WOOD CHEMICALS, A FLORIDA INDUSTRY

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ABSTRACT

The production of wood chemicals, also known as naval stores, is an industry of great importance in Florida. In fact, Jacksonville and Panama City feature some of the largest wood chemicals fractionation plants in the world.

In former days, the naval stores industry was primarily based on tapping live pine trees and collecting the resin. This resin would then be distilled into gum turpentine and gum rosin. At the present time, however, the industry depends on sulfate (kraft) pulp mills as a source of raw materials. A modern sulfate pulp mill will produce crude sulfate turpentine and tall oil as by-products. These two materials are then subject to purification and fractionation for the production of various terpene chemicals, fatty acids, and rosin.

This paper will attempt to survey the history of the industry, its impact on the economy of Florida, and the present state of its technology.

History of Naval Stores

The naval stores industry got started very early in the history of Florida and the U.S. The Spaniards were aware of the tar-yielding trees growing profusely in Florida. In fact in the year 1539, the expedition of Hernan de Soto used tar to pitch (water-proof) the ships that were used to take 300 men from Florida to Mexico. The chronicle of the ill-fated de Soto expedition describes, for the first time, the production and use of naval stores in North America. However, the actual start of the naval stores industry in America was due to England's need for naval stores to keep their navy and merchant vessels afloat, independent from the European countries. This need, although not as romantic as the search for gold, ranked high as an incentive for developing the new land.

After an early start in Virginia and New England, the industry moved to the South. Some of the early settlers found that southern pines (which were available in great abundance), unlike the pine of the north, exuded large quantities of gum which could be collected and make into tar, pitch, and turpentine.

A system of cutting a cup into the base of the tree, called a box, was developed to receive the oozing gum. Strips of bark above the box were removed periodically to keep the gum flowing. This method was used up to the 20th century, although very destructive and leading to conservation legislation when it became apparent that the forests were not inexhaustible.

While the tapping of live pine trees still goes on in the South as well as in many parts of the world, it was not until the advent of the sulfate (kraft) pulp process that the modern wood chemicals industry began. The pulping of coniferous trees (pine, fir, juniper, spruce) produces a steady and reliable stream of by-products used as feed materials in the modern wood chemicals industry. Due to the fact that the various southern pine varieties (Pinus palustris, Pinus taeda, Pinus elliottii, Pinus echinata) yield the greatest amount of turpentine and tall oil, the greatest concentration of wood chemicals and naval stores manufacturing operations in the world is in the South and particularly in northern Florida.

