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COMPOSITION AND FRACTIONATION OF AMERICAN STEAM-DISTILLED WOOD TURPENTINE.

PALKIN, S. ; CHADWICK, T.C. ; MATLACK, M.B.

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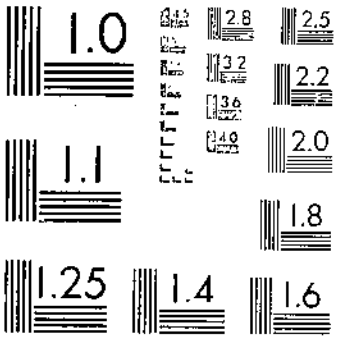

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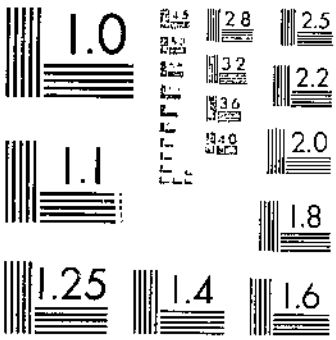

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UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

COMPOSITION AND FRACTIONATION OF AMERICAN STEAM-DISTILLED WOOD TURPENTINE [1] [2]

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INTRODUCTION

American steam-distilled wood turpentine is obtained chiefly from the stumps of two species of the southern pines—longleaf pine (*Pinus palustris* Miller) and slash pine (*P. caribaea* Morelet). Lightwood is also used. It consists of pieces with a high resin content from which the less durable portions with small resin content have been removed by decay. Both stumps and lightwood have generally been in or on the ground for many years after the trees were felled, and considerable change has taken place in the composition of their resinous content as compared with that in the living tree.

Turpentine is but one of a series of products obtained from the stumps and lightwood by the so-called steam and solvent process (*15, 27, 29*)[4] whereby the wood, after being reduced to chips, is subjected first to steam distillation and then to an extraction with a special petroleum solvent.

The oily condensate from the steam distillation contains the turpentine and also part of the pine oil, which must be removed by a series of processes in order to obtain the steam-distilled wood turpentine of commerce.

The composition and properties of the turpentine are controlled and uniformity of quality of the marketed product is obtained by observing certain empiric uniformity in processing and refining. This processing is generally carried out in well-equipped, centralized plants, of which there are about 9 or 10 in the entire country.

[1] Received for publication May 27, 1937.
[2] Drawings of the apparatus were made by Irl Bauserman, draftsman, Chemical Engineering Division.
[3] Member of the Naval Stores Research Division at the time this work was done.
[4] Italic numbers in parentheses refer to Literature Cited, p. 27.

Gum spirits of turpentine, on the other hand, is obtained from many separate stills. More than 1,100 are distributed over the producing area.[5] Because the separation of the two products of the gum, turpentine and rosin, is much more easily effected, chemical control is rarely necessary. Thus, although both steam-distilled wood turpentine and gum spirits are derived from the same species of pine, the raw material from which they are prepared, fresh gum in the case of gum spirits, and stump oleoresin in the case of steam-distilled wood turpentine, as well as their methods of preparation differ markedly. It is a matter of interest that the fresh gum spirits is, in the main, markedly uniform in composition (*20*). This uniformity is due to a number of contributing factors, and here certain contrasting features between wood turpentine and gum spirits are of interest. In every case, gum spirits represents the whole of the volatile oil obtained from the oleoresin, and not a fraction, as is the case with steam-distilled wood turpentine; it is not subjected to any special processing or refining; the hydrocarbon portion, which constitutes about 95 percent of the gum spirits, is comparatively simple, consisting almost wholly of the two dicyclic terpenes, α- and β-pinene. As has been shown previously (*20*) the proportions of these two constituents do not differ greatly for the two contributing species. While α-pinene is the principal constituent in both turpentines, very little β-pinene is present in wood turpentine. An appreciable proportion of the hydrocarbons of the latter consists of monocyclic terpenes. As will be evident from the experimental part later, even more marked differences characterize the nonhydrocarbon and "tailings" portions of these two kinds of turpentines.

Steam-distilled wood turpentine has been on the American market for about 25 years. While some data regarding its composition have appeared in the literature from time to time, these consist merely of statements of composition unaccompanied by detailed experimental data or methods of examination (*17*, *27*, *29*, *31*, *41*). The authors are aware of but one publication,[6] a comparatively recent report by Dupont, Rambaud, and Bonichon (*11*), in which the product has received a fairly systematic analytical examination. The results of this examination were based in the main on the application of Raman spectra methods to a series of fractions obtained by one fractional distillation. The conclusion reached by these authors was essentially that steam-distilled wood turpentine consists wholly of terpene hydrocarbons, dicyclic and monocyclic. Estimated percentages of the several hydrocarbons, totaling 100 percent, are also given, thus leaving the clear implication that the various "pine oil" compounds from which the turpentine was separated in plant operation have been completely removed by the refining process. This thought is indeed in harmony with the prevailing impression that steam-distilled wood turpentine consists entirely of hydrocarbons. As will be shown in the present investigation, this conclusion is not warranted.

Considerable published information is however available on the composition of the volatile oil as a whole obtained from the wood. A valuable contribution to the subject was made by the laboratories

[5] ELDREDGE, J. F. STATISTICS ON GUM NAVAL STORES PRODUCTION. U. S. Dept. Agr. Forest Survey Release 17, 13 pp. Dec. 31, 1935. [Mimeographed.]

[6] An investigation on steam-distilled wood turpentine was made in 1927 by E. K. Nelson, of this Bureau. The summary of his unpublished report reads as follows: "Examination of the minor constituents of wood turpentine revealed the presence of traces of benzaldehyde, small amounts of fenchyl alcohol and borneol, and larger amounts of terpineol."

of Schimmel & Co. some years ago, in which a systematic investigation of the composition of "yellow pine oil" was discussed (*34*). Considerable attention was also given to the more volatile constituents that are now known to be present in steam-distilled wood turpentine. However, the composition of what might correspond to steam-distilled wood turpentine as a separate entity was not given consideration.

Interstate commerce in steam-distilled wood turpentine, like that of gum spirits, comes within the purview of the Naval Stores Act. In connection with the enforcement of the act, it is desirable to have as complete information as possible on the basic chemical and physical differences between these two kinds of turpentine, because continued improvement in the process of refining steam-distilled wood turpentine has rendered distinction between it and gum spirits less and less obvious by the usual methods. Such data constitute a basis for chemically differentiating between the two and for the development of definite analytical ways and means of detecting reasonable quantities of one in the other. The question has also arisen as to the relative suitability of turpentines from these two sources for various specific industrial uses.

As part of the general program on the study of the composition and properties of American turpentines, the investigation reported in this bulletin has for its object the development of a suitable technique for the examination of products of this nature, the establishment of qualitative and quantitative data on the composition of steam-distilled wood turpentine, and such other information as may serve to bring out basic differences or similarities between this product, gum spirits, and turpentines from other sources.

METHODS AND EQUIPMENT

DISTILLATION PROCEDURE

The fractionations were carried out in the fractionating assemblies at suitable pressures maintained constant by an improved pressure control mechanism. Operations at fixed, accurately controlled pressures rendered possible a more intelligent "cutting" of the distillate into appropriate fractions. Also, because of large quantities of material involved, a number of separate batch distillations were necessary. Accurate pressure control made possible the subsequent uniting of corresponding fractions to form larger composite fractions on the basis of distillation temperatures. Temperature served also as as a guide in the properly timed introduction of individual fractions into the still pot for systematic refractionation.

In order to render possible check examination of the more complex higher boiling portion, actually only one-half of the total residue remaining after the first 39 fractions (table 2) was used in completing the systematic fractionation of series 2 (turpentine as a whole). For purposes of calculation in the table, therefore, weights of the respective fractions obtained from this point on were doubled. The second half of this residue was subjected to a schematic treatment described under Chemical Treatment of Higher Boiling Portion. This was done independently of the chemical-analytical examination of the individual fractions of that portion listed in table 2 and described under Systematic Fractional Distillation.

EQUIPMENT

A uniform type of assembly was used in all the fractional distillations, whether the column proper was large or small, of plate or packed type. The assembly as a whole, as shown in detail in figure 1, is divided into its four principal parts.

Parts of the assembly for which improved design is given here are as follows:

A pressure-control unit serving both the column system and an independent vapor jacket, each at its own pressure.

An independent vapor jacket for insulating the column, in which the temperature is controlled by regulation of pressure.

An improved precision gage.

MAIN PRESSURE-CONTROL UNIT

In previous publications (*23*, *24*) a design embodying a dual system of pressure control was described, the essential features of which are as follows: One vessel is in continuous communication with the distillation system, the pressure of which is maintained constant by means of a valve operated by a magnet, controlled in turn by a Herschberg-Huntress sulphuric acid manostat and thermionic relay. Another vessel is in continuous communication with the pump, but in intermittent communication with the first vessel. This constitutes the low-pressure system, the pressure of which is maintained only approximately constant. The pump operates occasionally and is in turn controlled by a mercury manostat and relay.

In the assembly shown in figure 1, the design of the control apparatus has been improved and simplified, and better coordination with the distillation apparatus is obtained.

For the detailed measurements and construction of the essential parts of the control assembly, the reader is referred to previous publications (*23*, *24*).

The low-pressure system, both for the main control unit and for the auxiliary jacket control unit is indicated in the drawing by heavy, dark lines.

The parts comprising the improved main control units and their new arrangement (fig. 1, *A*) are as follows: (*f*) and (*k*) are round-bottomed, short-necked flasks (6 and 3 l, respectively) that serve as ballast and provide a means for multiple connections. (*f*) also contains the sensitive valve mechanism consisting of the metal tube (*e*) with the capillary opening (*ec*), and the magnet (*g*) which is controlled by the thermionic relay (*a*) and the Herschberg-Huntress sulphuric acid manostat (*b*). (*c*) is a brass swivel. The low-pressure flask (*k*) is normally in communication with (*f*) by way of the metal tube and capillary valve, as indicated, but a bypass (*h*) provides a direct communication between high- and low-pressure systems when necessary. The branch (*d*) provides a connection between the auxiliary pressure-control unit *C* and the low-pressure system. The principal communication between the control unit and the column distillation system is made by way of the trap tube (7), fig. 1, *B*, manometers m_1 and m_2, and precision gage *D* joining at (*x*). Pressure in the low-pressure system is controlled by the mercury manostat (*v*) and pump relay (*r*). Stopcock (*u*) provides an opening to the atmosphere when necessary.

