Pine-Oil

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Introduction :—

ACCORDING to the National Formulary[1] "Pine-oil is a volatile oil composed chiefly of secondary and tertiary alcohols like terpineol, borneol and fenchol". Because of its ready availability at a low price, this one-time unwanted bye-product has found diverse uses in a number of industries. In fact the demand for pine-oil far exceeds the supply and as such attempts are made to prepare synthetic pine-oil. India imports 600 tons of pine-oil costing Rs. 13,64,000 mainly from the hard currency areas. As pine-oil could be obtained either directly or indirectly from pine trees it is of interest to know more about this material so that it could be produced from indigenous raw-materials.

Properties :—

Pine-oil is available in two grades, mainly distinguished by colour. Ordinary pine-oil has a pale yellow colour, while the superior quality is practically colourless. The more important properties of pine-oil, as per U.S. Federal Specifications[2] are as follows :—

Water content (% by wt.)	1.00	Maximum
Terpene alcohols (% by wt.)	65.00	Minimum
Specific Gravity, 15.5°	0.930 – 0.945	
Polymerisation Residue (% by vol.)	2.50	Maximum

Boiling range (% by volume) :—

Distillate below 185°	5.00	Maximum
Distillate below 200°	30.00	Maximum
Distillate below 225°	90.00	Minimum

The chemical composition of pine oil according to Pickett and Schantz[3] is as follows :—

(1) Terpene hydrocarbons	5—10%
(2) Berneol	5—10%
(3) Fenchyl alcohol	5—10%
(4) α Terpineol	50—60%
(5) Other terpineols	15—25%
(6) Terpene ether	5—10%
(7) Terpene ketones	2—00%

However Gravie[4] reports slightly different values for high-grade pine-oil.

(i) α Terpineol	68.5%
(ii) Methanols	4.2%
(iii) Fenchyl alcohol	8.0%
(iv) Borneol	9.0%
(v) Methyl chavicol (Phenol ether)	10.0%
(vi) Moisture	0.3%

The chemical composition of pine-oil is, of really secondary importance as the material is mainly employed because of its specific physical and physico-chemical properties. The surface tension and interfacial-tension (against water) are the two important properties.

Types of pine-oil :—

Three types of pine-oil are known, namely (i) Destructively distilled pine-oil (ii) Steam-distilled pine-oil (iii) Artificial or synthetic pine-oil.

(i) *Destructively distilled pine-oil :—*

Pine-stumps are subjected to destructive distillation and the volatile products coming over are collected. The volatiles contain appreciable amounts of tarry-materials and the product as such

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finds very little use. Steam-distillation of the product does give a superior product in low yields. The method however is of historical importance only, though small quantities are produced in isolated places both in this country and elsewhere.

(ii) *Steam-distilled pine-oil :—*

Steam-distilled pine-oil is obtained by subjecting pine-stumps to steam-distillation. An alternate method is to first extract the pine-stumps with low boiling petroleum hydrocarbon solvents, and subsequently subject the solvent-free extract to steam distillation. The method is perhaps the most important as commercial pine-oil at present is mainly obtained by this method. The yield, composition and the properties of pine-oil so obtained, however, are dependent on a number of factors. Thus the species of pine-trees, their age at the time of felling, the period the stumps remained as such in the ground, the weathering conditions, if any, prior to the chipping are all important factors that influence the quality of pine-oil. It is therefore not surprising that properties of pine-oil vary considerably and there is reason to belive that the usual pine-oils are not "Straight" products but are "Blends" of natural and "Synthetic" materials.

Synthetic pine-oil :—

Synthetic pine-oil is made from pinenes Many methods have been described in literature but in principle the process is one of hydration of pinenes to terpineol or its isomers. The hydration is carried out in two steps.

In the first step a dihydroxy derivative is formed by treatment with sulphuric acid or similar reagent and in the second step, the dihydroxy product is converted into a mono-unsaturated, monohydroxy derivative. The composition of the original pinenes will naturally determine the composition of the pine-oil.