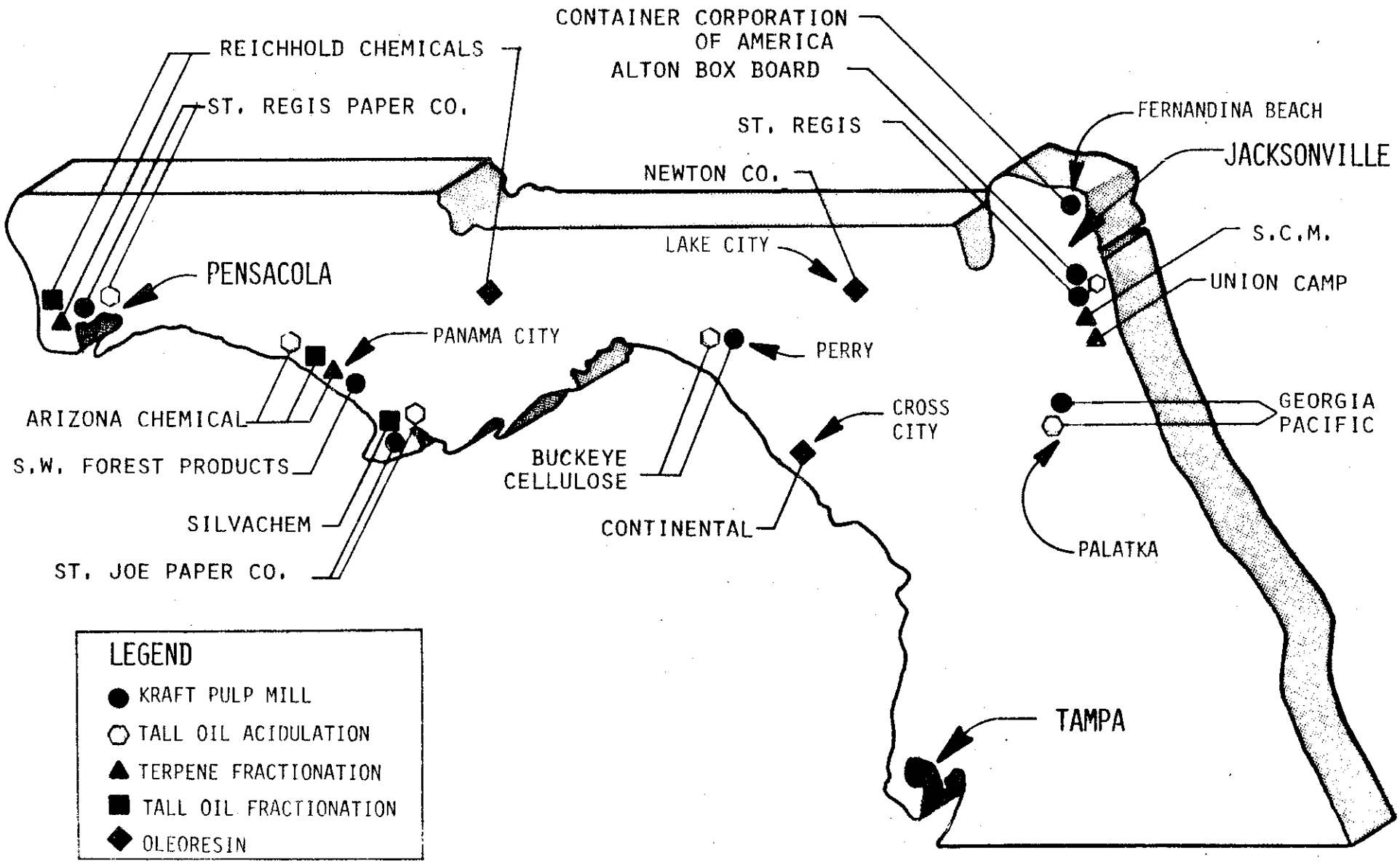
One of the leaders of the industry is Arizona Chemical which in 1949 brought on stream in Panama City the world's first tall oil fractionation plant specifically

designed to produce high quality tall oil fatty acids. Today Arizona Chemical operates a chemical complex in Panama City for the production of terpene and tall oil derivatives. Another leader in the naval stores industry is Union Camp Corporation. Their present Jacksonville facility dates back to 1935 when Nelio Rosin Company built a plant for the production of rosin. A terpene plant was built in 1962 which has undergone continuous growth ever since. The Jacksonville plant became part of the Union Camp organization in 1964. In conjuntion with their Savannah plant, Union Camp's wood-based chemical operations are the largest totally owned by any firm in the forest products industry today.

Other companies also maintain naval stores and wood chemical operations in Florida. Among the largest are S.C.M. (Glidden Division) in Jacksonville, Silvachem in Port St. Joe, and Reichhold Chemicals in Pensacola. In addition, most sulfate pulp mills have tall oil acidulation facilities on their premises with the most modern being Georgia Pacific's in Palatka.

The attached map indicates the location and type of wood chemical manufacturing sites in Florida.

WOOD CHEMICALS MANUFACTURING SITES
IN FLORIDA



Source of Raw Materials

Pine tress are the starting point in the production of pulp, paper, and all the derived wood chemicals such as terpenes and tall oil. The trees are felled, sawed into lengths, and shipped to the pulp mill where thousands of cords of wood are stored in huge wood yards. The various sections of the wood yard are filled and emptied in rotation. This maintains the maximum amount of pulp-wood storage with minimum, uniform storage time, thereby insuring both quality and yield of chemical and paper products.