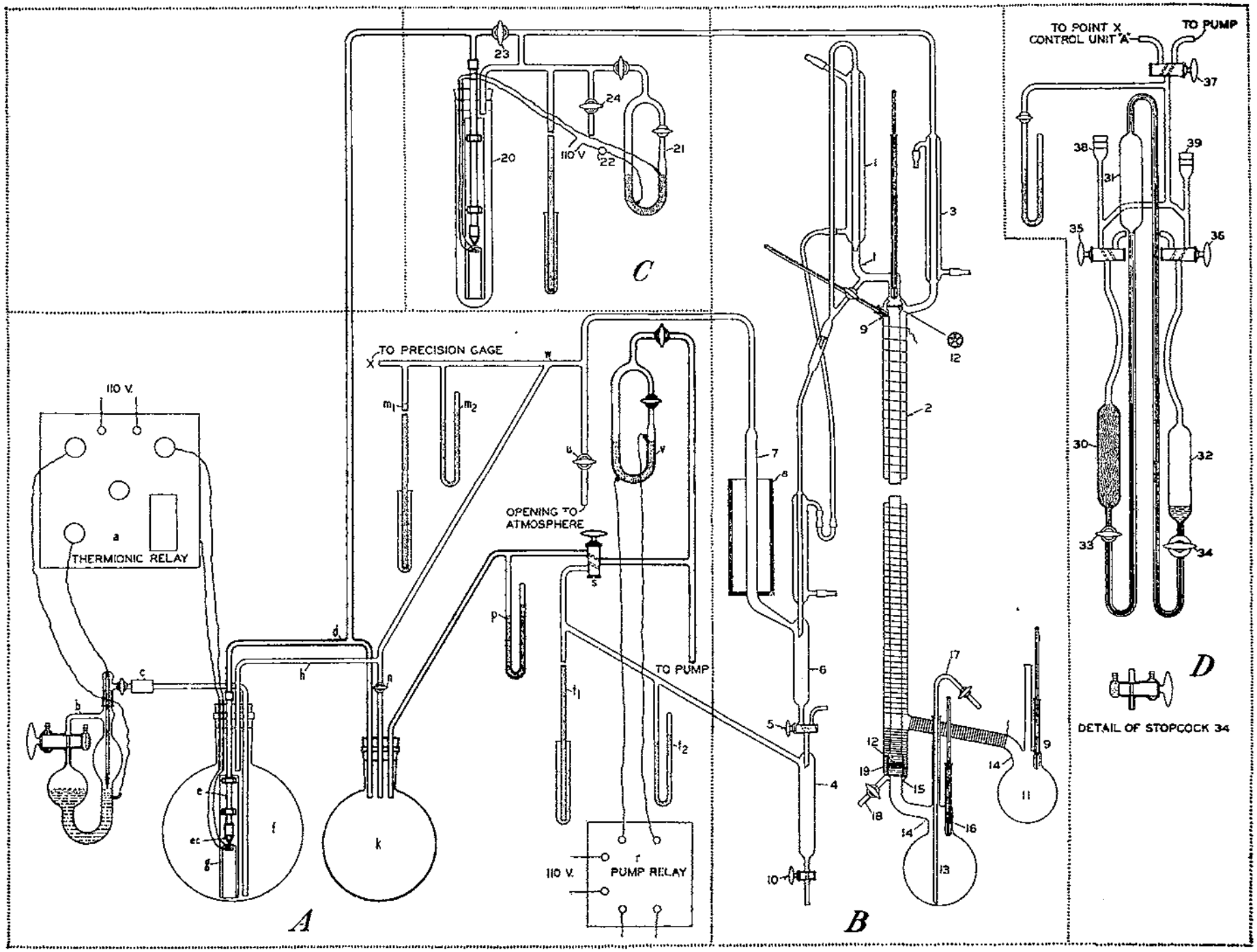

FIGURE 1.—Complete fractionating assembly: *A*, Main pressure-control unit; *B*, distillation apparatus proper; *C*, auxiliary pressure-control unit; *D*, precision oil gage.

Both barometric [7] and short U-tube type manometers are used in order to provide full range of pressure up to atmospheric, and are distributed in the various parts of the apparatus as shown so that pressure in all parts of the assembly, including the distillation system, the jacket system shown in *B*, and their respective control units (low- and high-pressure parts), and the distillate reservoir (4) may be observed at any time.

Three-way stopcock (*s*) normally provides communication between the pumping system and the low-pressure flask (*k*), the pressure of which is indicated on manometer (*p*).

The two distillate-receiving reservoirs (4) and (6), figure 1, *B*, are in communication with the pressure-control unit at points shown, and are joined to each other by the three-way stopcock (5) to facilitate taking a fraction and reestablishing column pressure in (4) afterwards. The arrangement has been so simplified that, after taking a fraction of distillate from (4) and locking the stopcocks (5) and (*s*), reevacuation of (4) is accomplished with the manipulation of but two stopcocks, (*s*) of the control unit and (5) of the distillate reservoirs. This is done as follows: Three-way stopcock (*s*) is opened to reservoir (4). The pump thus automatically started by the mercury manostat (*v*) and relay (*r*) exhausts the reservoir (4) and when the proper pressure (equal to distillation pressure) has been reached, as indicated by the manometers t_1 or t_2, stopcock (*s*) is turned back to its original position, that is, open to low-pressure flask (*k*), and stopcock (5) is opened to (6), bringing it back into communication with the column distillation system. No other manipulations are necessary, as all other operations are taken care of automatically.

Simultaneous operation of several stills, each at a different pressure, requires additional valve and manostat arrangements similar to that described for maintaining the still and jacket at their respective pressures.

DISTILLATION APPARATUS PROPER

The distillation assembly proper, comprising the column, the condenser, and the independent vapor jacket with its condenser, are shown in figure 1, *B*.

For the distillation of large batches, the column proper used was of the gauze-plate type (32-plate) previously described (*20*). From 1,000 to 1,200 g constituted a single charge, and all but the last 50 to 100 g were fractionated in the large apparatus. For small quantities, several types of semimicro columns were used, depending upon the quantity and character of the material available. One of these, a semimicro gauze-plate type (15-mm column-tube diameter and 20 plates), has been described (*21*).

Columns made entirely of glass, both of large size and of micro type, were also used in the latter part of the work. These consisted of the following:

(1) A packed column (fig. 1, *B*) filled with single glass spirals of the Wilson-Parker-Laughlin type (*45*).

(2) A semimicro type with the same kind of packing (fig. 2), similar to the small column described by Tongberg, Quiggle, and Fenske (*40*), but modified to provide controlled jacket temperature independently of the fractionating liquid.

[7] With correction for variation in atmospheric pressure.

The problem of effectively insulating the column so as to confine all condensation at the top is one that has given considerable difficulty, and a number of devices have been described in the literature, including the well-known type using magnesia-asbestos covering, the vacuum jacket (*7, 32*), the vapor jacket using vapor from the still pot (*40, 44*), and the type involving the heated air jacket (*3, 30*).

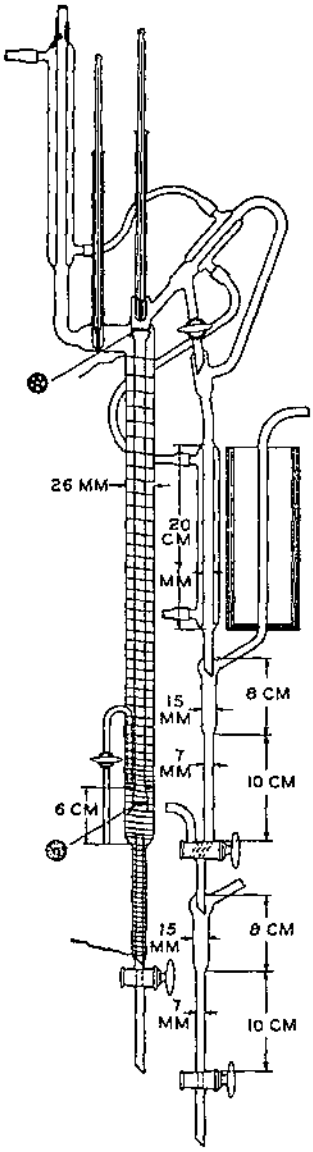

FIGURE 2.—Semimicro fractionation column.

In this latter type, heat compensation is generally provided by a series of independent resistance-wire windings on segments of the jacket, each rheostat-controlled. A set of thermometers distributed in various parts of the jacket is used for observing the temperature gradient.

With this type of heat-compensating insulation, difficulty was experienced in coordinating the four or five separate heating units so that the temperatures at the top and bottom of the jacket reasonably matched, respectively, the top and bottom of the column. This difficulty was not so obvious at first, but was shown experimentally with products with previously determined distillation properties in the following manner:

On making a suitable setting of the rheostats before beginning distillation, and seeing that the jacket temperatures after reaching equilibrium approximately equaled the previously determined top and bottom temperatures, respectively, of the column, it was found that when actual distillation was in progress the jacket temperatures invariably rose considerably above the column temperatures, and the rheostats had to be readjusted in order to provide less jacket heat. After each readjustment, moreover, an appreciable period of time was required to reestablish equilibrium. Thus it became obvious that heat was being transmitted from the column to the jacket, and that condensation of vapors must have taken place within the column before they reached the top, an effect generally recognized as highly undesirable for efficient rectification. Ultimate temperature of any part of the jacket thus represented the net result of several factors: the heat input of the jacket, the rate of heat loss by radiation, and the heat

transmitted to the jacket from the column by the column proper. These factors are not easily coordinated.

In the type where the vapor from the still pot containing the liquid to be fractionated is used to heat the jacket, as in the Widmer (*44*) and the Tongberg columns (*40*), a near approach to an automatic means for matching the temperature is provided. For a column of any length, however, it involves a serious hold-up of the liquid being fractionated, thus detracting in a large measure from the rectifying efficiency. Where an appreciable difference in vapor temperatures at top and bottom of the column exists, it also lacks provision for a proper gradient.

The vapor jacket here described utilizes a boiling liquid independent of the one being fractionated and provides a relatively simple means for temperature control by controlling the pressure in the jacket.

