added to 2.73 grams of freshly precipitated and well washed mercuric oxide (from 3.43 grams of mercuric chloride). gave no evidence of any reduction having taken place at the end of 24 hours. After working up in the usual way 0.92 gram of the unchanged acid was recovered.

LONG LEAF PINE OIL.

By J. E. Teeple.

Received January 2, 1908.

Long leaf pine oil, as its name indicates, is an oil derived from the *pinus palustris* or long leaf pine. Specifically, it is that particular pine oil which is obtained as a by-product in the extraction of turpentine from lightwood by means of steam. It merits our consideration here first because it is a new product commercially; second because of the great variety of uses which have been found for it; and third because its uniformity and the large quantities in which it can be furnished indicate that it will probably become a permanent source of valuable terpene derivatives.

The statements regarding long leaf pine oil given here refer only to the product made by steam distillation.[1] The rosin bath process and the destructive distillation systems, of course, give fractions of oil having more or less similar properties, but in the one case they are contaminated with products of rosin distillation and in the other case with creosote-like compounds.

Three years ago the sale of long leaf pine oil was almost negligible, and the greater portions of those fractions of the distillate which contained the oil were thrown away without purification. To-day the product is sold regularly in carload lots. As to its uses it has been found that it will dissolve any of the ordinary varnish gums cold, whereas in the usual methods of manufacturing varnishes the gums must be melted before they dissolve properly. This same solvent power makes it valuable in varnish works for washing filter cloths. It is likewise one of the best solvents for rubber. It can be added to a lacquer made from nitrocellulose dissolved in amyl acetate without precipitating the nitrocellulose. It is not of itself a rapid hard drying oil and so is often used in the coating of insulated cables. The high price of oil of camphor and the more stringent laws regarding the use of benzine have led to the substitution of pine oil almost exclusively for these two products in the manufacture of metal polishes. When properly refined it has a very pleasant odor which leads to its use by the essential oil trade in general and by soap makers in particular for perfuming cheaper soaps.

Regarding the composition of the long leaf pine oil, it has been generally

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[1] J. S. C. I., 26, 811.

understood and repeatedly stated during the last three years in what may be called the commercial literature, that its chief constituent is terpineol. In the scientific literature however, I can find only one single reference to its composition. Walker,[1] from its distillation and from its formation of a hydrochloride melting at about 50°, surmised that it might contain a terpineol. His experiments, however, were made on a small amount of material produced on a laboratory scale only.

The commercial long leaf oil, as it comes on the market, is either clear and water white, containing 3 or 4 per cent. of dissolved water, or it may have a very faint yellow color and be free from dissolved water. The specific gravity ranges from 0.935 to 0.947, depending on freedom from lower boiling terpenes. A good commercial product will begin distilling at about 206° to 210° and 75 per cent. of it will distil between the limits 211°–218°, and 50 per cent. of it between 213–217°. A sample having a density of 0.945 at 15.5° showed a specific rotation of about $[\alpha]_D^{20^\circ}$ —11°, and an index of refraction of N_D 1.4830. In fractional distillation of the oil the specific gravity of the various distillates rises regularly with increasing temperature, becoming steady at about 0.947 at 217°.

If the oil consists essentially of terpineol, $C_{10}H_{18}O$, it should be easy to convert it into terpin hydrate, $C_{10}H_{20}O_2+H_2O$, by the method of Tiemann, and Schmidt.[2] The conversion was found to proceed easily when the oil was treated with 5 per cent. sulphuric acid, either with or without admixture with benzene. If agitated continuously, the reaction is complete within 3 or 4 days. If, on the other hand, the mixture is allowed to stand quietly, the formation of terpin hydrate extends over several months and produces most beautiful large crystals, which, without recrystallizing, melt at 117–118°. When recrystallized from ethyl acetate they melt at 118°. Yield, about 60 per cent. of the theoretical. This forms such a simple, cheap and convenient method of making terpin hydrate that it will doubtless supersede the usual manufacture from turpentine, alcohol and nitric acid, and instead of terpin hydrate serving as raw material for the manufacture of terpineol, as heretofore, the reverse will be the case.

Terpineol Nitrosochloride. — This compound was made in the usual manner from amyl nitrite, glacial acetic acid and hydrochloric acid. The yield was good and the product, after crystallization from ethyl acetate, proved to be very stable. Melting point 101–103°.

Terpineol Nitropiperidide.—This compound was made from the nitrosochloride and piperidine according to Wallach's method. The once recrystallized product melted at 158–159° and formed well-shaped crystals from methyl alcohol.

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[1] Massachusetts Institute of Technology Bulletin, September, 1905.

[2] Ber., 28, 1781.

Terpineol nitranilide was made from the nitrosochloride and aniline dissolved in alcohol. On dilution of the reaction mixture with a little water good crystals of the nitranilide were obtained.

Dehydration Products.—Wallach[1] found that when 25 grams of terpineol were heated with dilute sulphuric acid, there resulted 16 cc. terpinene and cineol boiling at 177–180°, 4 cc. boiling at 181–185°, and 1.5 cc. boiling at 185–187°, containing terpinolene. This experiment was repeated, using a sample of long leaf pine oil, of which nearly the whole distilled at 216–218°. 100 grams of this oil heated for one hour with 400 cc. of dilute sulphuric acid (1 : 2) and then distilled with steam and dried over sodium, gave 85 cc. of oils volatile with steam. On redistillation the following fractions were obtained: 5 cc. at 165–175°, 56 cc. at 175–180°, 6 cc. at 181–185°, and 15 cc. at 186–192°. The largest fraction had a specific gravity of 0.860 and evidently consisted essentially of terpinene. It will be seen that these results agree quite closely with those obtained by Wallach from pure terpineol.

In conclusion, the specific gravity, index of refraction and boiling point of the long leaf pine oil, its absorption of bromine in quantity corresponding to a dibromide, the formation of a nitrosochloride, nitropiperidide and nitranilide, the formation of terpinene by dehydration and the easy conversion and large yield of terpin hydrate leave little doubt that the essential constituent of long leaf pine oil is a terpineol and is probably the optically active levo modification of α-terpineol (Δ'-*p*-menthenol(8)) boiling at 217–218°.

This seems to be the first recorded occurrence of terpineol in any member of the pine family. Even in this case it was obtained not from the living tree but from lightwood, *i. e.*, from portions of the tree which had been cut at least three years and were very resinous. It is the common belief of those familiar with lightwood that its resinous content increases regularly from the time it is cut from the tree or from the death of the tree. If any such action occurs the appearance of terpineol here would seem quite natural, as its formation from pinene requires only the addition of one molecule of water accompanied by splitting the tetra ring of pinene.

The investigation of this oil is being continued.

164 Front St., New York City,
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TRANSPARENT SOAP—A SUPERCOOLED SOLUTION.

By W. D. Richardson.

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The alkali-metal salts of the fatty acids—commonly called soaps—have been usually considered crystalloids by the older authorities and by others in recent years as colloids.[2]

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[1] Wallach, Ann., **230,** 225.

[2] Leimdorfer, Seifensied. Ztg. **1906,** Nos. 24-29; Merklen, Chem. Abs. **1907,** 2416; Lewkowitsch, J. Soc. Chem. Ind., **26,** 590 (1907).