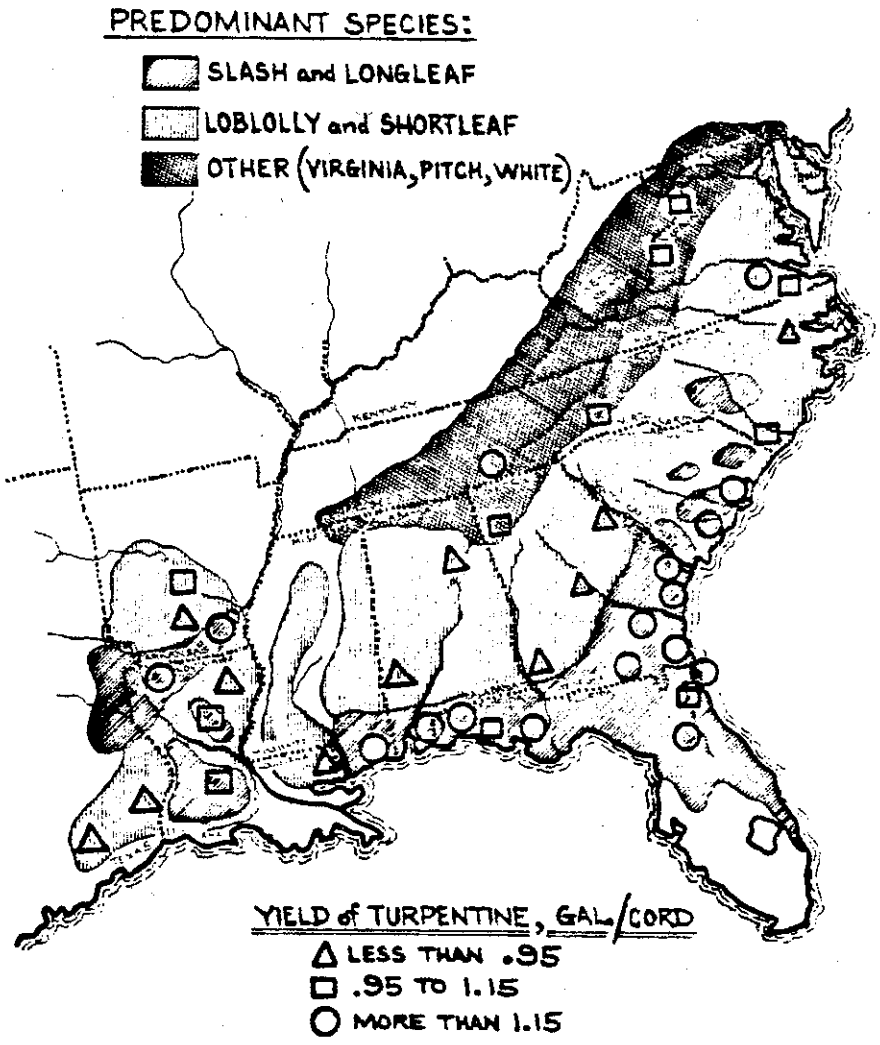
From the wood yard, the logs are transported to the debarking drums. The drums are huge open-end cylinders lined with steel bars. As the drums revolve, the logs tumble against each other, loosening the bark by friction. The logs are then reduced to chips by giant tool steel knives revolving at high speed. Quality control requires that chips be screened to uniform size to insure processing quality. Oversize chips are reprocessed. Tiny chips and sawdust are burned as fuel. Chips are regularly analyzed for size, moisture content, and density.

The chips are then conveyed to storage bins which feed directly into the digesters. Cooking liquor (a carefully controlled solution of sodium sulfide and sodium hydroxide) is added and the chips are cooked under pressure for hours. During the cook, the digesters are vented at regular intervals. The released gases contain crude sulfate turpentine which is condensed and sent to the refinery.

After cooking is completed, the pulp is blown from the digester; and a sample is tested to determine the amount of lignin remaining. Spent chemicals and dissolved lignin are removed by washing the pulp. From this point, the pulp is further processed into paper, paperboard, and converted products. The spent chemicals (black liquor) are processed to reclaim their chemical content.