As shown in Figure 1, *B*, the jacket (2) is sealed to the column. The annular space between the jacket and the column is about 4 mm. The jacket is provided with a reflux condenser (3). Thermometers in the thermometer wells (9), which contain mercury, permit observation of the jacket temperature. Flask (11) contains the boiling liquid for the jacket and serves as the independent still. Heat for this distillation and for compensation against excessive heat loss in the upper part of the jacket is furnished by an electric heater and nichrome resistance winding, rheostat controlled. The delivery tube from flask (11) is joined at a point sufficiently above the lowest part of the jacket to permit the use of a secondary "boiler" (19) and thus maintain the lower part of the column at the temperature of the boiling jacket liquid. Thus, by using a mixture of liquids with sufficient differences in boiling points, benzene and xylene, for example, it is not only possible to establish a temperature matching the distillation temperature at the top of the column, but at the same time to provide a lag between the top and the bottom.

Means for reflux control, reservoirs for receiving distillate, and form of trapping device were uniform except for differences in size for the various columns used.

In this connection the simple trap tube (7) cooled with solid carbon dioxide was found very serviceable.[8] The importance of having not only a tight system but efficient trapping, in pressure-controlled fractionation, can hardly be overemphasized, particularly when the intermittent-pumping type of control is used.

From an analytical standpoint this reflux form of trap tube has the additional advantage, pointed out by Podbielniak (*33*), that the more volatile vapors thus condensed are returned continuously to the fractions in the order of progress of the distillation rather than at the end of the operation.

This tube, jacketed with an ordinary cylindrical shipping carton and insulated with several layers of corrugated paper, has served very well with powdered solid carbon dioxide as the refrigerant. An additional glass jacket sealed to the lower part of the tube, and the whole in turn insulated as described, has also been used where liquid refrigerant contact was desired.

[8] A similar trap tube, but one in which the "light volatile" distillate was held back and not blended with the fractions, was used in the early part of the work. Fraction A of table 1 was obtained in this manner.

The still pot (13) constructed in Claisen form has the advantage of a two-point rigid support (14) and (15), particularly desirable where a long, heavy column is involved.

The sealed-in thermometer well (16) insures easy thermometer readings, free from distortions by fog, and the capillary tube (17) serves for charging, for withdrawal of residue, and for introducing inert gas as an antibumping mechanism. Stopcock and capillary (18) serve for drainage of the jacket liquid.

AUXILIARY PRESSURE-CONTROL UNIT

Pressure, and therefore temperature, in the vapor jacket of the column is regulated by means of the auxiliary pressure-control unit (fig. 1, *C*). The latter is similar to that of the large control unit figure 1, *A*, but simpler, and consists of a capillary valve-magnet mechanism set in the large test tube (20), and a mercury manostat (21).

The magnet operating the valve receives the current from the 110-volt circuit in series with a 7½-watt lamp (22) which provides the necessary resistance. The mercury manostat (21) acts as both manostat and switch, thus obviating the need for a relay. Pressure-control precision of the high order of the sulphuric acid manostat is not necessary. Stopcock (23) serves as a bypass. Capillary stopcock (24) provides communication of the jacket system with the atmosphere when necessary.

Any stable liquid with a boiling point conveniently higher than that of the liquid fractionated may be used in the jacket.

As the distillation proceeds and higher jacket temperatures are necessary, the boiling temperature of the jacket liquid is raised by readjusting the jacket pressure. This is done by letting in air through the stopcock (24). Temperature changes are prompt and definite.

PRECISION OIL GAGE

The ordinary U-tube type mercury manometer, the most commonly used laboratory pressure gage, is relatively coarse and insensitive. With the advance, in recent years, in pressure-control technique for low-pressure fractional distillations and other vacuum practice, there is a real need for pressure gages capable of measuring gas pressures with a high degree of precision, particularly in the range below 40 mm. With the exception of the Hickman gage (*14*), which requires the use of a high-vacuum diffusion pump for its use, no gages of sufficient sensitivity and precision for this pressure range are available. Gages of the McLeod type are serviceable for a very limited range only.

On the sensitive oil gage shown, a pressure difference of 1 mm is equivalent to less than one-fifteenth of a millimeter of mercury, and thus variations of one-thirtieth of a millimeter of mercury (one-half millimeter on the scale) may be readily observed. The gage is essentially a double U-tube manometer utilizing both oil and mercury, but the latter serves only as a backing medium to render possible the production of a Torricellian vacuum for the reference side of the oil gage. Complete detailed description of the construction and operation of this gage has been given (*22*).

EXPERIMENTAL DATA

SYSTEMATIC FRACTIONAL DISTILLATION

Factory-sealed containers of steam-distilled wood turpentine were purchased from the stock of a dealer. This was done, rather than by obtaining it directly from the manufacturer, in order to make certain that the sample was representative of the commercial product actually on the market. Records of shipment were examined to insure authenticity of origin and reasonable freshness of the sample.

The original turpentine had the following properties when tested in accordance with the methods of the American Society for Testing Materials: Refractive index, $n_D^{25°}$, 1.4668; rotation, $\alpha_D^{20°}$, + 22.2; density, $\frac{15.5°}{15.5°}$, 0.859; distilling below 170° C., 92 percent.

In order to handle the 15 kg of turpentine necessary for the determinations contemplated, the material was divided into 12 batches of about 1,200 g each, and these were fractionated in column stills, yielding six fractions and a residue from each batch. The corresponding fractions were then combined, making seven composite fractions designated A, B, C, D, E, F, and G, respectively. Distillation data and properties of the respective composite fractions are given in table 1.

This series of composite fractions, designated series 1, was then systematically refractionated several times, yielding ultimately the new series of fractions 1 to 73, inclusive, designated series 2, which are shown in table 2. Since the bulk of the fractionated material consisted of α-pinene, further fractionating was confined to two portions, the forerun (heads), or lower boiling portion, representing about 0.68 percent; and the higher boiling portion, representing the last 17.6 percent, which consisted largely of monocyclic terpenes. Data on these two series of fractions are given in tables 3 and 4, respectively, and designated fractions H–1 to H–12 (series 3) and fractions T–1 to T–54 (series 4), respectively. One refractionation of a middle portion representing α-pinene was made for the purpose of special purification only (table 5).

TABLE 1.—*Physical data on the 7 composite fractions of the turpentine*

Composite fractions (series 1)	Distillation temperature at 20 mm	Refractive index	Optical rotation	Density	Weight	Ratio of each fraction to the whole	Sum of fractions
	° C.	$n_D^{25°}$	$\alpha_D^{20°}$	$\frac{15°}{4°}$	Grams	Percent	Percent
A (light volatile)	Below 50.0	1.4380	(1)		64	0.43	0.43
B	50.0	1.4582	+22.9°	0.8560	570	3.83	4.26
C	50.5	1.4623	+25.7°	.8596	1,985	13.32	17.58
D	51.0	1.4630	+25.8°	.8611	5,057	30.98	57.56
E	51.0	1.4630	+25.0°	.8611	3,142	21.09	78.65
F	60.0	1.4608	+16.8°	.8525	1,299	8.72	87.37
G (residue)	Above 60.0	1.4603	+5.9°	.8514	1,882	12.63	100.00

[1] Practically inactive.

TABLE 2.—*Systematic refractionation of composite fractions of table 1, and properties of new fractions obtained*

Fraction no. (series 2)	Distillation temperature at 20 mm	Refractive index	Optical rotation	Density	Ratio of each fraction to the whole	Sum of fractions
	° C.	$n_D^{25°}$	$\alpha_D^{20°}$	$\frac{15°}{4°}$	*Percent*	*Percent*
1	[1] 10-18	1.4258			0.048	0.048
2	[1] 22	1.4255			.062	.11
3	[1] 28	1.4145			.11	.22
4	[1] 42	1.4278	+1.5		.18	.40
5	[1] 40	1.4549	+16.6		.27	.68
6	50.5	1.4612	+23.0	0.8599	.37	1.04
7	50.5	1.4621	+25.5	.8617	.36	1.40
8	50.5	1.4625	+25.7	.8624	.73	2.13
9	50.5	1.4630	+26.1	.8626	.61	2.74
10	50.5	1.4630	+26.4	.8626	.63	3.37
11	50.5	1.4632	+26.4	.8626	.67	4.04
12	50.3	1.4619		.8601	1.73	5.77
13	50.3	1.4627	+25.8	.8617	1.69	7.46
14	50.5	1.4628	+25.9	.8617	1.71	9.17
15	50.5	1.4629	+26.0	.8622	1.69	10.87
16	50.5	1.4630	+26.1	.8622	1.74	12.61
17	50.8	1.4631	+26.2	.8624	1.70	14.31
18	50.6	1.4633	+26.2	.8626	1.22	15.54
19	50.0	1.4631	+25.7	.8622	3.71	19.24
20	50.2	1.4631	+25.9	.8622	10.96	30.20
21	50.2	1.4634	+25.9	.8632	6.21	36.41
22	50.2	1.4633	+25.9	.8631	5.56	41.97
23	50.2	1.4634	+25.8	.8631	4.60	46.57
24	50.2	1.4637	+25.6	.8635	5.23	51.81
25	50.5	1.4638		.8638	2.74	54.54
26	51.0	1.4631		.8637	.49	55.03
27	50.5	1.4631	+26.1	.8629	2.86	57.89
28	50.5	1.4632	+25.9	.8627	2.23	60.12
29	50.8	1.4633	+25.9	.8625	3.47	63.59
30	50.8	1.4633	+25.7	.8630	2.08	65.67
31	50.8	1.4634	+25.4	.8629	2.42	68.08
32	51.0	1.4634	+25.2	.8627	3.49	71.57
33	51.5	1.4640	+25.2	.8631	2.26	73.83
34	51.4	1.4640	+25.5	.8638	1.82	75.65
35	51.5	1.4640	+25.6	.8638	2.63	78.28
36	51.5	1.4640	+24.5	.8640	1.12	79.41
37	51.8	1.4640	+23.9	.8641	.78	80.18
38	52.0	1.4642	+24.0	.8639	1.13	81.31
39	52.9	1.4643	+24.0	.8639	1.09	82.40
40 [2]	53.3	1.4647	+21.4	.8637	1.34	83.74
41	53.5	1.4650	+21.1	.8633	.35	84.09
42	54.0	1.4652	+18.8	.8[illegible]1	.12	84.21
43	54.1	1.4653	+17.7	.8647	.12	84.33
44	55.0	1.4654	+16.2	.8633	.29	84.63
45	55.9	1.4654	+12.5	.8630	.16	84.79
46	56.8	1.4653	+9.4	.8613	.19	84.97
47	57.8	1.4645	+5.7	.8589	.15	85.12
48	59.0	1.4640	+2.4	.8544	.21	85.33
49	59.0	1.4608	+9.5	.8515	.49	85.82
50	61.0	1.4607	+4.2	.8489	.38	86.20
51	61.3	1.4593	+10.0	.8515	.37	86.57
52	61.5	1.4558	+5.2	.8461	.39	86.96
53	62.0	1.4527	+.5	.8291	.61	87.58
54	63.6	1.4525	+1.2	.8289	.45	88.03
55	66.0	1.4525	+1.4	.8214	.61	88.64
56	66.3	1.4573	+3.3	.8301	.91	89.55
57	67.2	1.4579	+3.5	.8307	1.17	90.72
58	68.0	1.4582	+3.8	.8307	.78	91.50
59	69.0	1.4618	+5.0	.8360	.39	91.89
60	69.3	1.4641	+6.1	.8367	.83	92.72
61	69.5	1.4642	+6.2	.8393	.91	93.63
62	70.0	1.4645	+6.2	.8396	.94	94.57
63	71.0	1.4702	+8.5	.8472	.93	95.50
64	72.0	1.4720	+9.8	.8506	1.39	96.89
65	73.0	1.4740	+9.4	.8550	.31	97.20
66	79.0	1.4773	+6.5	.8646	.45	97.65
67	80.0	1.4823	+3.3	.8653	.29	97.94

