The chlorine compounds made thus far are oils, no matter how much or how little chlorine has entered the compound. These oils are difficult to purify inasmuch as all of them decompose before the boiling-point is reached. We have had several compounds in hand but have as yet been unable to purify them. On the contrary both firpene and pinene when first converted into the hydrochlorides, form crystalline compounds of chlorine, the melting-point rising with the increase of chlorine until the decachlor compound is reached. Substitution products from these various chlorides are now in preparation.

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THE PITCH AND THE TERPENES OF THE NORWAY PINE AND THE DOUGLAS FIR.

BY G. B. FRANKFORTER.

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PRELIMINARY.

IT HAS been known for several years that the Norway pine and the Douglas fir are rich in the terpenes and resin. During a few days in the spring, the Norway pine seems almost as rich in pitch and turpentine as its southern sister species but the conditions are such that "boxing" as practised in the south is out of the question. A series of "boxing" experiments resulted in collecting a considerable quantity of pitch for chemical examination and incidentally proved the impracticability of this method in the north. Although boxing does not seem practicable in the north and west, so far as I have been able to determine, the reason seems to be largely due to climatic conditions so that if the pitch and turpentine of the north and west are to be utilized, other methods than the common method of the south must be employed.

At the present time, nothing has been done by the lumbering industries either in the north or west toward utilizing the large amount of waste pitchy material. As a result, enormous quantities of wood, too rich in pitch to be of any value to the lumbering industries are burned or thrown aside as worthless. The enormous profits in lumber have made it unnecessary for lumbering industries to look to any of the by-products in order to earn large dividends on capital invested. As a natural consequence

no effort has been made by these corporations to utilize the waste products, and to produce pitch and turpentine in the north.

At the present time, practically all the turpentine used in the north and west comes from the south. The small quantity made in the north and west is scarcely worth considering. The tars and resins likewise come almost wholly from the south and from foreign countries. The rapid increase in the demand for these products has increased the already rapid destruction of the forests of the south to such an extent that at the present rate of destruction it is only a matter of a few years when the southern forests will be completely destroyed. This condition of affairs makes it absolutely necessary that new and modern methods of orcharding should be resorted to at once and that new fields should be opened by utilizing the waste products regarded at present as worthless. The United States Department of Agriculture has already fully realized the present conditions and has sounded a warning through one of its officials, Dr. Charles H. Herty, who in an admirable paper on "Turpentine Orcharding," shows that the southern industry will disappear in the near future unless the present methods are radically changed. That new fields may be developed seems both essential and certain, but much pioneer work must yet be done before these new fields become producers of turpentine, colophonium and tar.

This work was begun several years ago with the object of studying the northern turpentine problem from the industrial standpoint and especially with the idea of comparing the products of these hitherto unknown species with those of the south from the chemical point of view. 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. Other important species will be taken up later.

Both of the above-named species contain considerable pitch but neither will yield an appreciable quantity by the "boxing" method of the south. Of these two species, the Norway comes the nearer to the southern pine, but the fir wood is on the whole a little richer in both resin and in turpentine than the Norway pine.

The Norway Pine.—The so-called "northern pine." or *Pinus resinosa*, is one of the important species of the north. It is one of the two great lumbering species of the northwestern states. The "white pine," the other species, is preferable for lumber on

account of the smaller amount of resin it contains, but the northern pine is sought after because the trees are, as a rule, larger. It very seldom happens that a tree is so full of pitch that it can not be used for lumber, although frequently trees are found to contain so much pitch that the lumber can only be used for certain purposes.

During the past twelve years the problem of recovering the pitch from the Norway pine has been studied. It was found that, 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 in the roots. It seemed, therefore, that the greater part of the pitch might, in some way, be extracted from the stumps and from the waste material in the lumbering business. This has been the prime object of the experiments which are given below.

So far as could be ascertained, the northern pine had not been studied when this work was begun several years ago. Professor Henry Trimble, in a monograph on the pine family, briefly refers to one of the above-named species but no systematic work was done on it further than the study of the twigs and needles together with a brief examination of the wood itself. Nothing definite was known either of the amount of pitch in the wood or of the amount of turpentine in the pitch. Through kindness of the Weyerhauser Lumber Company,[1] the writer was able to obtain a quantity of water-white pitch just as it came from the trees by the "boxing process." This and the pitch obtained from the stumps and other waste material have been examined. The pitch from the stumps was recovered by extraction, by steam distillation and by slow destructive distillation. From these experiments, it is evident that in the near future, these waste products will be utilized, not only in the production of the turpentine but also of tar and other by-products.

Among the problems to be solved were, first the amount of colophonium and turpentine present in the various grades of wood, and second a method for the saving of these products.

That the exact amount of pitch might be ascertained, a large number of determinations were made on the various samples of wood, ranging from the richest to the poorest in pitch. Various

[1] I am especially indebted to Mrs. J. R. Jewett, through whose influence the first Norway pitch was collected in any quantity.

methods were used in the extraction. The following numbers are averages of several determinations each:

Lean wood gave an average of 6.2 per cent. of pitch.

Average wood gave an average of 8.6 per cent. of pitch.

Stumps gave an average of 19.4 per cent. of pitch.

Pitchy wood gave 39.1 per cent. of pitch.

Very pitchy wood gave 42.6 per cent. of pitch.