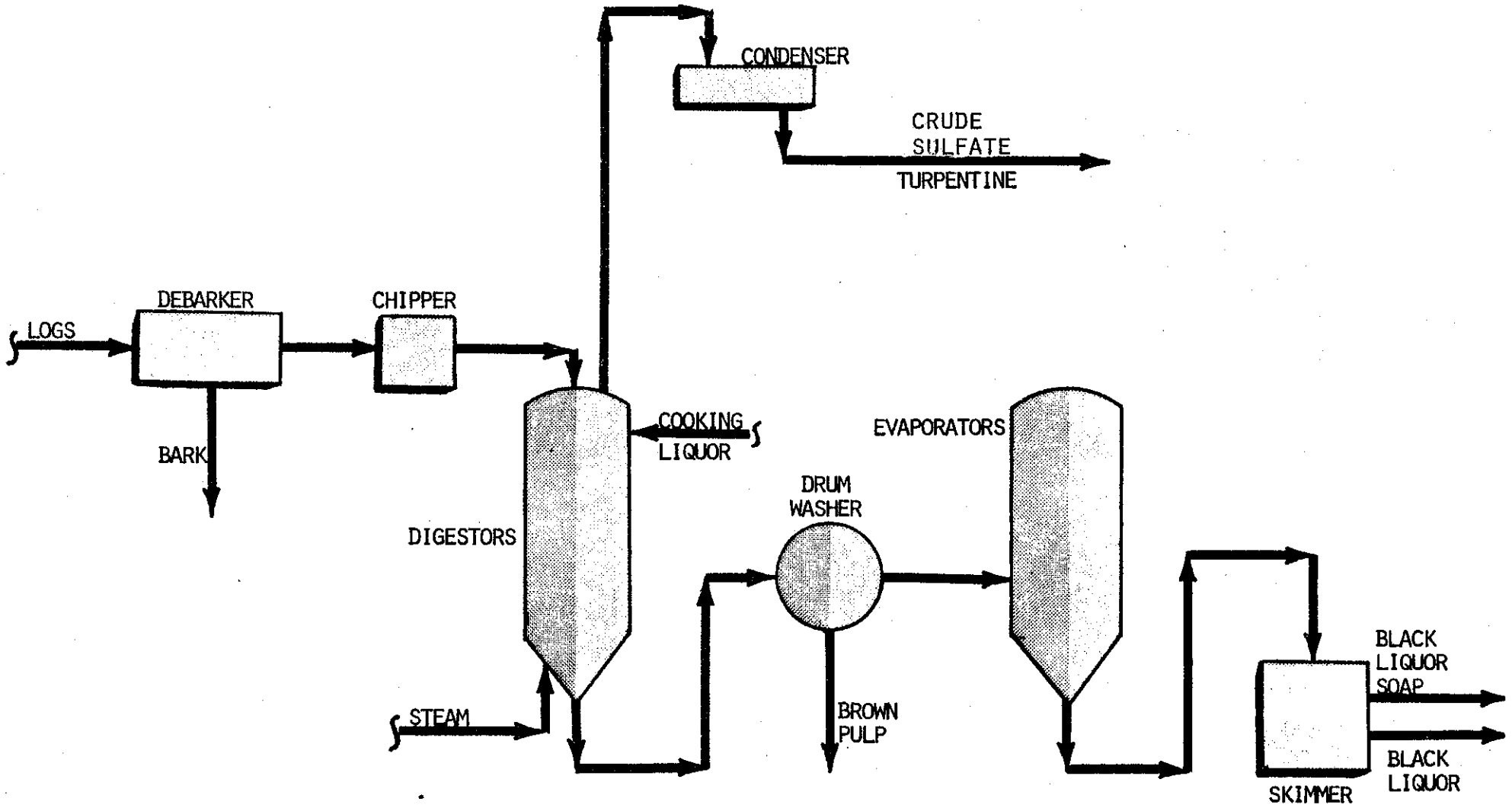
The first step in chemical recovery from black liquor is the removal of water in multiple stage evaporators. After partial evaporation, the black liquor is allowed to settle in tanks, and the soap formed by the fatty and rosin acids content float to the top. This soap is pumped off as "black-liquor skimmings". The rest of the liquor is further evaporated and burned to recover chemical content and for fuel value. The black liquor skimmings are sent to the tall oil acidulation plant for conversion into crude tall oil.

The attached map illustrates the predominant pine species which are used in sulfate pulp mills in the South. The diagram shows the simplified operation of a typical sulfate pulp mill.



Credit: Sulfate Turpentine Recovery, Pulp Chemicals Association, Page 127.