[1] These are approximate values calculated for 20 mm from actual distillation temperatures as follows: 1, 34.5°–42.5°/70 mm; 2, 35°–39°/50 mm; 3, 39°–47.5°/50 mm; 4, 40.2°–53.5°/35 mm; 5, 53.5°–60.5°/35 mm.

[2] At this point the remainder of the series was divided into 2 equal parts and refractionation continued using one-half of the total. Weights were multiplied by 2 from this point on.

TABLE 2.—*Systematic refractionation of composite fractions of table 1, and properties of new fractions obtained*—Continued

Fraction no. (series 2)	Distillation temperature at 20 mm	Refractive index	Optical rotation	Density	Ratio of each fraction to the whole	Sum of fractions
	°C.	$n_D^{20°}$	$\alpha_D^{20°}$	$\frac{15°}{4°}$	*Percent*	*Percent*
68 [3]	80.5	1.4845	+1.7	0.8825	9.80	98.74
69 [4]	50.0/3 mm	1.4894	−3.1		.12	98.86
70	83.0/7.5 mm	1.4892	−.7		.45	99.31
71	80.0/8 mm	1.4869	+4.2		.18	99.49
72	93.0/7.7 mm	1.4872	+14.2		.37	99.86
73	[5] 93.0/7.7 mm	1.4874	+20.3		.14	100.00

[3] Gave crystals found to be sobrerol.
[4] Distillation temperatures for fractions 69 to 73 calculated (roughly) to 20 mm for plottings of distribution graphs.
[5] Above 93.0°/7.7 mm.

TABLE 3.—*Refractionation of "light volatile" fractions 1 to 5 of table 2*

Fraction no. (series 3)	Distillation temperature at atmospheric pressure	Refractive index	Ratio of each fraction to the whole	Sum of fractions	Fraction no. (series 3)	Distillation temperature at atmospheric pressure	Refractive index	Ratio of each fraction to the whole	Sum of fractions
	°C.	$n_D^{20°}$	*Percent*	*Percent*		°C.	$n_D^{20°}$	*Percent*	*Percent*
H-1	106–111	1.4243	4.45	4.45	H-8	133	1.4360	6.2	54.31
H-2	115	1.4269	9.7	14.15	H-9	140	1.4361	5.66	59.97
H-3	120	1.4177	8.1	22.25	H-10	146	1.4430	8.09	68.06
H-4	122	1.4163	7.4	29.65	H-11	151	1.4516	7.8	75.86
H-5	125	1.4131	3.5	33.15	H-12	154	1.4577	7.55	83.41
H-6	129	1.4172	9.16	42.31	Residue	[1] 154	1.4627	16.58	99.99
H-7	131	1.4130	5.8	48.11					

[1] Above 154°.

TABLE 4.—*Systematic refractionation of fractions 40 to 57 of table 2* [1]

Fraction no. (series 4)	Distillation temperature [2]	Refractive index	Optical rotation	Density	Ratio of each fraction to the whole	Sum of fractions
	°C.	$n_D^{20°}$	$\alpha_D^{20°}$	$\frac{15°}{4°}$	*Percent*	*Percent*
T-1	52.5	1.4642	+24.30	0.8641	9.98	9.98
T-2	52.5	1.4646	+23.53	.8650	4.73	14.71
T-3	52.5	1.4648	+22.52	.8652	6.48	21.19
T-4	52.8	1.4651	+22.25	.8649	2.85	23.85
T-5	53.3	1.4654	+21.55	.8650	1.10	24.95
T-6	53.6	1.4654	+20.15	.8649	2.01	26.96
T-7	53.9	1.4655	+19.01	.8651	1.68	28.64
T-8	53.4	1.4654	+20.95	.8649	1.88	30.52
T-9	53.6	1.4657	+19.77	.8649	1.36	31.88
T-10	54.1	1.4660	+18.21		.91	32.79
T-11	54.5	1.4664	+16.20	.8667	1.23	34.02
T-12	55.8	1.4669	+13.42		.78	34.80
T-13	56.5	1.4673	+9.51		.52	35.32
T-14	57.6	1.4670	+5.68		.72	36.04
T-15	58.5	1.4663	+1.33		1.10	37.14
T-16	59.5	1.4654	−2.02		.78	37.92
T-17	60.4	1.4652	−5.37	.8549	1.10	39.02
T-18	60.7	1.4631	−7.97		.46	39.48
T-19	60.5	1.4617	−4.59		.91	40.39
T-20	61.2	1.4584	−4.17	.8418	1.36	41.75
T-21	61.8	1.4552	−4.27	.8347	1.16	42.91

[1] Represents the last 17.60 percent.
[2] Fractions T-1 to T-33, inclusive, were determined at 20 mm. Fractions T-34 to T-53, inclusive, were determined at 10 mm (values given in table), but for purposes of plotting distribution graphs, were calculated roughly to 20 mm.

TABLE 4.—*Systematic refractionation of fractions 40 to 57 of table 2*—Continued

Fraction no.	Distillation temperature	Refractive index	Optical rotation	Density	Ratio of each fraction to the whole	Sum of fractions
	°C.	$n_D^{25°}$	$\alpha_D^{20°}$	$\frac{15°}{4°}$	*Percent*	*Percent*
T-22	62.2	1.4520	−3.97	0.8282	1.16	44.07
T-23	62.8	1.4482	−2.78	.8198	1.29	45.36
T-24	63.2	1.4443	−1.20	.8127	1.04	46.40
T-25	63.8	1.4419	−.17	----------	.91	47.31
T-26	----------	1.4424	+.59	----------	.39	47.70
T-27	----------	1.4423	+3.11	----------	.52	48.22
T-28	65.0	1.4492	+.11	.8201	3.69	51.91
T-29	65.6	1.4506	+1.11	.8209	3.63	55.54
T-30	66.0	1.4521	+2.14	.8231	2.53	58.07
T-31	67.0	1.4541	+2.70	.8252	1.55	59.62
T-32	68.0	1.4569	+3.89	.8299	2.20	61.82
T-33	68.7	1.4623	+5.60	.8358	2.85	64.67
T-34	54.8	1.4669	+7.03	.8424	1.49	66.16
T-35	56.0	1.4695	+5.83	.8431	3.76	69.92
T-36	56.4	1.4707	+6.03	.8481	1.23	71.15
T-37	57.0	1.4724	+6.41	.8506	3.76	74.91
T-38	57.2	1.4732	+8.81	.8506	2.79	77.70
T-39	57.4	1.4732	+9.04	.8511	2.27	79.97
T-40	57.8	1.4734	+9.20	.8514	3.24	83.21
T-41	58.3	1.4739	+9.25	.8526	3.43	86.64
T-42	59.7	1.4747	+8.97	.8546	2.23	88.97
T-43	61.0	1.4755	+8.4	.8566	1.03	90.00
T-44	63.0	1.4779	+6.4	.8625	1.36	91.36
T-45	65.0	1.4803	+4.5	.8681	1.03	92.39
T-46	66.0	1.4826	+2.6	----------	.78	93.17
T-47	67.0	1.4843	+1.8	----------	.98	94.15
T-48	67.6	1.4842	+1.6	.8811	1.03	95.18
T-49	74.0	1.4850	+1.7	.9252	1.03	96.21
T-50	80.0	1.4819	+0.9	.9634	.52	96.73
T-51	82.0	1.4793	−.2	.9681	.52	97.24
T-52	82.5	1.4784	−1.0	.9838	.50	97.84
T-53 (residue)	[3] 82.5	1.4924	+21.1	----------	2.14	99.98

[3] Above 82.5°.

TABLE 5.—*Refractionation of α-pinene fraction* [1]

Subfraction no.	Distillation temperature at 20 mm	Refractive index	Density	Optical rotation			Dispersion
	°C.	$n_D^{25°}$	$\frac{15°}{4°}$	$\alpha_D^{20°}$	$\alpha_J^{20°}$	$\alpha_V^{20°}$	$\alpha_V^{20°}/\alpha_J^{20°}$
1	50.2	1.4627	0.8616	+25.32	+26.57	+29.97	1.128
2	50.2	1.4631	.8626	+26.00	+27.31	+30.84	1.1295
3	50.5	1.4631	.8627	+26.01	+27.32	+30.86	1.1296
4	50.5	1.4631	.8627	+26.05	+27.33	+30.86	1.1292
5	50.6	1.4631	.8628	+26.14	+27.47	+31.01	1.1288
6	50.7	1.4633	.8629	+26.08	+27.41	+30.94	1.1287
7	50.7	1.4633	.8629	+26.08	+27.41	+30.93	1.1282

[1] Fraction no. 20, table 2.

