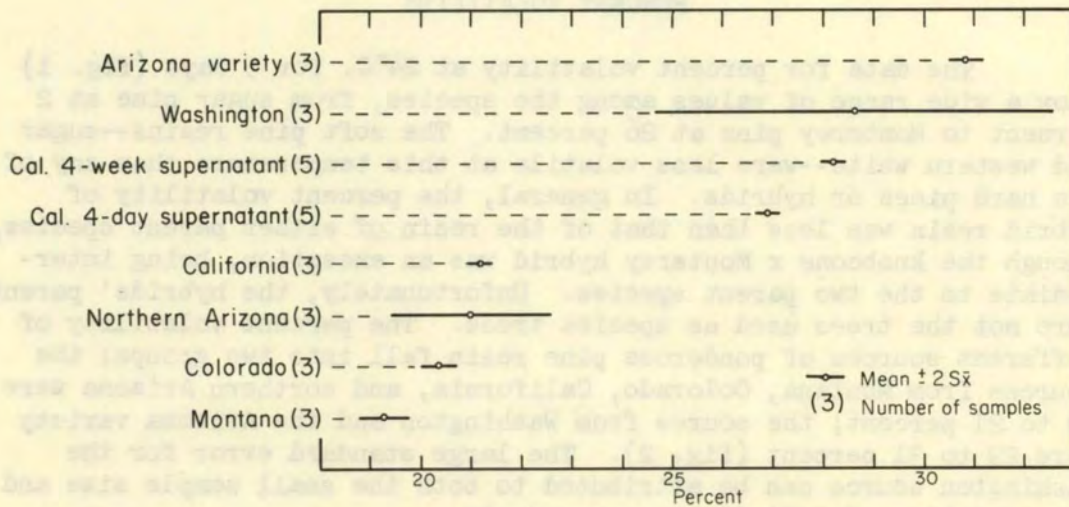


Figure 2.--Percent volatility of ponderosa pine resin sources and derivatives at $75^{\circ} \pm 3^{\circ}\text{F}$. for 5 days, all samples for one source from a single tree.

The volatility of the soft pine resins increased by 15 to 20 percent, and most of the hard pines increased by 5 to 10 percent. The greater increase in the soft pine resins suggests some relationship between the volatile and nonvolatile phases of resin. Two of the Jeffrey x ponderosa hybrids (#1 and #2) had different Jeffrey parents but the same ponderosa parent; the dissimilarities shown could reflect differences in the Jeffrey parents. The Jeffrey x Coulter hybrid resin was either intermediate or similar to the two parent species for the various temperature intervals.

At the conclusion of the 100°C. treatment the sources of ponderosa pine fell into the same two groups which could be distinguished at room temperature; the Montana, Colorado, California, and northern Arizona sources varied from 24 to 26 percent while Washington and the Arizona pine source varied in volatility from 33 to 36 percent (fig. 4). However, there is some dissimilarity in the pattern of volatility in response to intermediate temperatures; the Washington and Colorado sources had a noticeable increase in volatility at 60°C., while the increase at this temperature was much less for the other four sources. The percent volatility of the two supernatant liquids of ponderosa pine were very similar to each other at the temperature intervals but they differed noticeably from fresh resin.

The values for the percent volatility at 100°C. are generally considerably higher than those given by Mirov and are more in line with those by Williams and Bannister, at least in the three species common to all three works (table 1). These comparisons are not of the same tree but merely the same species. The differences in table 1 could be an expression of tree variation, but more than likely they reflect the difference between an open-faced collection of resin (Mirov) and a closed-faced collection (Smith; Williams and Bannister).

VAPOR SATURATION

Vapor saturation is defined as the weight of resin which, when vaporized at $73^{\circ} \pm 2^{\circ}\text{F.}$, will saturate the atmosphere in 150 cc. There was a wide range in this value among the pines used; at one extreme were Coulter and sugar pines having a vapor saturation of about 2.0 mg. and at the other Digger and Jeffrey pine about 20.0 mg. (fig. 5). The range in values for one tree may be partially an expression of experimental error; however, it could be the result of variation from other causes, such as, seasonal change (fig. 6). Mirov⁵ does not feel that there is a likelihood of seasonal variations in resin quality though he gives evidence both for and against this contention. The results of the work reported here suggest that there are seasonal variations.

The vapor saturation of ponderosa pine resin from different sources and of resin derivatives of ponderosa pine, except turpentine, ranges from 3 to 5 mg. (fig. 7). Though quantitative differences in molecular constituents could account for some of this variation, it is

⁵/ Op. cit., p. 5.