TYPICAL SULFATE PULPING PROCESS



Terpenes: Manufacture and End Products

The terms terpenes and turpentine have been used interchangable, however, there is a distinction betwen the two. Terpenes is the general class of volatile chemicals found in coniferous (evergreen) trees. Turpentine, a mixture of terpenes, is a product of commerce and is strictly defined by the Naval Stores Act of 1923 according to the method of production. Four types of turpentine are commercially available in the United States as defined by the Act:

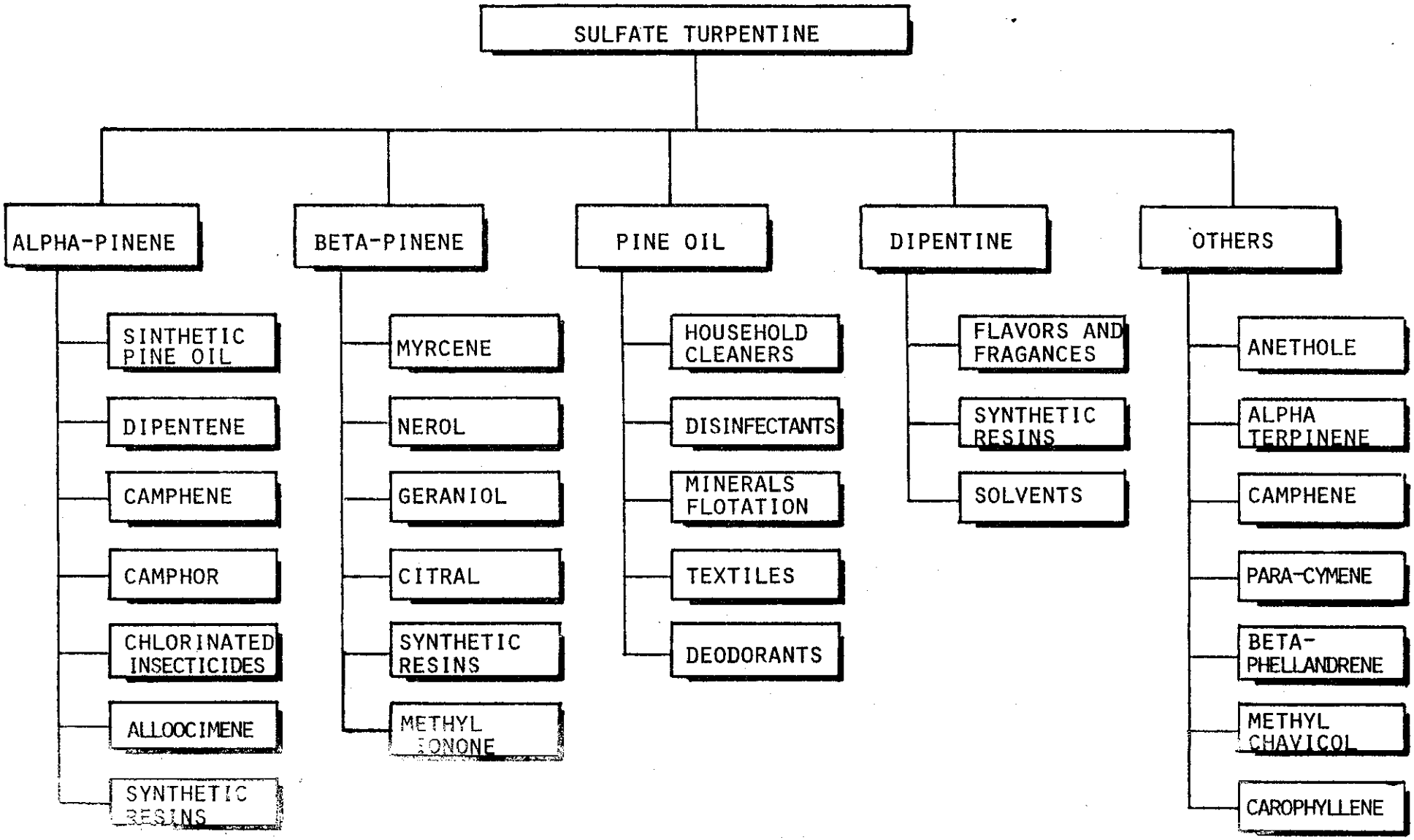
> Gum spirits of turpentine obtained by distillation of oleoresin (gum) from living trees.
>
> Steam-distilled wood turpentine produced by steam distillation of the oleoresin component of wood whether in the presence of the wood or after solvent extraction from the wood.
>
> Destructively distilled wood turpentine obtained by the destructive distillation (pyrolysis) of wood.
>
> Sulfate turpentine obtaned by the condensation of "off-gases" recovered in the sulfate (kraft) process of cooking wood pulp.

