RESEARCHES ON PINE CHEMICALS IN CHINA*

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Abstract: Abundant pine oleoresin resources are available in China. Its output is more than 500 kt/a, taking the first place in the world. Three development periods and main research units for pine chemicals industry in China are mentioned. The Section of Oleoresin Chemistry, the pine chemicals research center in China, in Institute of Chemical Industry of Forest Products, CAF, was founded in 1960. Re-processed products in pine chemicals, produced commercially, were reviewed. Today, China can produce nearly all reprocessed products available in the world, a total producing capacity more than 100 kt/a. Meanwhile, some new research results on polymeric materials, fine chemicals, new catalysts and perfumes, were reviewed. Some basic studies supported by Chinese Natural Science Foundation were also mentioned. Numerous valuable data for chemotaxonomy of pine species were obtained through systematic studies on chemical composition of oleoresin of nearly 60 pine species.

Key words: oleoresin; rosin; turpentine; pine chemicals

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中国松香松节油的研究概况

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摘 要: 中国有丰富的松脂资源,其产量 50 多万 t/a,居世界第一位。本文提到了中国松脂工业的 3 个发展阶段和主要的研究单位。于 1960 年成立的林产化学工业研究所松脂化学研究室是全国松香松节油研究中心。回顾了松香松节油再加工产品的生产情况,目前中国已基本上能生产世界上现有的再加工产品,其生产能力已达 10 多万 t/a。同时,也回顾了最近在高分子材料、精细化学品、新型催化剂和香料等方面的研究成果。最后提到了由国家自然科学基金多次资助的基础研究工作,通过对近 60 个松树树种的松脂化学成分的系统研究,得到了松树化学分类的许多有用证据。

关键词: 松脂; 松香; 松节油; 松脂化学品

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Biography: SONG Zhan-qian (1942-), male, Shanghailander, professor, Member of Chinese Academy of Engineering, Chief Scientist in Chinese Academy of Forestry. He has been engaged in study of chemical modification and application of forest products resources, especially in pine chemicals for the past 40 years.
宋湛谦(1942-),男,上海人,研究员,中国工程院院士,中国林科院首席科学家,40 年来一直从事于林产资源的化学改性和应用研究,特别是松脂资源的深加工利用研究。

1 Pine oleoresin resources and pine chemicals industry in China

1.1 Pine oleoresin resources

Abundant pine oleoresin resources are available in China. There are about 22 pine species and 10 varieties, nearly 30 pine species such as *Pinus elliottii*, *P. caribaea*, introduced from abroad since the 1970′s. The total area of pine forest amounts to 16 million hm^2, distributed mainly among Yunnan, Guangxi, Guangdong, Hubei, Fujian, Jiangxi, Hunan Provinces in China, in latitude N 22- 23°, longitude E 105- 122°.

The output of pine oleoresin in China is more than 700 kt/a, but the potential output is 1.5 million tons. *P. massoniana*, *P. yunnanensis*, *P. langbianensis and P. latteri* are main pine species for oleoresin production, generally 2.5- 5 kg/tree per year and 10 kg from *P. latteri*. Rosin and turpentine, the important industrial raw materials, can be obtained through processing of gum oleoresin.

There has been a long history of tapping pine oleoresin in China. Oleoresin was used as medicine for improving health and curing ulcers and sores 1 700 years ago. The technology of tapping oleoresin was illustrated in the 17th century. However, high grade rosin had to be imported from abroad because of primitive technology, lower output and inferior quality before 1950.

1.2 Pine chemicals industry

The pine chemicals industry in China was developed very rapidly over the past 50 years. In 1980, China became the biggest production country, the output exceeded the U S. Since then, it consistently took the first place in the world, with output of rosin more than 500 kt/a and that of turpentine about 80 kt/a.

Table 1 Output and export of rosin in China (1991- 2002) $\times 10^4$ t

years	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
output	32.0	42.0	43.0	32.0	38.5	37.0	52.8	39.0	40.0	39.5	42.0	51.0	58.2
export	22.8	22.0	23.0	19.0	24.5	23.4	29.6	30.4	26.1	28.1	30.2	35.6	35.9

The development of pine chemicals industry in China can be divided into three periods: before 1960, rosin and turpentine were produced as primary raw material; 1960- 1980, re-processed products of rosin and turpentine were developed; since 1990, deep-processed products are studied creatively.

Pine oil, terpineol, synthetic camphor, and borneol since the 1970′s, and hydrogenated rosin, disproportionated rosin and polymerizated rosin since the 1980′s have been exported successively. The processing technology of polyterpene resin was exported in 1998. Currently the output of reprocessed products is more than 100 kt/a, accounting for 20 % of rosin and 50 % of turpentine output. At the same time, rosin is also one of Chinese main export commodities, exporting more than 300 kt/a and accounting for 60 % of world trade. The pine chemicals industry has become the pillar of forest chemicals industry in China.

