OLEORESIN ENHANCEMENT IN THE LIVING PINE TREE

AN ALTERNATE SOURCE OF ENERGY AND REPLACEMENT FOR PETROLEUM DERIVATIVES

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The naval stores industry is the oldest American industry with the first export shipment in 1608 consisting primarily of naval stores products. Throughout our history the pine tree has played a prominent role. The first coins struck by the colonists were pine tree shillings and the early American flags at the time of the Revolutionary War pictured the pine tree. The tall pine trees furnished masts for the ships and tar for caulking ships, treating ropes, and waterproofing tarpaulins - from whence comes the term "naval stores."

In the early colonial days, New England was the primary source of naval stores but as the trees were cut out and conservation legislation was enacted, the industry moved south and by the latter nineteenth century and early twentieth century, large acreages of timber lands were used for naval stores production with the then-familiar scarred "catface" and rosin cup on each tree. This method of collecting turpentine and rosin was referred to as the gum naval stores industry.

As labor costs increased, gum naval stores became less and less profitable, and about the same time the wood naval stores industry began to grow. The wood naval stores industry is based on the solvent extraction of turpentine and rosin from virgin pine stumps. As these pine stumps are used up and since second growth stumps do not yield quantities large enough to make the operation economically feasible, there has been a slow decline in this operation over the past 25 years.

Fortunately for the naval stores industry, as each process has declined in importance, a new process has become available. The pulp and paper industry has found the Southern pine to be ideally suited to make paper and as more and more paper mills were built, by-products of crude sulfate turpentine and crude tall oil have made up for the decline in the wood naval stores industry. It is interesting to note that, except for war years, the quantity of naval stores produced by all methods has been fairly constant since 1900.

Crude sulfate turpentine is produced in vapor stream of the wood digestion step in the paper mill and although it has the characteristic paper mill odor, this is easily removed in the first distillation step. It is a versatile raw material with its components going into a wide variety of products including cleaners, disinfectants, solvents, insecticides, flavoring and perfumery chemicals, vitamins, resins, and a large number of essential oils such as lemon, lime, spearmint, peppermint, black pepper, nutmeg, and cinnamon oils.

Crude tall oil is made by acidulating tall oil soap from the black liquor evaporation step in the chemical recovery section of the paper mill. This crude tall oil is fractionated into tall oil fatty acids, tall oil rosin, and distilled tall oil. These products find wide use in such products as resins, synthetic lubricants, plasticizers, detergents, soaps, surfactants, pharmaceuticals, coatings, paper size, paints, varnishes, printing inks, floor tiles, fungicides, flotation agents, and shoe polish.

Annual production of crude sulfate turpentine is about 30,000,000 gallons and annual production of crude tall oil is about 750,000 tons.

Since these two by-products are so versatile and can be used in so many applications, a lot of study has been given to methods of increasing their recovery. Many improvements have been made in the paper mill, but there has been some negative effects also such as outside chip storage, continuous digesters, and increased usage of hardwoods.

Another method of increasing by-product recovery is to increase the by-product contents in the living tree. For many years the gum naval stores industry has been based on the slashing or wounding the living pine tree and collecting the oleoresin (containing rosin and turpentine) in small buckets below the wound. Sulfuric acid is applied to the open slash to stimulate the flow of the oleoresin, and several years ago the USDA Forest Service Laboratory in Olustee made an extensive study to find a substitute or improvement for sulfuric acid. Not much success was noted until about four years ago when the trees were cut. It was observed that the trees treated with an 8% paraquat solution showed a lighterwood formation as high as 30 feet above the area treated. Only trees treated with paraquat and diquat showed this lightering. Both paraquat and diquat are herbicides developed by Imperial Chemical Industries and distributed by Chevron Chemical Company in the U. S. Both have been used for years to kill off unwanted plant growth around citrus trees, potato fields and cotton fields. Although quite poisonous in their concentrated form, they are rendered harmless upon contact with the soil, making them very useful weed control chemicals.