Chemically, terpenes are a mixture of unsaturated, bicyclic, hydrocarbons of the $C_{10}H_{16}$ series. Terpenes and other compounds such as the sesquiterpenes ($C_{15}H_{24}$) and the diterpenes ($C_{20}H_{32}$) are all members of a much larger class of substances with carbon skeletons made of isoprene units (C_5H_8) and occurring in both plants and animals. It is common to refer to all members of the group as isoprenoid compounds.

Commercially available sulfate turpentine is primarily composed of alpha-pinene and beta-pinene. A variety of minority components such as camphene, limonene, -3-carene, terpineol, and others are also present. The exact composition of turpentine depends not only on its method of isolation, but also on the species and geographic location of parent tree.

Crude turpentine produced in kraft pulp mills is brought by tank car to processing facilities such as Union Camp's in Jacksonville, Arizona Chemical's in Panama City,

or Reichhold Chemical's in Pensacola. The first step in the manufacturing consists in elimination of impurities such as water and odoriferous sulfur compounds. This is done by distillation. Other distillation steps will separate the major constituents such as alpha-pinene, beta-pinene, and pine oil, and pinenes into aromatic compounds which possess a very high market value. The attached chart will illustrate the tremendous range of derivatives produced from crude turpentine.


SULFATE TURPENTINE
ALPHA-PINENE
BETA-PINENE
PINE OIL
DIPENTINE
OTHERS
SINTHETIC PINE OIL
DIPENTENE
CAMPHENE
CAMPHOR
CHLORINATED INSECTICIDES
ALLOOCIMENE
SYNTHETIC RESINS
MYRCENE
NEROL
GERANIOL
CITRAL
SYNTHETIC RESINS
METHYL IONONE
HOUSEHOLD CLEANERS
DISINFECTANTS
MINERALS FLOTATION
TEXTILES
DEODORANTS
FLAVORS AND FRAGANCES
SYNTHETIC RESINS
SOLVENTS
ANETHOLE
ALPHA TERPINENE
CAMPHENE
PARA-CYMENE
BETA-PHELLANDRENE
METHYL CHAVICOL
CAROPHYLLENE

