MASTER

FUEL PLANTATION RESEARCH

Progress Report

Jack Stubbs
Research Project Leader and
Principal Investigator

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Southeastern Forest Experiment Station
Aiken, South Carolina 29801

August 1977

PREPARED FOR THE
U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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ABSTRACT

This report summarizes research in chemical induction of lightwood that has resulted wholly or partially from the research agreement between the U. S. Energy Research and Development Administration (ERDA) and the USDA Forest Service, Southeastern Forest Experiment Station (SEFES). The report covers the period from October 10, 1975 through July, 1977. During this time the Southeastern Station received a total of \$501,000 from the Division of Biomedical and Environmental Research, ERDA. Four large-scale proof of concept studies have been installed that test five paraquat treatments on a total of 71,228 trees. This amounts to a volume of 10,580 cords and an area of 530 acres. This wood will be used in actual pulp mill and extraction plant runs to determine oleoresin recovery and possible processing problems. Nearly 3,000 wood samples have been collected to ascertain duration of treatment effects. Data collection procedures have been decided for the first pulp mill run, scheduled for January 1978. Results of complementary studies are also reported; most of these are concerned with optimization of paraquat application techniques and the effect of species differences on these methods. A large study was installed to field screen selected insecticides for insect pest control in lightwood operations, and interim results are presented. Dowco 214 (Reldon) proved to be an adequate substitute for BHC and 0.5% concentrations were as effective as 1%. In cooperation with the Forest Products Laboratory, ten northern and seven western conifer species were tested for their reaction to paraquat treatment. All members of

genus Pinus showed appreciable resin soaking but other coniferous genera did not. Feasibility of oleoresin substitution for petrochemicals was investigated through a grant to the Battelle Memorial Institute. Their report, which highlights several promising opportunities for expanded oleoresin use, is both summarized and presented in full. Selected research results attained through the sponsorship of the Lightwood Research Coordinating Council are given, involving a south-wide test with 20 cooperators. The bibliography lists 22 published papers made possible either wholly or partially by ERDA funds provided through this contract. Copies of all available reprints are included..

FUEL PLANTATION RESEARCH
Progress Report

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INTRODUCTION

The following report covers the period from October 10, 1975 through July 31, 1977. This joint venture in Fuel Plantation Research, which capitalizes on the discovery that paraquat-treated southern pines will produce lightwood, originated through the interest of Dr. J. L. Liverman (Director, Division of Biomedical and Environmental Research; or DBER, ERDA) that his Division sponsor some research directly related to energy matters. The USDA Forest Service management group (National Forest System, Southern Region; or R-8) at the Savannah River Plant (SRP) was contacted by DBER-HQ; in early 1975; they in turn queried the Southeastern Forest Experiment Station (also USDA Forest Service, referred to hereon as SEFES) concerning an appropriate research problem. During this period, Mr. Michael R. Lennartz was serving with the SRP Forest Service group as an Assistant Forest Manager for Research Coordination, on loan so to speak from the Southeastern Station for two years. Lennartz of course knew of the paraquat lightwood discovery, thus he and Dr. David Olson of SEFES prepared a preliminary proposal and sent it to DBER. They expressed interest, consequently through the SRP Forest Manager at that time, James Beavers, a meeting was arranged on April 14-15, 1975. This was attended by Dr. J. B. Hanson, DBER HQ; Dr. J. B. Hilmon, Director, SEFES and two members of his staff; Beavers and Lennartz of SRP Forestry; Dr. Todd Crawford of the Savannah River Laboratory (DuPont); Grover Smithwick of Savannah River Plant Operations (ERDA); and Dr. Duane Zinkel, Forest Products Laboratory (USDA Forest Service).

This meeting resulted in agreement on a research program comprised of four elements: 1) A large-scale test of lightering, amounting to Proof of

Concept experimentation (5 years, SRP); 2) Chemical determination of the oleoresins produced and their potential for industry; 3) Evaluation of need, economics, and technology; 4) Analysis of wood samples from lightwood studies. The Biomedical and Environmental Research Division (ERDA) decided to fund this effort with \$200,000 for FY-76. The 179 budget documents were written by Lennartz of SRP Forestry and submitted through their usual channel, Mr. Nat Stetson, Manager, Savannah River Plant.