In order to visualize the progressive improvement in separation and the distribution over given temperature ranges of the fractions obtained from these several fractionations, distribution curves are shown in figures 3, 4, 5, and 6 and rotation curves in figures 7 and 8. The relative complexity of the small quantity of forerun (series 3), and particularly that of the higher boiling portion (series 4), may be visualized from the respective distribution curves in figures 5 and 6, and also the refractive index curve (fig. 9) and rotation curve (fig. 10), plotted from data in tables 3 and 4, respectively.

The great bulk of the turpentine distillate, boiling around 50°–51° C. at 20 mm pressure, is α-pinene. While no difficulty was experienced in establishing the presence of β-pinene by chemical means in the appropriate fractions, it was present in too small a quantity in the original turpentine to appear in pure form in any one of the fractions. No attempt was made to calculate by optical means, by the method of Darmois-Dupont (*9*), the relative proportion of α- and β-pinene in the various fractions, as was done in the case of gum spirits (*20*), since the influence of the presence of several monocyclic hydrocarbons in the fractions involving β-pinene would render such calculations inaccurate. For similar reasons, no application of the Biot rule was made to calculate individual components, such as limonene, terpinene,

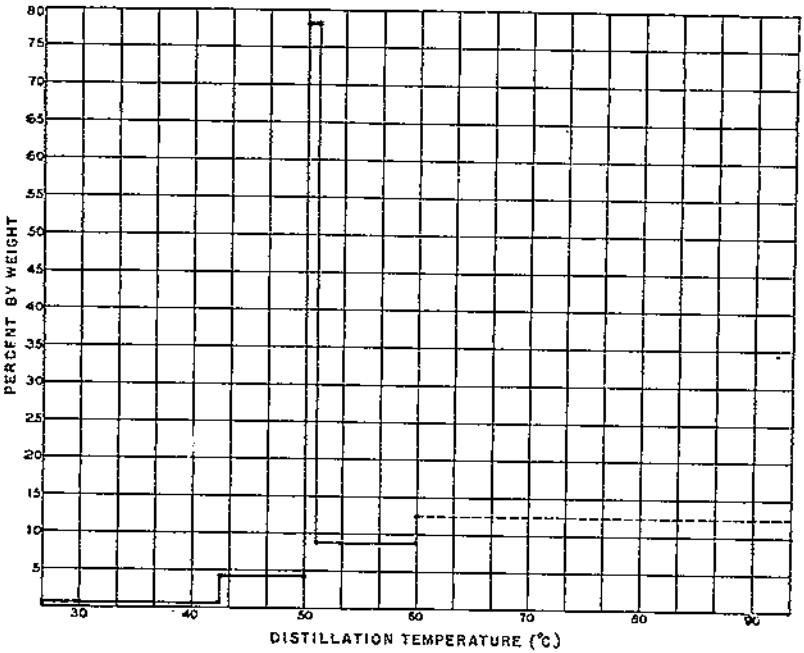

FIGURE 3.—Distribution (percent by weight), with respect to boiling range at 20 mm, of the first series of fractionations (composite) obtained by one fractionation of whole turpentine.

terpinolene, the several alcohols, etc., of the subsequent or high-boiling fractions.

The total quantity of higher-boiling residue was insufficient, the number of constituents too large, and their boiling points too close together to permit a physical separation of individual compounds in pure form, even by repeated fractionations, as is evident from the data on rotation, index of refraction, and density shown in table 4, and the plottings shown in figure 10.

Data on optical rotation were obtained with a Schmidt and Hänsch polarimeter equipped with a monochromator. Rotation measurements were made in the green (V=546 $m\mu$) and yellow (J=578 $m\mu$), in addition to the yellow (D=589 $m\mu$), where rotatory dispersion data were desired. Rotatory dispersion values have been shown by Darmois (*9*) to be particularly significant in characterizing and establishing

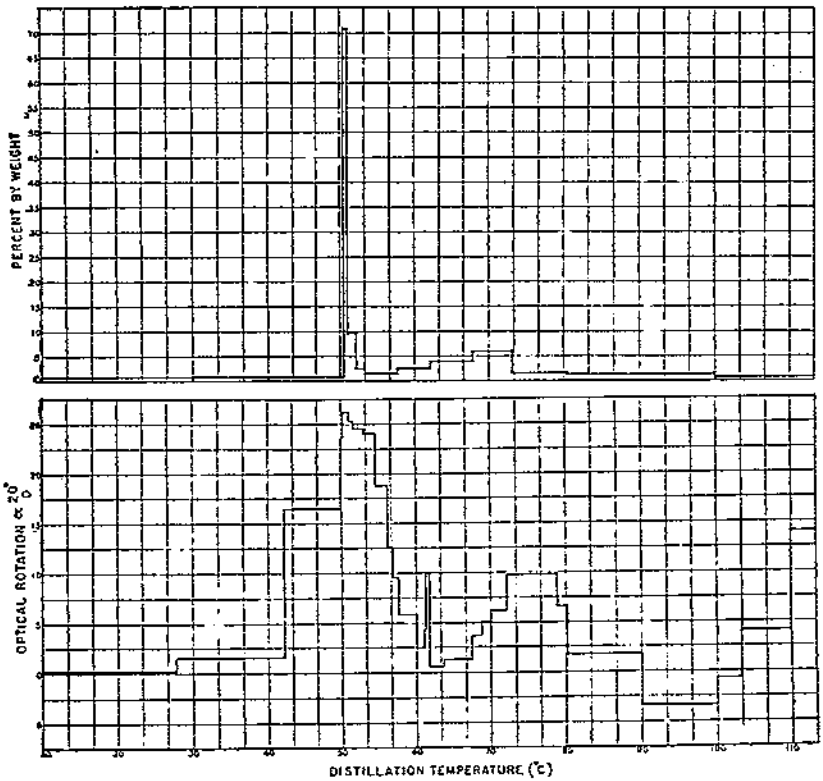

FIGURE 4.—Distribution (optical rotation and percent by weight), with respect to boiling range at 20 mm, of the second series of fractions obtained after several refractionations of all of first series.

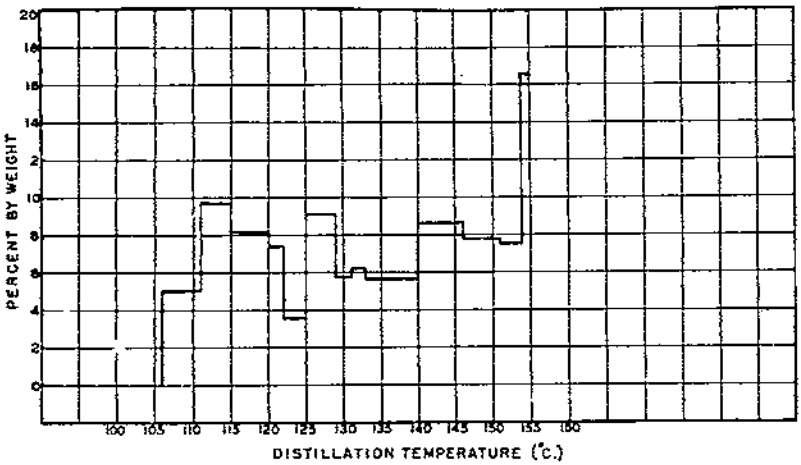

FIGURE 5.—Distribution (percent by weight), with respect to boiling range at atmospheric pressure, of the third series of fractions obtained by refractionation of first five fractions of series 2, representing the volatile part of turpentine only.

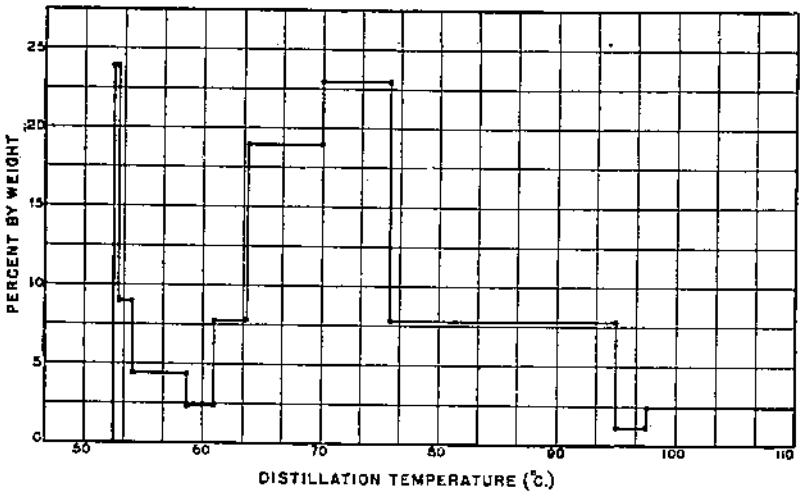

FIGURE 6.—Distribution (percent by weight), with respect to boiling range at 20 mm, of the fourth series of fractions obtained by refractionation of the last 34 fractions of series 2, representing the high boiling part only.

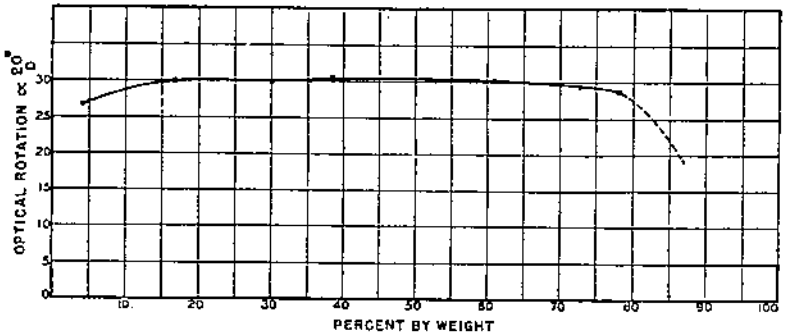

FIGURE 7.—Optical rotation, with respect to percent by weight, of the first series of fractions (composite) obtained by one fractionation of the whole turpentine.