Properties of Norway Pitch.—Norway pitch obtained from the trees by boxing is colorless and mobile while that obtained from the wood by extraction with the common solvents is slightly colored, otherwise their properties are identical.

Specific gravity of Norway pitch at 20°, 0.8137.

Index of refraction, 1.47869.

Optical activity at 20° is $(\alpha)_D = +4°$.

The pitch as obtained by the above methods of extraction contains about one-fifth of its weight of turpentine, the remainder being colophonium or resin with a very small quantity of water. An average of five determinations gave the following:

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

When exposed to the air the pitch loses turpentine so that after a month or two it becomes a semisolid or solid, depending upon the amount of turpentine remaining.

The colophonium has already been studied and the report on the work will follow this paper.

Fir Wood.—The Douglas fir is to the western states what the Norway pine is to the northern and the yellow pine is to the southern states. The species is interesting on account of the enormous size which it attains and on account of the wide variation in the amount of pitch which it contains. Owing to the high specific gravity of the pitchy wood, a series of specific gravity determinations was made on samples lean and rich in pitch, with the following results:

	Fir.	Norway.
Lean wood, sp. gr. at 20°, average of 5 tests.....	0.6074	0.6025
Medium wood, sp. gr. at 20°, average of 5 tests.....	0.6711	0.6432
Fat wood, sp. gr. at 20°, average of 5 tests.....	0.8225	0.7984
Very fat wood, sp. gr. at 20°, average of 5 tests.....	0.9456	0.9122
Roots (green), sp. gr. at 20°, average of 5 tests.....	0.9746	0.9321

Fir Pitch.—The Douglas fir likewise varies widely in the quantity of pitch. It frequently happens that fir logs are so pitchy

as to be worthless for lumber. They are therefore thrown away or burned. In order to determine the quantity of pitch in various grades of wood, a series of determinations was made by extracting with the various solvents and evaporating so as to avoid loss of the turpentine. The richest and the poorest samples of wood were selected for examination.

An average of five determinations in each of the samples given below, gave the following results:

Very lean wood gave 11.6 per cent. of pitch.

Lean wood gave 13.5 per cent. of pitch.

Medium wood gave 19.8 per cent. of pitch.

Rich wood gave 40.7 per cent. of pitch.

Very rich wood gave 42.4 per cent. of pitch.

Properties of Fir Pitch.—Fir pitch as it runs from the trees is a perfectly clear liquid varying somewhat in its properties. Usually it is water-white and quite mobile. On exposure to the air it changes its color and slowly becomes viscous. This change is due, as in the case of the Norway pitch, to loss of turpentine and to slow oxidation.

The water-white pitch was collected directly from the tree, placed in a closed vessel, so as to prevent oxidation, and kept in this condition until examined. On exposure to the air it was found to change. White pitch had the following properties: It is colorless with a peculiar aromatic odor.

Sp. gr. at 20°, 0.9821.

Index of refraction at 20°, 1.51745.

Optical activity $(\alpha)_D = -8.82$.

At a freezing temperature it is a solid, gradually changing until at 15° it is quite mobile. The amount of turpentine in the fir pitch was about 22 per cent., or the same as in the Norway pitch.

The Terpenes.—The terpenes from the Norway pine and the Douglas fir have been studied. They have been obtained from the pitch which had been recovered by "boxing" and from the pitch which had been extracted from the wood by the various solvents. In addition to these methods, they were obtained from the wood by destructive distillation. In each case it was found that the terpenes obtained by destructive distillation differed from those which were obtained from the wood and from the pitch by steam distillation or by extraction from the wood. Those

obtained from the wood by steam distillation and extraction seem to be of simpler nature than those obtained by destructive distillation. The terpenes obtained by destructive distillation have a wide variation of boiling-points, ranging from 149° to 208°. Even the properties of the compounds of the same boiling-points seemed to have been changed during the process of destructive distillation. The following is a comparison of the two terpenes.

	Norway terpene.		Fir terpene.	
	Steam Dist.	Destructive Dist.	Steam Dist.	Destructive Dist.
Specific gravity at 20°	0 8636	0.8666	0.8621	0.8662
Boiling-point.....	153–154°	158–160°	153.5–154°	157–160°
Index of refraction at 20°...	1.47127	1.4716	1.47299	1.47246
Optical activity.....$(\alpha)_D$ =	+ 17.39	—7.56°	—47.2	—29.4°

These terpenes are now being studied.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON OILS AND EXTRACTS.

BY EDWARD MACKAY CHACE.

Received July 13, 1906.

THE detection of the adulteration of lemon oils and extracts is a problem that has long been disturbing those chemists who are engaged in food and drug analyses. Methods for the detection of the crude forms of adulterations have been devised and are in the main satisfactory. Unfortunately, as the lemon oil industry has developed, certain by-products have come into existence and in the effort to cheapen the cost, these products have been used to produce a grade of impure oil.

With the introduction of these oils the detection of factitious oils and extracts has become a more difficult matter. When the adulteration consisted in the addition of foreign substances such as turpentine or of the substitution of other oils for lemon oil, determinations of the physical constants of the sample and of the first fractions of its distillate were generally sufficient. Now, however, when it consists in varying the proportion of the constituents themselves, physical constants alone are not sufficient.

Lemon oil is composed of 90 per cent. *d*-limonene, 4 to 6 per cent. citral, the remainder being other aldehydes and oxygenated bodies.