The author, Jack Stubbs, agreed to be the Principal Investigator for the Southeastern Station on August 13, 1975. As time from his other duties permitted, he began to familiarize himself with lightwood and naval stores technology and information, also with the requirements of this new position. This included a week's trip to Florida, visiting our laboratory at Olustee where paraquat research was being conducted, contacting several industrial cooperators, and inspecting numerous field studies. During this time, Michael Lennartz returned to the Southeastern Station and was replaced as Research Coordinator (USFS, R-8, SRP) by another Station scientist, James McMinn. A draft for a Research Agreement, ERDA and the Station, was completed by McMinn in early September. Following ERDA review and approval, the contract agreement was formally signed by Nat Stetson, Manager, SRP, and J. B. Hilmon, Director, SEFES on October 10, 1975. On that day the Station began to spend ERDA supplied funds, and this is where our story actually begins.

EARLY EFFORTS AND OVERALL RESEARCH PLANNING

As part of his job as Principal Investigator, Stubbs was also made Research Project Leader of the group at Olustee that had made the paraquat discovery and were continuing research in that field. While in Florida he also cast his net for a person to fill the Principal Technician's position at SRP, and found a very satisfactory candidate.

The SRP location being in effect a new unit for the SEFES, we began with nothing whatever - no office, office furniture, typewriter, vehicles, field equipment, or staffing. In the interval from October 10, 1975 to January, 1976, much time and effort was spent filling these voids (certain GSA items ordered in December, 1975 have not yet appeared!; we of course went to other sources if necessary). At this time we also worked on wood sample analysis costs and problems, coordinated complementary entomological research, made first attempts to obtain industrial cooperators for the Proof of Concept studies, prepared a budget for the ERDA funds, wrote position descriptions and did other personnel matters for staffing, and also other items, especially a 16-page Prospectus. This informal Prospectus (see Appendix H) summarized our views of the research problem and how it ought to be attacked. Although it is now obsolete in detail, largely due to the realities of what industrial cooperators are able to accomplish in their various plants, the general approach and plans have remained valid. Two later formal documents take the place of this Prospectus; the first is a Research Proposal submitted through Mr. Stetson to the Division of Solar Energy and also DBER, ERDA, on December 14, 1976. This Research Proposal

summarizes current knowledge of the lightwood technology and pertaining commercial questions, outlines our research plans, progress to that date, gives organization, staffing, and physical facilities, includes a cost proposal, and other matters. A copy of this ponderous document is not included in this report, partially because of practical considerations of thickness and weight, but more especially because all prospective recipients of this report already have a copy. The second formal document is a Statement of Work and Milestone Plan ("perk chart") submitted to ERDA (Mr. Stetson; Solar Energy and DBER) on June 24, 1977. This in effect summarizes the research plans of the Proposal, and resulted from a draft prepared by Mrs. Anne S. Fege (Solar Energy) during a meeting attended by Dr. Roscoe F. Ward and Anne Fege (Solar Energy), Dr. Robert L. Watters (DBER), J. B. Hilmon and Stubbs (SEFES) on May 26, 1977. We have used the tasks as given in this Statement of Work as the core outline for this report (the Statement of Work and Milestone Plan is given below in the third major section, "Plan of Work and Accomplishments").

FUNDING AND STAFFING

FUNDS AUTHORIZED

In this section we will present the amounts of various funds authorized by ERDA to SEFES, the dates that SEFES actually received them, and how these funds were used. Additional cost data broken down by individual studies is given below under: "Achievements, Task I Studies".

Table 1. -- Fuel plantation research funds.