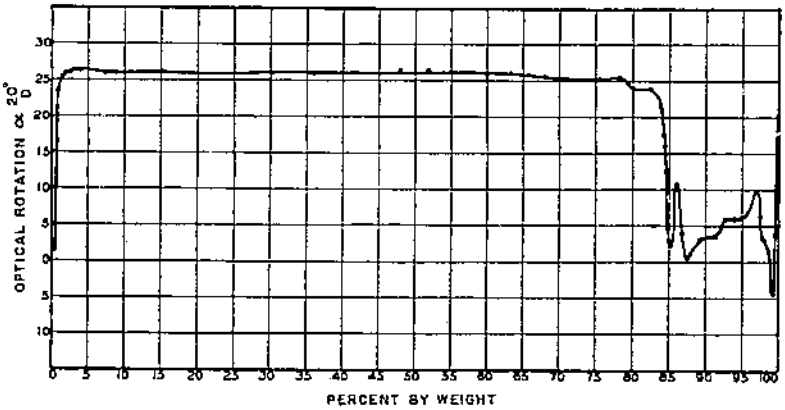

FIGURE 8.—Optical rotation, with respect to percent by weight, of the second series of fractions obtained after several refractionations of the first series.

the purity of α-pinene. Such rotatory dispersion data for fractions obtained by further fractionation of the α-pinene fractions are shown in table 5 together with other data. These data show that α-pinene of highest purity had been obtained in the previous fractionation (table 2).

Refractive indices were obtained in the usual manner with an Abbe refractometer. Specific gravity determinations were made with the Westphal balance and in some instances with pycnometers, values

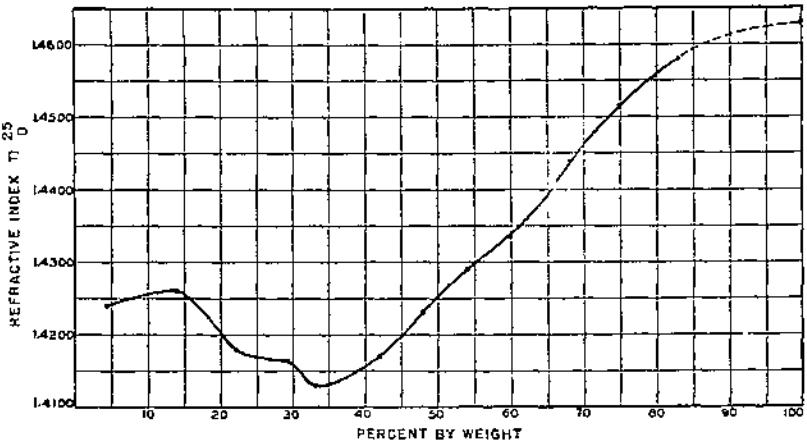

FIGURE 9.—Refractive indices, with respect to percent by weight, of the third series of fractions obtained by refractionation of the first five fractions of series 2, representing the volatile part of turpentine only.

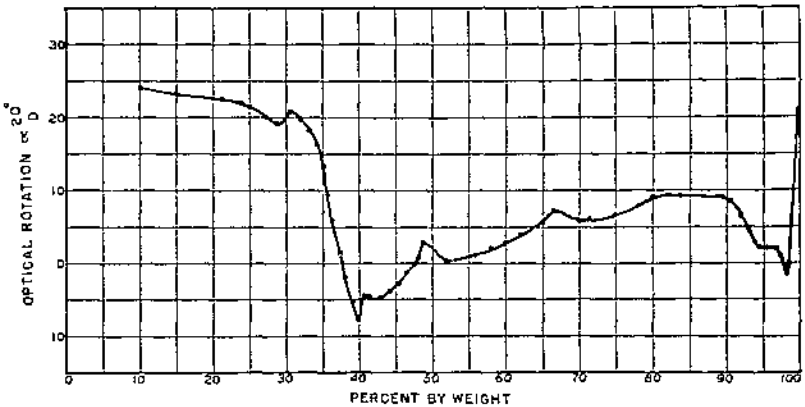

FIGURE 10.—Optical rotation, with respect to percent by weight, of the fourth series of fractions obtained by refractionation of the last 34 fractions of series 2, representing the high boiling part only.

being subsequently converted to density. In some instances the use of micro-pycnometers was necessary, in view of the very small quantities of fractions available. Micro boiling points were obtained in a number of instances as indicated, for fractions available in very small quantities.

Quantitative determinations of alcoholic and phenolic hydroxyl (*18*, *47*) and methoxyl (*5*) in connection with methyl ethers were also made on a number of fractions. These are described under Chemical Examination of Fractions.

CHEMICAL EXAMINATION OF FRACTIONS

ALDEHYDES

In view of the oily character (water insoluble) of the fractions involved, the test for aldehydes, using Schiff's reagent, was carried out as follows: 2 cc of aldehyde-free alcohol prepared by the method of Stout and Schutte (*37*) was added to about one-half cc of the fraction in a test tube, one or two drops of fuchsin reagent was added, and the tube was shaken. A parallel or blank test was made on the aldehyde-free alcohol, and the development of color noted in the two tubes.

Positive reactions for aldehydes were given by fractions 1 and 2, and doubtful reactions by fractions 3, 4, 5, and 6 (table 2). Positive reactions were also given by fractions T–4, T–6, T–7, T–8, T–10, T–12, T–16, T–18, T–20, T–22, T–24, T–26, T–49, T–50, T–51, and T–53 (table 4).

PHENOLS

Qualitative tests for phenols with diazo-p-nitrobenzene, known to be a sensitive test agent for phenols (*25*), gave pronounced dye reactions with fractions T–52 and T–53 (table 4).

FURFURAL

In the first fraction (tables 1 and 2) of low boiling distillate, there was present a lower aqueous layer of brownish color (about 1 cc) which, after removal from the upper layer of hydrocarbons, gave a positive reaction for aldehydes and a strong qualitative reaction for furfural with aniline acetate paper.[9] This brownish liquid was steam distilled, the distillate was extracted with ether, the extract was dried over anhydrous sodium sulphate, and the solvent was evaporated in vacuum. Two or three drops of a light-colored oily residue remained. This formed a phenyl hydrazone which, after two crystallizations from dilute alcohol, had a melting point of 95° C.

BENZALDEHYDE

The low-boiling hydrocarbon fractions 1, 2, and 3 (table 2) were extracted several times with saturated sodium bisulphite solution, the bisulphite solution was treated with sodium carbonate and extracted with ether, and the ether solution was dried over anhydrous sodium sulphate. A few drops of residue obtained on evaporation of the ether had a strong almond odor. A semicarbazide was obtained having a melting point of 212°–213° C., the semicarbazide of authentic benzaldehyde having a melting point of 214°. The presence of benzaldehyde in steam-distilled wood turpentine had been noted in this laboratory some years ago.[10]

PETROLEUM HYDROCARBONS

Properties of the low-boiling fractions pointed to petroleum hydrocarbons. Fractions 1–5 (table 2) were therefore subjected to further refractionating, giving series 3, whose properties are shown in table 3. The first few fractions of the new series were treated with sulphuric

[9] The presence of furfural in steam-distilled wood turpentine had been noted by C. F. Speh of this Division in an unpublished report dated 1914.

[10] See footnote 6, p. 2.

acid to free them from accompanying α-pinene and other unsaturates, as follows: The fractions were shaken in the cold three times with fuming sulphuric acid and twice with concentrated sulphuric acid, washed with water, then with dilute sodium hydroxide, again washed with water, steam distilled, and separated from the water layer. These fractions, which were now very small, had the properties, determined by micromethods, shown in table 6. The last two fractions, H–2 and H–3 (treated), after recombining and drying over calcium chloride, were redistilled, distillation temperature ranging from 112° to 117° C., and constants were determined as follows: Density, 20°/4°, 0.733; refractive index $n_D^{20°}$, 1.4097. The odor seemed to be similar to petroleum oil.

These low-boiling fractions were evidently mixtures of paraffin hydrocarbons with properties in the neighborhood of methylheptane and octane, but the quantities available were far too small to permit even an approximate separation of individual compounds.[11] Dimethylcyclopentenes were isolated by Chavannes (*4*) from French gum spirits, but the properties exhibited by these fractions were quite different from those described here.

ALPHA-PINENE

This hydrocarbon, found in fractions 7 to 35 (table 2), constitutes by far the major portion of wood turpentine, roughly 80 percent, and no difficulty was experienced in isolating it in a pure state, as evidenced by its physical properties (table 5), particularly by its rotatory dispersion (*9*).

CAMPHENE

The camphene in fraction T–12 (table 4) was hydrated by the method of Bertram and Walbaum (*1*). The resulting isoborneol, after three crystallizations from petroleum ether, had a melting point of 208°–209° C., the mixed melting point with authentic isoborneol showing no depression.

TABLE 6.—*Properties of fractions treated with sulphuric acid*

Fraction no. (treated)	Micro boiling point	Density	Refractive index
	°C.	$\frac{20°}{4°}$	$n_D^{20°}$
H–1	107	0.736	1.410
H–2	113	.734	1.409
H–3	114	.736	1.410

BETA-PINENE

Fractions T–14 and T–15 (table 4) were oxidized with potassium permanganate to nopinic acid, using the method of Dupont (*10*), with modifications and quantities of material as indicated: 28-g sample, 63 g of potassium permanganate in 900 cc of water, 11 g of potassium hydroxide, and 10 g of sodium carbonate. The following deviations were made from the Dupont procedure: Sodium carbonate was used

[11] No attempt is made in this connection to explain the origin of the trace of paraffin oils in steam-distilled wood turpentine, as these may come as contamination from plant processing, rather than as natural constituents in the turpentine.

in place of sodium sulphate and added as a saturated solution after the mixture had been filtered free of manganese dioxide and concentrated to a volume of 300 cc. On addition of sodium carbonate, 1.4 g of crystals separated from the reaction mixture, and another crop was obtained on further concentration of the filtrate.

The combined crystals were recrystallized from 95-percent alcohol, the first crop of crystals was converted to the free acid, using 10-percent sulphuric acid, and the resulting nopinic acid was recrystallized from benzene. The melting point was 127.5°–128° C.

PARA-MENTHANE

A 6-g portion of fraction T–26 (table 4) was treated with two to three times its volume of mild fuming sulphuric acid, allowed to separate, washed with water, distilled, again washed with water and sodium carbonate solution, and yielded finally 3.3 g of purified oily liquid. This had a refractive index, $n_D^{20°}$, of 1.4315; density, $\frac{20°}{4°}$, 0.7962; micro boiling point, 168°–169° C. A sample of authentic paramenthane had the following properties: Refractive index, $n_D^{20°}$, 1.440; density, $\frac{20°}{4°}$, 0.7996; boiling point, 167°–168°.