Table 2 Rosin output in China and the world

durations	output of world($kt \cdot a^{-1}$)	output of China($kt \cdot a^{-1}$)	percentage/%
1934- 1938	720	6	0.8
1956- 1960	913	90	9.9
1975- 1979	1000	271	27.1
1994- 1998	1100	404	36.7

2 Main research units

The Institute of Chemical Industry of Forest Products (ICIFP), Chinese Academy of Forestry, was founded in 1960 in Nanjing. It is the only specialized institute engaging in chemistry and utilization of forest products in China. National Quality Supervision and Inspection Station of Forest Chemicals, State Forestry

Administration, P. R. China, are set up at this institute. ICIFP comprises 8 research sections working in different fields of forest products resources. The Section of Oleoresin Chemistry is the pine chemicals research center in China, with more than 30 research scientists and technicians, as well as many Ms, PhD students and post-doctors. Its main research fields are: 1) tapping techniques and tools; 2) processing technology; 3) new re-processed and deep-processed products of rosin and turpentine; 4) composition of oleoresin and basic studies.

A lot of universities and institutes are engaged also in study of pine chemicals, such as Nanjing, North-east, Beijing and Central-south forestry universities; Guangxi Univ., Kunming Univ. of Technology & Science, Jiangxi Normal Univ. and Jiangxi Agricultural Univ.; Shanghai Organic Chemistry Institute and Guangzhou Chemistry Institute of Chinese Academy of Sciences; and some forestry research institutes in Sichuan, Guangdong, Guangxi and Fujian Provinces.

The above mentioned units conduct projects supported by National Natural Science Foundation, State Forestry Administration, P. R. China, provinces, as well as from pine chemicals enterprises.

3 Main research results

Before 1990, the document "Technical Instructions on Pine Oleoresin Production" was formulated. Different tapping methods for *P. massoniana* and several chemical stimulants were researched systematically. The waste sulfite pulping liquor provided enhanced effect on increasing oleoresin production. Some new tapping tools such as JHG-82 were also developed to increase labor efficiency and save cut face. The continuous distillation column system was for the first time designed and adopted by medium and large scale factories. A rectification column was designed successfully for producing high purity β-pinene (98%), used in perfumery. Nearly all re-processed products of rosin available in the world, such as polymerized rosin, disproportionated rosin, hydrogenated rosin, maleated rosin, rosin nitrile, rosin amine, rosin esters, etc., can be produced commercially in China. Pine oil, terpineol, synthetic camphor, borneol and polyterpene resins had been produced. Some perfumes were developed.

Since 1990, much of our researches have been devoted to finding practical ways of introducing functional groups into the molecules because the major problem in developing new uses for pine chemicals is the fact that it does not contain very useful functional groups, through which new products were developed as follows:

3.1 High polymeric materials

1) A new kind of epoxy resins, with excellent electrical insulating and mechanical properties and heat, weathering, and chemical resistances, could be made from maleopimaric acid and acrylpimaric acid, the addition products of rosin acid and dienophiles. After cured by organic anhydride or an amine, they could be used as coatings, injection molded articles, and outdoor materials. A curing agent for epoxy resins could also be made from rosin acid.

2) A polyimide or polyamideimiden with excellent heat, moisture and electrical insulating properties could be prepared by reacting maleopimaric acid with a diamine or a diisocyanate.

3) A rigid polyurethane foam with good heat resistance could be made from a diisocyanate and the polyesters, produced by esterification of maleopimaric acid with a dibasic alcohol.

4) Maleopimaric acid could be used as a substitute of phthalic anhydride for preparing fast-drying coating or water-soluble alkyd resins.

5) Unsaturated polyesters of low cost could be made by the cross-linkage between styrene and the reaction product of dimerized rosin acid, replacing phthalic anhydride, a dibasic alcohol and maleic anhydride.

6) Dehydroabietic acid metallic salt, which acts as a crystal-nucleating agent for crystalline polyolefins, could be made from disproportionated rosin.

7) Rosin can also be used for preparing coatings for road traffic lines. Turpentine can be used for polyurethane coatings and terpene-catechol resins.

3.2 Fine chemicals

1) A series of rosin-based surfactants, such as polyethoxylated rosin alcohol, polyethoxylated maleic rosin acid glycerol ester, polyethoxylated rosin-based imidazoline, with improved surface performance, which can correspond with those products made from fatty acid or fatty amine, were synthesized.

2) A non-toxic chemicals Synergist A_1, with acute oral toxicity LD_{50}> 10 000 mg/kg and acute dermal toxicity LD_{50}> 5 000 mg/kg, which was synthesized via isomerization of α-pinene, addition with maleic anhydride, and further modification in the presence of phase transfer catalyst, is being used in pyrethroids and carbamates insecticides with superior synergism results to replace piperonyl butoxide, imported from abroad.