Fiscal Year	ERDA Source	Class of Funds	Amount (Thousands of dollars)	Date Received
FY-76	DBER	Operating	200	Oct. 10, 1975
	DBER	Capital Equip.	7	June 8, 1976
FY-76-77 trans.	DBER	Operating	50	Aug. 4, 1976
		Capital Equip.	29	Sept. 21, 1976
FY-77	DBER	Operating	200	Dec. 16, 1976
		Capital Equip.	15	April 6, 1977
FY-77	Solar Energy	Operating	113	Not yet received
		Capital Equip.	7	Not yet received < come 1 Sept. 77
Totals:		Operating	563	
		Capital Equip.	58	

USE OF FUNDS

Uses of operating funds for FY-76, FY-76-77 transition quarter, and FY-77 through July 1977 are given in tables 2, 3, and 4 which follow. The numbered tasks given in these tables are: I-Paraquat treatment of test plots (proof of concept experiments); II-Determination of oleoresin yields; III-Evaluation of mill trials; IV-Exploratory and complementary

studies. In table 2: The Battelle grant was for a study to investigate the feasibility of substituting oleoresin for various petrochemical uses; The grant to the Forest Products Laboratory (USDA Forest Service) was for research in lightening response of northern and western conifers; Both of these endeavors are covered in sections further on in this report. The wood analysis contract also listed in table 2 was for laboratory analyses of wood samples taken from Task I experiments. Quantitative analyses are made for resin acids (rosin), turpentine, and turpentine constituents. In table 3 a grant to Clemson University is included; this was to Dr. Lawrence E. Nix to sponsor research in the effects of paraquat treatment on tree growth, anatomical and histological changes. His final report is due August 31, 1978. Items purchased with capital equipment funds are listed in table 5.

Table 2.--Use of Operating Funds in FY-76 (DBER, \$200,000)

Research Group	Task I	Task II	Task III	Task IV	Insect Res.	Res. Adm.	Other	Totals
(Thousands of dollars)								
SEFES, SRP								
<u>Salaries</u>								
Princ. Invest.	7.9	2.1	-	4.2	0.5	6.3	-	21.0
Superv. Techn.	6.3	-	-	-	-	0.7	-	7.0
Secretary	0.4	-	-	-	-	0.4	-	0.8
								<u>28.8</u>
Temp. Salaries	2.2	-	-	-	-	-	-	<u>2.2</u>
								31.0
<u>Operating Expenses</u>								
Vehicles (USFS)	0.4	-	-	-	-	0.1	-	0.5
Supplies, Equip.	21.3	1.2	-	-	-	0.2	-	<u>22.7</u>
								23.2
<u>Travel</u>								
Scientists	1.9	0.2	-	0.3	-	0.2	-	2.6
Moving (2 people)	-	-	-	-	-	5.8	-	<u>5.8</u>
								8.4
Sub-totals, SRP	<u>40.4</u>	<u>3.5</u>	<u>-</u>	<u>4.5</u>	<u>0.5</u>	<u>13.7</u>	<u>-</u>	<u>62.6</u>
INSECT RESEARCH								
<u>Operating Expenses</u>								
Vehicles (USFS)	-	-	-	-	0.6	-	-	0.6
Supplies, Equip.	-	-	-	-	0.5	-	-	0.5
Travel	-	-	-	-	2.3	-	-	<u>2.3</u>
Sub-totals, Insects	-	-	-	-	<u>3.4</u>	-	-	<u>3.4</u>
BATTELLE GRANT	-	-	-	-	-	-	43.4	<u>43.4</u>
FOR.PROD.LAB.GRANT	-	-	-	-	-	-	25.0	<u>25.0</u>
WOOD ANAL.CONTRACT	-	59.0	-	-	-	-	-	<u>59.0</u>
STATION RES.ADM.	-	-	-	-	-	-	10.0	<u>10.0</u>
GRAND TOTALS	40.4	62.5	-	4.5	3.9	13.7	78.4	<u>203.1</u>

Table 3.--Use of Operating Funds in FY-76-77 (DBER, \$50,000)