CINEOL

Fractions T–28, T–29, and T–30 (table 4) had a distinct cineollike odor. Fraction T–28 was shaken twice with 5 cc of 50-percent resorcinol solution. No crystalline product resulted. The combined resorcinol solutions were treated with 5-percent sodium hydroxide solution and extracted with ether, the ether was evaporated, and 1 cc of 50-percent resorcinol solution was added. The solution became turbid, but no definite precipitate was obtained. Five percent sodium hydroxide was added, and the mixture was distilled with steam. A few oily drops separated from the distillate. The distillate was extracted with petroleum ether and the extract was dried over anhydrous sodium sulphate, but no definite derivative of cineol was obtained in this manner.

The next fraction, T–29, was extracted several times with 50-percent resorcinol solution and treated in the manner already described. A few drops of a viscous liquid with a cineol odor was thus obtained. Tested with iodol, it gave crystals similar to those from the iodol derivative of authentic cineol. The melting point was not sharp—110° to 115° or 116° C. A mixed melting point with the derivative from authentic cineol, however, showed no lowering.

LIMONENE AND DIPENTENE

A 6-cc portion of fraction T–35 (table 4) was brominated according to the method of Godlewski (*6*). The precipitated bromide was filtered, washed with absolute alcohol, and air-dried. Two and seven-tenths grams of tetrabromide with a melting point of 120°–121° C. was thus obtained. This was recrystallized from absolute alcohol several times, and the melting point was then 123°–124°. No further elevation of the melting point resulted from two additional crystallizations.

CYMENE

Each of the three fractions T–35, T–37, and T–39 (table 4) was subjected to permanganate oxidation in the usual manner, and a small quantity of material obtained from fraction T–37 was sublimed, but found insufficient for identification.

TERPINENE

A 2-cc portion of fraction T–43 (table 4) was brominated according to the Godlewski method, the resulting crystals after recrystallization from alcohol having a melting point of 122° C. Further recrystallization, however, gave two crops which melted at 125°–126°. The melting point after recrystallization three times from absolute alcohol showed no change, and determination of the mixed melting point with authentic terpinene tetrabromide showed no depression.

TERPINOLENE

The original mother liquor yielded crystalline bromides with lower melting points, 116°–117° C., which were subjected to two more crystallizations without apparent change, but when a mixed melting-point determination was made with authentic terpinolene tetrabromide (116°–117°) a sharp depression of 26° in melting point resulted, thus indicating that no derivative of terpinolene had been isolated. It was identified, however, in a higher boiling fraction (T–48, table 4). A 1.5-cc portion of the hydrocarbons separated by distillation after treatment of this fraction with ethyl borate to hold back the alcohols was brominated in glacial acetic acid, yielding a crystalline bromide which, after two crystallizations from alcohol, gave a product with a melting point of 117° C. This showed no depression by mixed melting point determination with authentic terpinolene tetrabromide.

SOBREROL

A solid residue separated from fractions 67, 68, and 69 (table 2) which was removed by decantation. The oily liquid centaminating the crystals was not soluble in petroleum ether, but was readily removed by repeated washing with small quantities of methyl alcohol. The white crystalline residue was recrystallized from ethyl alcohol, after which the dried crystals showed softening at about 131° and clearing at 144° C. Rotation obtained by dissolving 0.295 g in 25 cc of alcohol gave $[\alpha]_D^{20°}$,+120°. Authentic sobrerol gave $[\alpha]_D^{20°}$,+122°.

The decanted methyl alcohol solutions and washings were evaporated, and the crystals thus obtained also showed a softening point of 130°–131° C., and melted to a pure oil at 139°. After recrystallization from water, the crystals melted at 149°–150°. When mixed with authentic sobrerol, no depression of the melting point resulted.

ALCOHOLS

The high-boiling fractions T–43, T–48, T–49, T–50, T–51, T–52, and T–53 (table 4) were each treated with ethyl borate for the removal of the alcohols as a whole by the Kaufmann procedure (*16*). The ethyl borate was prepared by the method of Webster and Dennis (*43*), using a large excess of boric anhydride. T–43 yielded no alcohol.

The others, with the exception of T–53, which consisted principally of alcohols, each yielded only a few cubic centimeters of alcohol after removal of the hydrocarbons.

Methods available for the separation of secondary and tertiary terpene alcohols from each other, as distinguished from methods for their quantitative determination, are far from satisfactory, as pointed out by Delaby and Sabetay (*8*), particularly when preservation of the tertiary alcohols is an essential requirement.

Experiments with synthetic mixtures of borneol, fenchyl alcohol, and terpineol by benzoylation in the cold in the presence of pyridine (*13*) did not give anything like a complete separation of the secondary alcohols from the tertiary alcohols because of the volatility of the benzoyl esters of the secondary alcohols. The acid phthalate method, which depends upon extraction for separation of unreacted tertiary alcohols, was found more satisfactory.

By a modification involving prolonged heating (24 to 40 hours) of the phthalic anhydride reaction mixture, Stephan's (*36*) low-temperature procedure using benzene, which is ordinarily regarded as suitable for primary alcohols only, was made applicable to secondary terpene alcohols. Experiments with synthetic mixtures showed the method to be relatively effective for separating borneol and fenchyl alcohol from terpineol without, apparently, any appreciable dehydration of the latter.

FENCHYL ALCOHOL

The alcoholic residues from T–48 and T–49 (table 4) were combined because of the small quantities available. Acid phthalates were prepared from this mixture and from the alcoholic residues from each of the other fractions, using the modified Stephan method described by Bournot (*2*). All of these were found to give esters which on several recrystallizations melted at 168°–169° C., corresponding to the fenchyl acid phthalate reported by Zeitschel and Todenhoffer (*35, 46*). Mixed melting-point determinations with authentic acid phthalate showed no depression.

BORNEOL

An attempt was made to separate bornyl acid phthalate by fractiona crystallization of the combined acid phthalate residues remaining after isolation of the fenchyl acid phthalate, but results were negative.

TERTIARY ALCOHOLS

The alcoholic residues not reacting with phthalic anhydride on first treatment were very small, and were combined (except T–53) and given a second treatment, yielding a small additional quantity of fenchyl acid phthalate. The combined tertiary alcoholic residue was then tested for terpineol by an attempted hydration with sulphuric acid (*38*) to terpinhydrate, and also by conversion to a phenyl-urethane, but with negative results.

ALPHA-TERPINEOL

The alcoholic residue from fraction T–53 (table 4) after distillation showed the following properties: Refractive index, $n_D^{25°}$, 1.4884; density, $\frac{20°}{4°}$, 0.9573; microboiling point, 208°–209° C.

While the properties of this residue approached those of α-terpineol, no solid phenyl-urethane could be obtained. It was therefore subjected to a further purification treatment, and ultimately yielded a phenyl-urethane, the procedure being as follows: 3.7 g of sample, 3.7 g of phthalic anhydride, and 8 cc of benzene were placed in a flask fitted with a reflux condenser and heated for 42 hours. The reaction mixture was poured into an excess of normal sodium hydroxide and shaken. The mixture was extracted twice with petroleum ether and the combined extract was washed with dilute sodium hydroxide and then with water. It was then filtered through paper, the petroleum ether was evaporated, and the residue was distilled in vacuum, yielding approximately 1.3 cc of distillate.

The phenyl-urethane was prepared as follows: 0.5 cc of distillate and 0.6 cc of phenyl isocyanate were heated for 1½ hours at 70° C. and then for one-half hour at 90°. The reaction mixture was treated with 1 cc of acetone containing 0.1 cc of water (*12*) and allowed to stand for 2 hours. The acetone was then removed by evaporation. The residue was extracted with petroleum ether, the petroleum ether was evaporated, and the extract was dissolved in 7 cc of 70-percent alcohol. After long standing at 10°, crystals separated which, after recrystallizing three times from dilute alcohol, had a melting point of 108°–109°. The mixed melting point with authentic α-terpineol phenyl-urethane showed no depression and indicated that the crystals obtained by this procedure were slightly impure terpineol phenyl-urethane.

KETONES

After removing the alcohols from fractions T–43 to T–51 (table 4) with ethyl borate, using the Kaufmann procedure (*16*), the residues were combined and treated with hydroxylamine in the usual manner. A very small quantity of gummy precipitate was obtained, but no crystalline oxime was formed.

METHYL CHAVICOL (ANETHOL)

The nonalcohol portion of fraction T–52 (table 4) was oxidized with 4-percent potassium permanganate and the solution, after removal of the manganese dioxide by filtration, was concentrated and acidified with hydrochloric acid. A precipitate was formed which, after three crystallizations, melted at 183.5° C. No depression was obtained by mixed melting-point determination with authentic anisic acid.

The acidified concentrate from the nonalcohol portion of T–52 was extracted with ether. A very small oily residue was obtained on evaporation of the ether which had a camphoraceous odor. On sublimation, it yielded only an oily product. No oxime of camphor could be obtained by the usual treatment with hydroxylamine.

CHEMICAL TREATMENT OF HIGHER BOILING PORTION

The second half of the high-boiling portion, not used for fractionation, was then subjected to schematic treatment for the successive removal of the aldehydes, phenols, and alcohols.

ALDEHYDES

The presence of aldehydes had already been shown by color tests on individual fractions, using the fuchsin reagent, and also by formation of derivatives of furfural and benzaldehyde.

This second half of the high-boiling portion was extracted four times with 50-cc portions of aqueous sodium bisulphite solution. Because of the minute quantities of aldehydes present, no crystalline bisulphite could be obtained. Extraction by the bisulphite solution was relied upon, however, as a means for the removal of these traces of aldehydes (*39*). The combined bisulphite extracts were made alkaline with sodium carbonate, and the regenerated aldehyde mixture was extracted with ether. The residue obtained on evaporation of the ether consisted of a very small quantity of viscous oil smelling strongly of benzaldehyde. No crystalline semicarbazone could be obtained, and the total quantity of aldehydic oil resulting from this extraction was too small to permit a purification treatment with the view to subsequent regeneration for preparation of derivatives.

PHENOLS

After extraction with bisulphite, the sample was subjected to repeated extraction with sodium hydroxide solution as follows:

Twelve extractions were made using 50-cc portions of 5-percent aqueous sodium hydroxide solution, followed by six extractions using 8-percent sodium hydroxide. Tests were made for completeness of extraction on portions of the final extracts by use of diazo-p-nitrobenzene (*25*). As these tests still showed traces of phenol, a portion was extracted 38 times with 5-percent sodium hydroxide, and even then tests of the extract did not show complete removal, but in view of the sensitivity of the test, the extraction was regarded, for practical purposes, as complete.