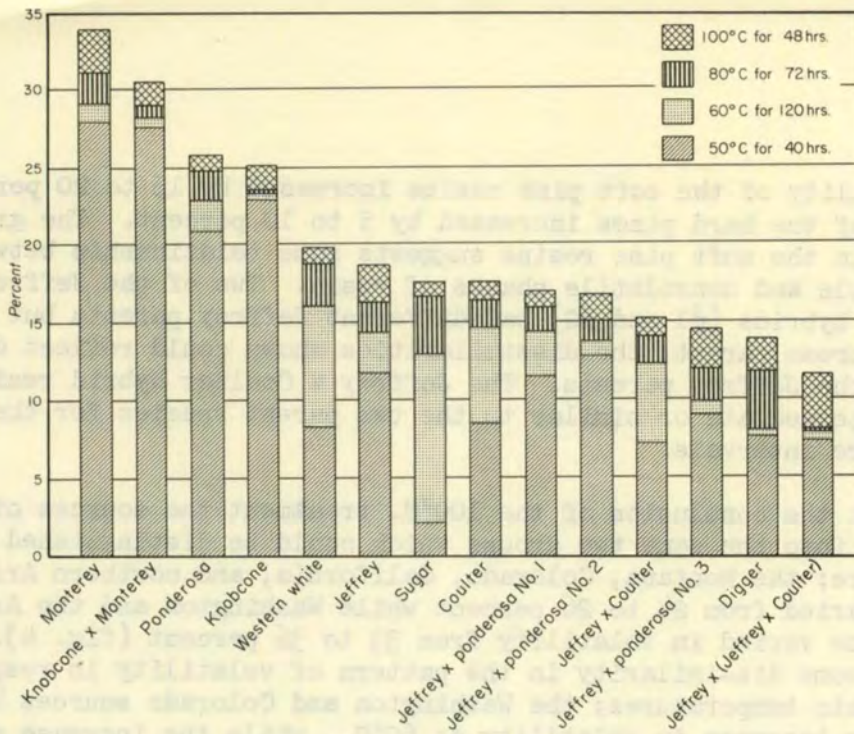


Figure 3.--Percent volatility of pine resins with temperature and time, each species represented by a single tree.

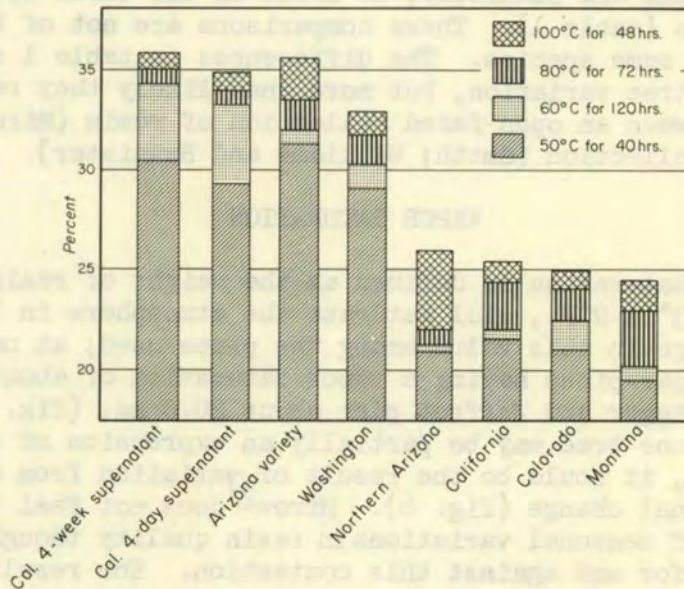


Figure 4.--Percent volatility of sources and derivatives of ponderosa pine with temperature and time, each source represented by a single tree.

quite possible that qualitative differences exist also. It will be noted that the vapor saturation of fresh resin of ponderosa pine is almost identical with its supernatant liquid. The supernatant liquid is much less viscous than fresh resin. We can assume that supernatant liquid has a higher concentration of volatile fraction than fresh resin, but the same proportional representation of the various molecules of the volatile fraction.

Table 1.--Percent volatility of pine resins as determined by different workers

<u>Pinus</u>	: Smith, at : 100°C.	: Mirov, at desig- : nated temperature	: Williams and : Bannister, : with steam
- - - - - Percent - - - - -			
<u>lambertiana</u>	17.6	16.4 (steam) 18.4 (200°C.)	--
<u>monticola</u>	19.8	18.2 (steam) 20.0 (180°C.)	--
<u>jeffreyi</u>	18.7	9-11 (steam)	--
<u>coulteri</u>	17.6	17.0 (steam)	17.5
<u>sabiniana</u>	14.0	11.4 (steam)	14.2
<u>ponderosa</u>			
Montana	24.6	17.7 (200°C.)	--
California	25.9	18.5 (steam)	23.8
Colorado	25.0	20.0 (200°C.)	--
Arizona	26.1	19.6 (steam)	--
<u>attenuata</u>	25.1	23-24 (200°C.)	--
<u>radiata</u>	33.9	16.8 (190°C.)	--

There was a large difference in the vapor saturation of fresh resin of ponderosa pine and turpentine obtained by fractionation of the fresh resin at 165°C. This difference could indicate (a) that the volatile constituents are changed during fractionation, (b) that large changes in the concentration of the liquid form of a mixture of volatile substances will change the vapor saturation of the whole, or (c) that properties of the volatile constituents change in the absence of the solid portions of the complex mixture of molecules found in resin.