Research Group	Task I	Task II	Task III	Task IV	Insect Res.	Res. Adm.	Other	Totals
(Thousands of dollars)								
SEFES, SRP								
<u>Salaries</u>								
Princ. Invest.	3.0	0.3	1.0	1.2	0.3	1.5	-	7.3
Superv. Techn.	3.2	-	-	-	-	0.4	-	3.6
Secretary	0.3	-	-	-	-	0.3	-	0.6
								<u>11.5</u>
Temp. Salaries	7.0	-	-	-	2.0	-	-	<u>9.0</u>
								20.5
<u>Operating Expenses</u>								
Vehicles (USFS)	1.3	-	-	-	-	-	-	1.3
Vehicles (ERDA)	2.2	-	-	-	-	-	-	2.2
Supplies & Equip.	6.0	1.4	-	-	-	-	-	<u>7.4</u>
								10.9
<u>Travel</u>								
Scientists	1.4	-	-	0.8	-	0.2	-	2.4
Sub-totals, SRP	<u>24.4</u>	<u>1.7</u>	<u>1.0</u>	<u>2.0</u>	<u>2.3</u>	<u>2.4</u>	<u>-</u>	<u>33.8</u>
INSECT RESEARCH								
<u>Operating Expenses</u>								
Vehicles (USFS)	-	-	-	-	0.2	-	-	0.2
Supplies, Equip.	-	-	-	-	0.7	-	-	0.7
Travel	-	-	-	-	0.5	-	-	0.5
Sub-totals, Insects	<u>-</u>	<u>-</u>	<u>-</u>	<u>-</u>	<u>1.4</u>	<u>-</u>	<u>-</u>	<u>1.4</u>
GRANT, CLEMSON U.	-	-	-	-	-	-	15.0	<u>15.0</u>
GRAND TOTALS	<u>24.4</u>	<u>1.7</u>	<u>1.0</u>	<u>2.0</u>	<u>3.7</u>	<u>2.4</u>	<u>15.0</u>	<u>50.2</u>

Table 4.--Use of Operating Funds in FY-77 (DBER, \$200,000)

Research Group	Task I	Task II	Task III	Task IV	Insect Res.	Res. Adm.	Other	Totals
(Thousands of dollars)								
SEFES, SRP								
<u>Salaries</u>								
Princ. Invest.	8.4	1.5	3.3	5.4	0.3	8.1	-	27.0
Superv. Techn.	3.9	7.7	-	-	-	1.3	-	12.9
Secretary	2.2	0.4	0.9	1.0	-	3.0	-	7.5
								<u>47.4</u>
Temp Salaries	84.6	4.9	-	-	2.6	-	-	<u>92.1</u>
								139.5
<u>Operating Expenses</u>								
Vehicles (USFS)	2.6	0.3	-	-	0.2	-	-	3.1
Vehicles (ERDA)	4.6	0.3	-	-	-	-	-	4.9
Supplies, Equip.	8.0	10.9	-	-	-	0.3	-	<u>19.2</u>
								27.2
<u>Travel</u>								
Scientists	0.6	-	-	1.0	-	0.2	-	1.8
Sample Trans.	-	1.3	-	-	-	-	-	<u>1.3</u>
								3.1
Sub-totals, SRP	<u>114.9</u>	<u>27.3</u>	<u>4.2</u>	<u>7.4</u>	<u>3.1</u>	<u>12.9</u>	<u>-</u>	<u>169.8</u>
INSECT RESEARCH								
<u>Salaries</u>								
Scientist	-	-	-	-	5.8	-	-	5.8
Techn.	-	-	-	-	3.3	-	-	3.3
								<u>9.1</u>
<u>Operating Expenses</u>								
Vehicles (USFS)	-	-	-	-	0.5	-	-	0.5
Supplies, Equip.	-	-	-	-	0.7	-	-	0.7
Travel	-	-	-	-	2.1	-	-	<u>2.1</u>
								3.3
Sub-totals, Insects	-	-	-	-	12.4	-	-	<u>12.4</u>
STATION-RES. ADM.	-	-	-	-	-	-	10.0	<u>10.0</u>
GRAND TOTALS	114.9	27.3	4.2	7.4	15.5	12.9	10.0	<u>192.2</u>

Table 5.--Items Purchased with Capital Equipment Funds by
Fiscal Years (DBER, \$51,000; Solar Energy, \$7,000)