This discovery prompted the formation of a cooperative study and experimental group known as the Lightwood Research Coordinating Council made up of paper mills, by-product processors, university and government personnel. Annual meetings have been held for the past four years and a wide variety of reports have been given on such subjects as methods of treatment; various chemicals used; amount of enhancement versus time, species of tree, season and degree of treatment; analytical methods used; toxicity; physiological effects within the tree; insect activity and control and the feasibility of using oleoresin from pines as a substitute for fuels and petrochemicals. A brief summary of some of these topics follows.

The early tests showed that only paraquat and diquat induced oleoresin enhancement in pine trees. Several methods have been used to get the chemical into the tree such as cutting a narrow section of the bark away for 1/3 to 1/2 of the circumference (known as "streaking") and then spraying the chemical on the exposed xylem layer, using a high pressure needle injection, gashing with a Hypo-Hatchet and various types of tree injectors and drilling one or more holes into the tree at various levels. Various automated methods have been suggested such as a tractor pulled device, a modified chain saw streaking tool, a modified grease gun and a portable gasoline driven injector. A large number of chemicals were tested with only paraquat and diquat showing the greatest enhancement. A lesser increase was found using Ethrel (2-chloroethyl phosphonic acid) and a few of the amines. The increase of oleoresin starts at the point of treatment and moves inward radially to the center and upward in the tree at a rate of about one foot per month. About 40% of the resin soaked volume is oleoresin. The maximum amount in the tree occurs about 15 months after treatment. Ethrel added to paraquat or diquat appears to act as a synergist. Depending on species of tree and type of treatment, the turpentine increase was about four times and the rosin increase was about three times that of untreated trees. The components of turpentine that increased the most percentagewise were β-pinene and β-phellandrene and rosin acids showed a larger percentage increase than fatty acids.

One problem encountered with the physical wounding of the tree was an increase of insect attacks. There were correlations between the degree of attack and the type of treatment and the concentration of chemical used. In some cases the number of dead and dying trees forced changes in the testing program. Various types of insecticides were used as well as insect repellents and attractants with relatively little success. Recent tests have been made using the treatment chemicals mixed with various penetrants and surfactants and then sprayed on the bark of the tree. This type of treatment does solve the insect problem and although it is too early to make a good comparison on the increase in oleoresin content, this does appear to be less than that in the methods that wound the tree.

Three large scale mill trials have been made using various percentages of paraquat treated wood. In all of these trials, there were no problems encountered in handling, chipping and pulping the wood. Some additional foaming was encountered in the washing step, as was to be expected, but this caused no problems. The additional by-products recovered makes the use of treated wood a profitable venture for the paper mills.

In the past, the quantity of rosin and turpentine produced has not been large enough to warrant attention as a petrochemical substitute. However, the possibility of increased amounts of oleoresin as a result of chemical treatment of trees has caused private industry and the government to reconsider the substitution of oleoresin for petrochemicals. This would only represent a small percentage of the total amount of petrochemicals produced and at the present time it is not economical to substitute oleoresins for many of the petrochemicals. Oleoresins can be used in many of the following petrochemical areas: resins, urethane foams, synthetic lubricants, mellitic acids, adhesives, terephthalic acid for polyester fibers and isoprene.

Turpentine is suitable for use as a fuel, although at the present time it is not economically feasible. The energy content of a gallon of turpentine is 130,000 to 140,000 Btu's whereas a gallon of gasoline is in the 120,000 to 130,000 Btu range. If all of the turpentine produced were substituted for gasoline, at the present usage this would be about 0.1% of gasoline consumption. A private research organization has applied for a patent to replace gasoline with turpentine as a motor fuel, claiming high road mileage.

In conclusion, I would like to point out that, even though the naval stores industry is America's oldest industry, there are lots of new developments in it and as a renewable resource we can expect even newer developments in the future.