The alkaline extract was acidified with 10-percent sulphuric acid, the liberated phenols were extracted with ether, and the ether was evaporated, leaving a brown viscous residue which was subjected to steam distillation. An arbitrary division of distillate was made, (1) distilling easily, and (2) requiring prolonged steam distillation. As all of the phenol material was not steam-volatile, the residue remaining in the distillation flask (3) was reextracted with sodium hydroxide solution, the phenols were liberated with acid and extracted with ether, and the ether extract was washed and dried over anhydrous sodium sulphate. All three phenolic fractions were found to consist, in part at least, of methyl ethers as shown by the following determinations of methoxyl:

	Percent methoxyl
(1) Steam volatile part (more volatile with steam)	1.1
(2) Steam volatile part (less volatile with steam)	3.8
(3) Residue (not volatile with steam)	3.3

The quantities of phenols were too small for separation into fractions, either by distillation or by fractional crystallization of alkali salts, and it was not found possible to prepare dinitrobenzoates or other solid derivatives. Methyl chavicol (anethol) had been identified in fraction T–52 (table 4) by oxidation to anisic acid (p. 22).

ALCOHOLS

The residual oil, after extraction of phenolic and aldehydic compounds, was dried and treated in two batches (630 cc each) for removal of alcohols by means of ethyl borate as described by Kaufmann (*16*).

The quantity of ethyl borate reagent used was in excess of that calculated on the basis of Zerevitinoff determination (*47*) on a 2-g sample. This showed that the residual oil had a total alcohol content,

calculated as $C_{10}H_{18}O$, of 12.8 percent. This would indicate a total alcohol content of about 2 percent, calculated on the original turpentine.

The hydrocarbons were distilled from the reaction mixture, beginning at about 15 mm pressure and 45° C. and completing the distillation at about 8 mm, at a temperature not exceeding 100°.

The residue of boric esters remaining was then subjected to steam distillation, most of the regenerated alcohols distilling with the first liter of distillate. In order to insure complete hydrolysis of the alcohol-boric-esters, 100 cc of 5-percent sodium hydroxide was added to the reaction mixture toward the end of the distillation. The ether solution of the total alcohols was dried over anhydrous sodium sulphate and the ether was removed, the yield being 93 cc of terpene alcohols.

The hydrocarbon portion was treated a second time with ethyl borate, but practically no further yield of alcohol was obtained. A Zerevitinoff determination (*47*) made on the hydrocarbon distillate showed virtually complete removal of the alcohols.

To test the character of the residue from the boric ester hydrolysis, it was acidified with 10-percent sulphuric acid and extracted with ether, and the ether solution was dried over anhydrous sodium sulphate. The evaporation of the ether left a very small, brown, viscous residue, which, when distilled with superheated steam, yielded only a trace of oily material and gave a strong phenolic reaction.

SECONDARY ALCOHOLS

The mixed alcohols were heated for 24 hours in a benzene solution with an equal weight of phthalic anhydride, using the Stephan procedure (*36*) except for time of heating, the flask with the reaction mixture having been set down in a steam bath to insure heating at 100° C. The resulting acid phthalates were fractionally crystallized from benzene-petroleum ether and from dilute alcohol.

FENCHYL ALCOHOL

Impure fenchyl acid phthalate was obtained from the benzene-petroleum ether mother liquors, which, after several recrystallizations from 50-percent alcohol, had a melting point of 169°–169.5° C. A mixed melting-point determination with authentic fenchyl acid phthalate showed no depression.

BORNEOL

After repeated crystallization of the acid phthalates from benzene-petroleum ether, bornyl acid phthalate, melting point 161°–162° C., was obtained. A mixed melting-point determination with authentic bornyl acid phthalate showed no depression.

TERTIARY ALCOHOL

The residue not reacting with phthalic anhydride, after separation from the alkalized reaction mixture by extraction with ether, was purified by steam distillation in the presence of a little 5-percent sodium hydroxide to hold back traces of phthalic acid, the oily distillate was extracted with ether, the ether solution was dried over sodium sulphate, and the residual alcohol obtained after evaporation of the ether was distilled in vacuum to insure complete removal of traces of moisture and ethyl alcohol.

ALPHA-TERPINEOL

A portion of the tertiary alcohols was shaken with 5 percent sulphuric acid (*38*) at intervals over a period of 5 days, the unreacted oil was removed with petroleum ether and the aqueous solution, after neutralization, was evaporated in vacuum. The residue was extracted with alcohol. The alcohol solution was evaporated and the resulting solid, after recrystallization from water, melted at 110.5°—111.5° C. A mixture with authentic terpinhydrate, melting point 115°–116°,melted at 110.5°–112.5°.

Second and third portions of the tertiary alcohols, when reacted with phenyl isocyanate and p-nitrophenyl isocyanate, respectively, yielded only noncrystallizable oils.

A fourth part of the tertiary alcohols was again treated with phthalic anhydride in benzene, this time for 42 hours, to insure complete removal of traces of secondary alcohols. The purified alcohols yielded a phenyl-urethane, melting point 110.5°–111.5° C., by the procedure described on page 22. A mixed melting point with the phenylurethane of authentic α-terpineol gave no depression.

In view of the difficulties experienced in obtaining diagnostic derivatives, a fifth portion of the tertiary alcohols was subjected to fractionation in vacuum. The apparatus is shown in figure 2 and described under equipment. The fractions shown in table 7 were obtained.

TABLE 7.—*Fractionation of tertiary alcohols*

Fraction no.	Distillation temperature	Pressure	Density	Alcohol,[1] calculated as $C_{10}H_{18}O$
	°C.	*Mm*	$\frac{20°}{4°}$	*Percent*
1	88—95.5	20	0.935	68
2	87—92	10	.947	94
3	92—95.5	10	.946	91
4	88	5	.951	93

[1] Determined by the Zerevitinoff method (*47*).

Fraction 4 (table 7) yielded a nitrosyl chloride by the following procedure (*26, 42*): To a mixture of 1.3 g of terpene alcohol, 1.3 cc of ethyl alcohol, and 1.3 cc of ethyl nitrite in an ice bath was added 1.1 cc of 8 N alcoholic hydrochloric acid solution, drop by drop, and the reaction mixture was left in the ice bath for 2 hours, after which 5 cc of alcohol in 10 cc of water was added. The crude nitrosyl chloride came down as a pasty mass, which, after several washings by decantation with cold water, was dried in an Abderhalden oven at 50° C. and 5 mm pressure. It was then recrystallized twice from ethyl acetate, yielding 0.06 g of nitrosyl chloride which had a melting point of 113°–116°.

The nitrosyl chloride was dissolved in 4 cc of alcohol, treated with 0.1 g of aniline (*42*), heated on the steam bath for about 8 minutes, cooled, and 3 cc of water was added. An oil separated which, after a few minutes, solidified to a crystalline mass. This was filtered and washed with 25-percent alcohol, crystallized from about 2 cc of 40-percent alcohol, and dried in vacuum. The melting point was 155°–156° C. No depression was observed in a mixed melting-point determination made with the anilide prepared from authentic terpineol.

SUMMARY AND CONCLUSIONS

Steam-distilled wood turpentine, representative of material sold to conform to specifications of the American Society for Testing Materials, was subjected to systematic fractional distillation followed by physical and chemical examination of the individual fractions. The results are compared to those obtained previously for gum spirits of turpentine. Equipment and procedure suitable for the fractionation in vacuum of turpentine are described in full or given by citation.

The investigation here reported shows that steam-distilled wood turpentine consists chiefly, but not entirely, of terpene hydrocarbons, the major portion of which, roughly 80 percent, is α-pinene. β-Pinene, which constitutes a large percentage of gum spirits, is present, but only in small amount. The only other dicyclic hydrocarbon found is camphene, which is probably also present only in small amount. The remainder of the hydrocarbon portion consists of monocyclic hydrocarbons, notably dipentene, limonene, terpinene, and terpinolene.

The nonhydrocarbon portion, which in the aggregate probably does not exceed 2 percent of the turpentine, consists of secondary and tertiary terpene alcohols, aldehydes, phenols, phenolic ethers, and oxidation and polymerization products. Of the secondary alcohols, both borneol and fenchyl alcohol are found, but the latter is more characteristic. The tertiary alcohols, of which α-terpineol was identified, constitute a substantial part of the total alcohols.

The presence of benzaldehyde in very small amount was definitely established, confirming previous findings. Furfural, which had been reported previously, based on color test only, was definitely identified by means of the phenylhydrazone, although present in very small amount.

A trace of cineol was present. Sobrerol was found in more than traces. The presence of camphor and cymene was indicated, but the quantities present were too small for identification. Very small quantities of phenols, evidently mixtures, were found, but the individual phenols were not identified. Phenolic ethers were present, and methyl chavicol (anethol) was identified.

The presence of very small quantities of low-boiling hydrocarbons of a paraffin nature was established, but whether these are naturally present or merely residual petroleum contaminants due to the process used in commercial extraction cannot be positively stated.

The principal characteristic differences then between steam-distilled wood turpentine and gum spirits may be summarized as follows: (1) While the hydrocarbon portion constitutes by far the major part of both products, virtually all the hydrocarbon components in gum spirits consist of dicyclic terpenes, whereas the hydrocarbons in steam-distilled wood turpentine consist of appreciable proportions of monocyclic terpenes, notably dipentene (limonene), terpinene, and terpinolene; (2) the dicyclic terpene α-pinene is present in a considerably larger proportion in steam-distilled wood turpentine than in gum spirits—about 80 percent in the former to about 60 percent in the latter; (3) β-pinene is present in substantial proportions in gum spirits, but only in negligible quantities in steam-distilled wood turpentine.

These gross differences in composition between steam-distilled wood turpentine and gum spirits, while not evident from Engler

distillations and the usual routine examination of constants and properties, become manifest in a systematic fractional distillation.

The pine-oil type of constituents, such as terpene alcohols, phenols, and phenolic ethers, characterizes the high-boiling portion of steam-distilled wood turpentine. With the possible exception of traces of phenols, these are absent in gum spirits. Together with the presence of benzaldehyde and monocyclic hydrocarbons in this turpentine, these constitute striking and characteristic differences between it and gum spirits.

Several complete fractional distillation assemblies suitable for work in vacuum, together with pressure-control apparatus, are described.

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