Fiscal Year	Amount	Items Purchased
(Thousands of dollars)		
FY-76 (DBER)	7.0	<ol style="list-style-type: none"> 1. Fire-proof data cabinet 2. All-terrain vehicle ("Pug") 3. Tractor mounted sprayer 4. X-ray film processor
FY-76-77 Transition Qtr. (DBER)	29.0	<ol style="list-style-type: none"> 1. 3/4 ton truck 2. 12-passenger van 3. Walk-in freezer 4. Tractor (wheeled) 5. Tractor mounted sprayer 6. Typewriter 7. Vehicle 2-way radio, 2 ea.
FY-77 (DBER)	15.0 <i>April 6</i> <i>1977</i>	<ol style="list-style-type: none"> 1. All-terrain vehicle, 2 ea. 2. 3/4 ton truck 3. Tractor mounted sprayer 4. Vehicle 2-way radio, 2 ea. 5. "Handy-talky" repeater radio, 3 ea.
FY-77 (Solar Energy)	7.0	<p>Funds not yet received, but have authorization in principle from SRO for:</p> <ol style="list-style-type: none"> 1. Cyclone wood sample grinder

STAFFING

Staffing has been a continuing problem with our research team here at the SRP. The primary difficulty, as with all other Federal Agencies, has been the personnel ceilings that have been imposed. This has resulted in delay in filling a position for an additional scientist. However, it now appears that this position will be filled by September 1, 1977 (we have replies to inquiries of availability sent to seven people on the Civil Service list supplied to us, and five are available as candidates). Our position of Supervisory Technician was well filled in January, 1976 and presents no problem. But we have not been able to fill two additional technician slots, again because of ceiling restrictions. Instead we have hired technicians on 180 working-day temporary appointments -- a less than ideal practice because after getting them reasonably trained in their approximately 9 month stay with us, they are gone. We now have permission from Civil Service to set up two term appoints, each for two years, which are still temporary positions but at least are not limited to the 180-day proviso. I have two fine candidates that have previously worked with us, for these two technician positions.

For the secretaries position, we started dealing with the Civil Service Commission in December 1975 and the position was not filled until April 11, 1976. After working here 4 months (until August 13, 1976) this lady took a job paying considerably more money, and it was October 18, 1976 before this position was again filled. During the interval covered by this report, nearly 22 months, we have been without a permanent, full-time secretary about 8 months. Fortunately, we have had the assistance of a secretary with Forest Service volunteer status during this time. This...

gracious lady has contributed hundreds of hours of unpaid work.

Our Forest Worker crews are also on 180-day temporary status, and are employed through the hiring authority of R-8, SRP (and we are very grateful for this assistance). As with temporary technicians, well-trained crews are lost. In the last two weeks, I have interviewed, corrected and graded applications of 38 applicants to fill Forrest Worker jobs; 16 of these have been hired. Our present group of Forest Workers totals 23, 4 women and 19 men, of which seven are black.

In summary, our staff presently consists of:

1. Principal Investigator (Research Forester and Project Leader):
Jack Stubbs
2. Scientist (Research Forester): This position will be filled by
September 1, 1977
3. Supervisory Forest Technician: Edgar L. Davenport
4. Two Forest Technicians:—G. Michael Gossett and Kenneth C. Simmons....
They are presently on 180-day temporary tours, but both will be
placed in 2-year term appointments in a few weeks.
5. Secretary: Evelyn M. Sowell
6. Forest Workers: 23 presently on duty; two and possibly three of
these people will be promoted to Crew Leader positions.

Total personnel, SEFES, SRP: 28 people.

Also, for the Entomological Studies we work in cooperation with another Research Work Unit of SEFES, RWU-2209, Forest Insect Detection,

Evaluation and Control. The Project Leader is Dr. H. Allen Thomas, and they are located at our Forestry Sciences Laboratory at Research Triangle Park, N. C. Assigned from this work unit to cooperate with us at the SRP are:

1. Research Entomologist: Gordon E. Moore
2. Biological Lab. Technician: Thomas Merritt

PLAN OF WORK AND ACCOMPLISHMENTS

On the next few pages is found our Statement of Work. The tasks described therein are the basis for the bulk of this report. Other research endeavors which our agreement with ERDA has funded, and which are given on tables 2, 3, and 4, are discussed further on in this report; these include Insect Control Research, Paraquat Tests with Northern and Western Conifers, and The Battelle Report (Feasibility of Oleoresin Substitution for Petrochemicals).