The vapor saturation of hybrid resins tended to be intermediate between the two parents, as illustrated by the data for Jeffrey x ponderosa, Jeffrey x Coulter, and Jeffrey x (Jeffrey x Coulter). The values for the

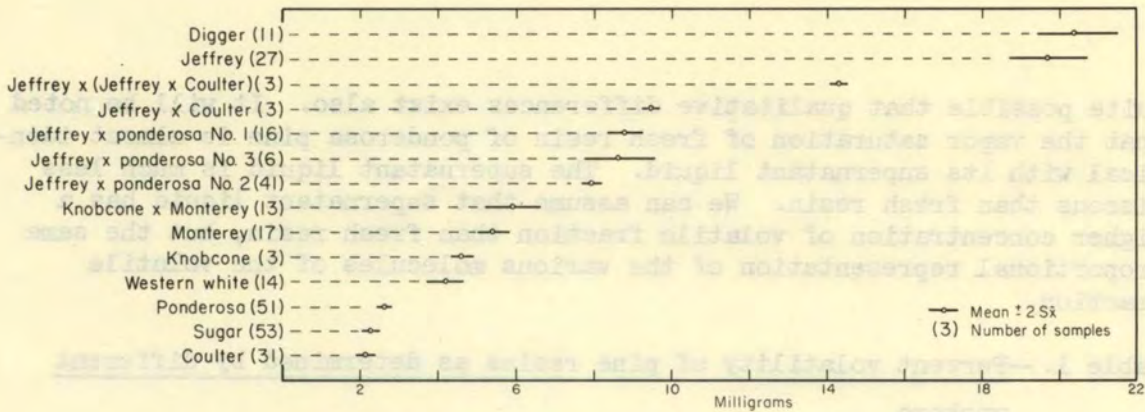


Figure 5.--Vapor saturation weight of pine resins in 150 cc. volume at $73^{\circ} \pm 3^{\circ}\text{F.}$, all samples for one species from a single tree.

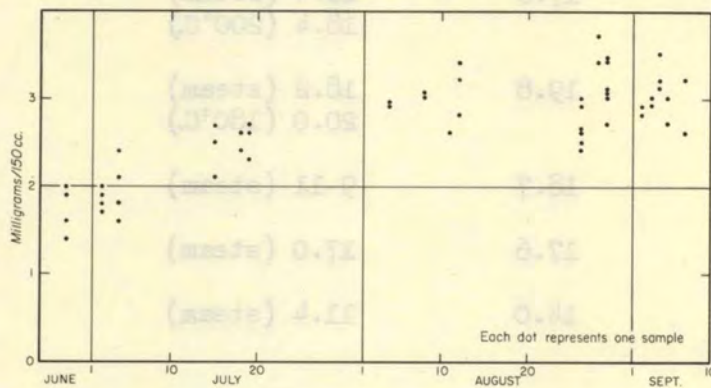


Figure 6.--Seasonal variation in vapor saturation weight of ponderosa pine resin from one tree at $73^{\circ} \pm 2^{\circ}\text{F.}$ in 150-cc. volume.

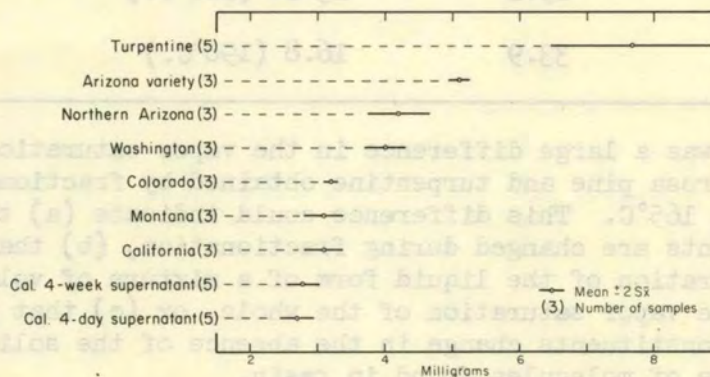


Figure 7.--Vapor saturation weight of ponderosa pine resin sources and derivatives in 150 cc. volume at $73^{\circ} \pm 2^{\circ}\text{F.}$, all samples for one source from a single tree.

knobcone x Monterey hybrid overlap those for parents which do not differ significantly from each other. A study of vapor saturation and volatility in hybrids could be worthwhile since, generally, one is less than either parent and the other intermediate to them.

There seems to be no relationship between volatility and vapor saturation. This, plus the lack of uniform increase in volatility with increased temperature, once again suggests a relationship between the volatile and nonvolatile phases of resin.