3) Pinane hydroperoxide, catalyst of polymerization of butadiene and styrene, was prepared through oxidation and hydrogenation of pinane, which can be prepared from hydrogenated of turpentine. Recently, success was achieved by replacing oxygen with air for oxidation of pinane.

4) Today, synthesis of juvenile hormone analogs from turpentine have been studied.

5) A new modified rosin used in soldering flux with superior weldability, heat resistance and fluidity capability had been developed which is suitable for automatic welding with satisfactory results.

6) Many units engage in developing anion dispersion rosin size, cationic dispersion rosin size and neutral sizing of rosin esters for the development of paper-making industry.

7) The encapsulational material was prepared though rosin and tung oil can be used for coated urea. For coated urea with two coating layers and one outer sealing layer, urea dissolution percentage is 12.7 % for 24 h in water, and lapsed time in water is about 11 days when the accumulative dissolution percent reaches 80 %.

8) The natural antioxidant, pycnogenol, can be extracted from barks of *P. massoniana*, *Acacia mearnsii*.

9) Rosin is also used in Chinese medicine preparation and external medicine.

3.3 New catalysts

Raw earth, solid superacid, phase transfer and extra-fine catalysts applied in chemical reactions of rosin and turpentine are studied.

1) The qualified disproportionated rosin can be prepared by non-noble metal catalyst, which is prepared by hydrolysis of metal alkoxide.

2) Rare-earth metal oxides and organic tin compound are used as catalyst in rosin esterification.

3) Solid superacid or selective catalyst is used in isomerization of α-pinene, esterification of pine oil alcohol, and synthesis of *p*-cymene.

4) Phase transfer catalysts are used in hydration of pine oil alcohol.

5) Aluminum chloride supported on mesoporous molecular sieves as catalyst is used in polymerization of α-pinene.

3.4 Perfumes

1) Linalool, the intermediate of perfume and V_E, has been produced from α-pinene in the scale of 500 t/a.

2) Synthetic sandal serial products are synthesized through light-sensitive oxidization of α-pinene.

3) Perillartine from α-pinene and perilla alcohol from β-pinene are prepared.

4) β -caryophyllene, a perfume and a medicine, is extracted from by-products produced during hydration of longifolene.

3.5 Developing new process

1) An oleoresin stimulating agent containing rare-earth elements, sprayed one time each month, has been applied in a commercial scale, which can increase oleoresin 20 %- 30 % and decrease labor intensity 20 %- 30 %.

2) Emulsion series products were prepared by means of different rosin esters or rosin and used in emulsion adhesive to increase adhesion and to reduce cost.

3) Light-colored rosin with color lower than 1 (Garder) are produced commercially.

4) Some new technologies are developed and applied in production successively such as polymerization of rosin without acid residue, hydrogenation of rosin with higher tetrahydroabietic acid content, new processes of terpineol, synthetic camphor or borneol in order to reduce production cost.

3.6 Basic studies

A lot of projects were accomplished under support of National Natural Science Foundation.

1) ICIFP studied chemical constituents of oleoresin from 60 pine species in China systematically. Valuable data and results were obtained by GC-MS method, which indicated that the chemical composition of oleoresin from different pine species varies. Also some characteristic features in the composition of oleoresin from different origins do exist. The oleoresins from Subgen. Stroubs and Subgen. *Pinus* are obviously different in the contents of some diterpenes acids. The former contains a lot of lambertianic acid (> 10 %), while most species of the later do not contain such acid. The inherent chemical characteristics of oleoresins from the introduced pine tree in China are similar to that of the species in their native countries.

2) The mechanism of rosin crystallization and preventing methods were proposed. It was found that the amount of abietic-type resin acids in rosin from *P. massoniana* is as high as 75 %, which results in higher crystallization potential, and that controlling the isomerization process by temperature and time both in distillation and cooling can prevent the formation of rosin crystals.

3) By the study on rosin color, the Chinese optical standard of six-color-grade X, WW, WG, N, K and M are provided.

4) Some reaction mechanisms of rosin are explored. In polymerization of rosin, two main reactions——isomerization and polymerization of abietic-type resin acids do occurr, the rate of the former is much greater than that of the latter. A study on the disproportionation of rosin indicated that rosin from *P. massoniana* is disproportionated much easily than that from *P. elliottii*. The hydrogenation dynamics of rosin are also researched in detail.

Today, many scientists are devoted to developing fine chemicals from pine oleoresin in stead of petroleum raw materials. Scientists in China, as a country of the biggest output of pine oleoresin in the world, would like to strengthen co-operative researches with scientists from different countries for developing more new deep-processed naval stores products and making new contributions to the world economy.

References are omitted.