Production in India :—

As far it is known pine-oil is not being produced in this country. Possibly one of the reasons is that Indian-pines from which the oleo-resins are obtained belong to a different species from the American and French pines. Secondly pine-forests are generally situated in the sub-Himalayan region of the country, there being no attempts to cultivate pine-trees on plantation basis ;—the basic raw-material namely the pine-stumps, are not readily accessible. Also if the composition of Indian turpentine is to be taken as a criterian for the pinene content of the pine-stumps then it is extremely unlikely that the product from Indian pine-stumps will be anywhere near that obtained from American pine-stumps. Indian turpentine contains only 35% pinenes, the rest being Δ^3 and Δ^4 carenes and longiofolene. Thus even if it is possible to collect pine-stumps, any oil recovered from them is unlikely to have properties comparable to imported pine-oil. It may perhaps be more prudent and economical to use turpentine as a raw-material for which, in any case there is little or no use at present.

The first step naturally will be to fractionate turpentine to get a product with at least 80% pinenes which could be subsequently converted into synthetic pine-oil. No information is available on the recovery of pinene from Indian-turpentine, but it is known that the problem is under investigation at one of the Research-Institutes in the country. So far as conversion of pines to pine-oil is concerned Gulati and co-workers[5] have described a simple process which consists essentially of hydration of pinenes emulsfied with glue, using 28.5% sulphuric acid and subsequently dehydrating the dihydroxy product to a monohydroxy derivative with dilute sulphuric acid. Yields of the order of 77% have been claimed but the properties of pine-oil so prepared are not recorded.

probably because the investigators' main aim was to prepare terpineol.

Uses :—

Pine-oil as such finds uses in a large number of industries and it is also a basic raw-material for the production of certain chemicals, quite a few of them finding an important place in perfumery. The major use of pine-oil is in the metallurgical industries where it is employed as a frothing agent in the benefication of metalliferous ores. With the emphasis now on upgrading of ores with low metal content the demand for pine-oil is on the increase. Next only to use as a froth-flotation agent pine-oil finds an important application in the textile industry. Practically every aspect of wet-processing of fibres or fabrics—be they cotton, rayon or silk—employ pine-oil at some stage or the other. Other uses for pine-oil are as an auxiliary in laundry-detergents, in toilet and other soaps, as a disinfectant, auxiliary in dyeing and finishing of leather, in various types of polishes such as metal, automobile, furniture etc.

Pine-oil is also an important raw-material for the preparation of many terpene chemicals. Thus α-terpineol can be readily separated by fractional crystallization. It should be pointed out that the "α-terpineol" so obtained is different from the "β-terpineol" which is used in perfumery. The latter, however, can be readily prepared from α-terpineol by isomerisation.

From the mother-liquor, after the removal of α-terpineol crystals, a number of other bye-products could be obtained by fractional-distillation, the more important being methyl-chavicol, anethol, borneol and fenchol. The last two products can be oxidised or rather dehydrogenated to the corresponding ketones by heating under reflux in the presence of 2% by weight of nickel or copper carbonate or a mixture of the two for several hours. Small quantities of camphor may also be formed simultaneously.

The pine-oil is an important material and is essential for the development and maintenance of the metallurgical and allied industries, textile industry and the soap and the cosmetics. In view of the fact that the raw materials required for its production are readily available and the finished product has a well-established market, the production of pine-oil should prove to be an economically attractive proposition and it is gratifying to note that the N.R.D.C. has a project under active consideration.

References :

1. Pine-oil, United States Dispensary, 24th Edition, p. 890.
2. Guenther, E., "Essential Oils" 1952, VI, 298.
3. Picket and Schantz, Ind. Eng. Chem., 1934, 26, 709.
4. Gravie, Chemical Industries, 384.
5. Gulati and co-workers, Ed., 1944, 62.