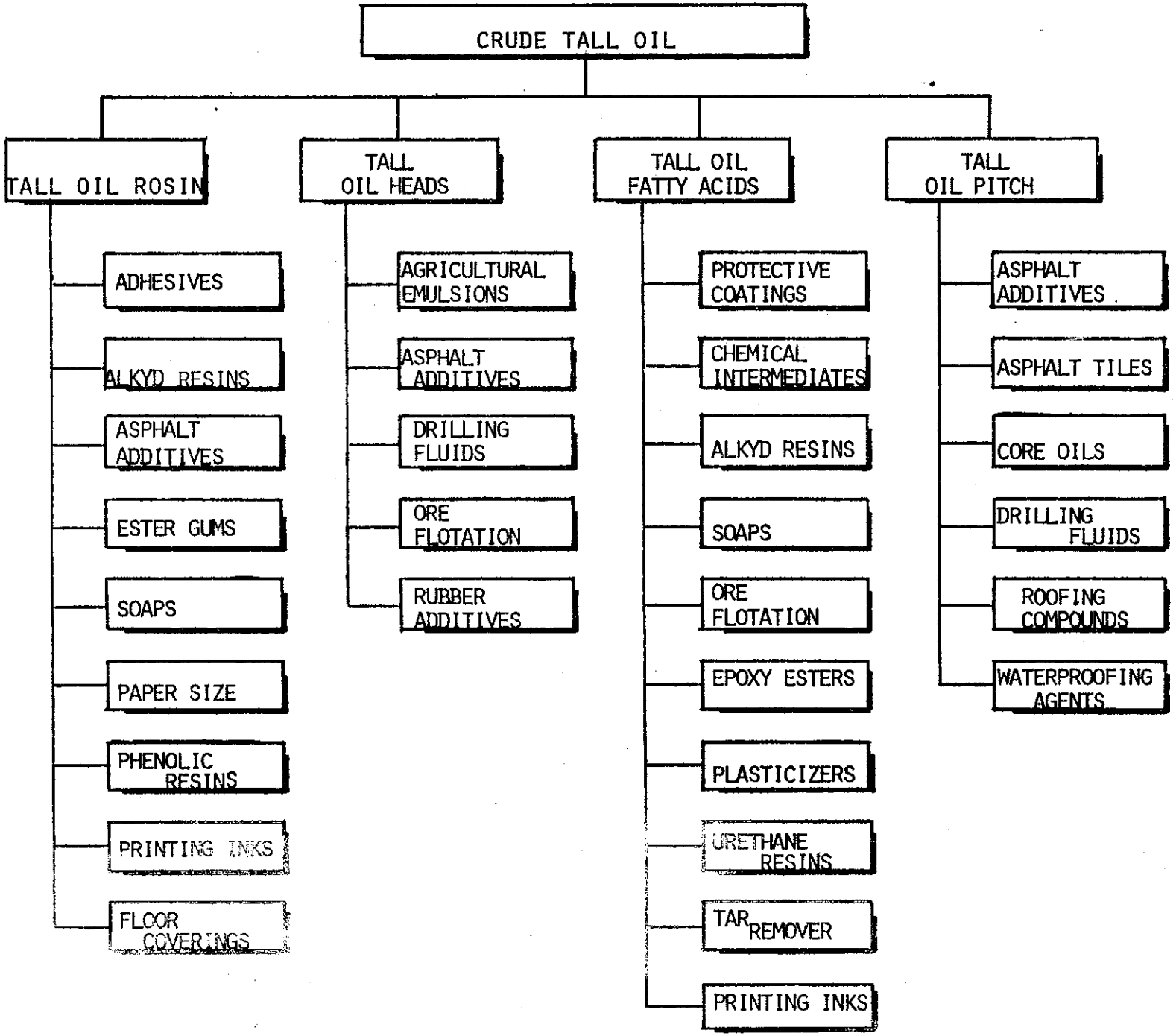
Tall Oil: Manufacture and End Products

The term "tall oil" is an anglicization of the Swedish work "tallolja" or "oil of the pine" -- the dark and soapy liquid by-product which results when pinewood is converted into pulp through a sulfate process. Although tall oil has been around since the late 1800's, it has only been since mid-century that tall oil by-products have been in ever-increasing demand. Where in the past tall oil was simply burned off as waste, today this by-product's main constituents (fatty acids and resins) are separated for use in the manufacture of such diverse products as soaps and detergents; protective coating, inks, and driers; sizing for paper; masonry products; and other applications formerly held by wood and/or gum rosins.

Black liquor skimmings (soap) recovered in the pulp mills comprise the raw material for crude tall oil. All soap skimmings are carefully analyzed for potential yield and are stored for several days to ensure separation of any remaining cooking liquor. In some cases, the soap is washed countercurrently with a sodium sulfate solution to further remove residual cooking liquor and lignin fibers. The soap is then acidulated with sulfuric acid at high temperature to form crude tall oil. The acidulation process can either be continuous or batch. The crude tall oil is then either centrifuged or allowed to settle to remove the excess acid and aqueous reaction products.

Most tall oil acidulation plants are located adjacent to the pulp mill. The crude tall oil is then sent to a central refining facility for conversion into finished products. This refining, which is usually done by fractional vacuum distillation, will remove the odoriferous compounds and will separate the unsaponifiable "heads", fatty acids, rosin acids, and pitch.

The various distillation components can be sold as final products or converted into derivatives by further chemical processing. The attached chart shows the major products obtained from tall oil.


CRUDE TALL OIL
TALL OIL ROSIN
TALL OIL HEADS
TALL OIL FATTY ACIDS
TALL OIL PITCH
ADHESIVES
ALKYD RESINS
ASPHALT ADDITIVES
ESTER GUMS
SOAPS
PAPER SIZE
PHENOLIC RESINS
PRINTING INKS
FLOOR COVERINGS
AGRICULTURAL EMULSIONS
ASPHALT ADDITIVES
DRILLING FLUIDS
ORE FLOTATION
RUBBER ADDITIVES
PROTECTIVE COATINGS
CHEMICAL INTERMEDIATES
ALKYD RESINS
SOAPS
ORE FLOTATION
EPOXY ESTERS
PLASTICIZERS
URETHANE RESINS
TAR REMOVER
PRINTING INKS
ASPHALT ADDITIVES
ASPHALT TILES
CORE OILS
DRILLING FLUIDS
ROOFING COMPOUNDS
WATERPROOFING AGENTS

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