STATEMENT OF WORK

Agreement Number EY-76-A-09-0903, Fuel Plantation Research,
between

The Savannah River Plant, ERDA
and

The Southeastern Forest Experiment Station, USDA Forest Service

Principal Investigator: Jack Stubbs

Task I: Paraquat treatment of test plots

The Southeastern Forest Experiment Station shall:

1. Design an experimental program at the Savannah River Plant site to test the effects of the following variables on the oleoresin yield:
 - a. method of application
 - b. season of treatment
 - c. concentration and volume of paraquat applied
 - d. tree species (slash pine and loblolly pine)
2. Treat up to 600 acres of loblolly and slash pine with paraquat.
3. Control insects and disease, applying BHC at least once per treatment application.
4. Determine the cost of each method of application.

Task II: Determination of oleoresin yields

The Southeastern Forest Experiment Station shall:

1. Determine the yields at 6, 9, 12, 15 and 18 months following treatment as appropriate for the specific study duration, sampling from 30 trees per treatment plot.
2. Prepare up to 5000 samples for analysis.
3. Perform analysis for turpentine and resin acids on each sample.
4. Analyze data and compare to untreated trees to determine the effect of the treatment variables on oleoresin yields.
5. Evaluate the costs of various treatment methods on yield.
6. Provide discs or chips from treated trees to Georgia Institute of Technology, with the support of labor from Georgia Institute of Technology. The number and volume of samples to be provided shall be determined by mutual agreement between the ERDA Program Manager, Georgia Institute of Technology, and the Southeastern Forest Experiment Station.

Task II: Determination of oleoresin yields Continued

7. Submit quarterly reports to ERDA.
8. Submit preliminary report to ERDA on September 1, 1977, summarizing work completed under Division of Biomedical and Environmental Research (ERDA) funding, since October 10, 1975.

Task III: Evaluation of mill trials

The Southeastern Forest Experimental Station shall:

1. Establish cooperative agreements with two additional cooperative pulp and paper or naval stores industries, to bring total number of cooperators to 6 cooperators.
2. Supervise timber operations for the removal of paraquat-treated trees by cooperative industries.
3. Evaluate modifications made to the mill processes during the extraction of turpentine, resins and other wood chemicals.
4. Through their industrial cooperators, perform materials balance studies during mill runs to determine oleoresin yields. The Station will correlate these with yields from sample analysis.
5. Submit preliminary report to ERDA on all work completed prior to August 1, 1978.
6. Submit final report to ERDA on work completed under Tasks I, II and III. (Element I, Research Proposal of December 14, 1976, SEFES).

Task IV: Exploratory and complementary studies

The Southeastern Forest Experiment Station shall:

1. Design one or more experiments to test the effect of the following variables or combinations of variables on oleoresin yields:
 - a. new wound and chemical application treatment techniques.
 - b. new chemicals and chemical combinations.
 - c. multiple treatments over time.
 - d. tree size and age.
 - e. fertilization.
 - f. soil moisture stress.
 - g. stand site index.
 - h. stand stocking.
 - i. tree crown class and live crown ratio.
 - j. site preparation methods, control of competing vegetation, and other cultural methods.

Task IV: Exploratory and complementary studies Continued

2. Treat up to 50 acres of loblolly and slash pine with lightwood inducing chemicals.
3. Control insects and disease.
4. Sample trees at 3, 6, 9, 12 and 15 months after treatment, as appropriate for the specific study duration.
5. Prepare up to 5000 samples for analysis.
6. Perform analysis for turpentine and resin acids on each sample.
7. Evaluate the effect of the specified variables on yield.
8. Submit quarterly reports to ERDA.
9. Submit preliminary reports each August 15, summarizing work completed to date. First report due in August, 1978.
10. Submit final report to ERDA on Exploratory and Complementary Studies (Element II, Research Proposal).

MILTON JONES, UDEL / INDIATION / RESEARCH

TASK I

1. Prog
desi
2. Treat
trees
3. Control
insects
4. Application
costs

Key: ▽ Complete
○ Report
◇ Decision Point
FY-78 Funding

TASK II

1. Sample trees
2. Prepare samples
3. Analyse samples
4. Treatment results
5. Treatment costs

- 6. Coop. with Ga. Tech.
- 7. Quarterly reports
- 8. Preliminary report

TASK III

1. Coop. agreements
Industry
2. Westvaco
Continental Group
Union-Camp
Reichhold Chemical
2 other cooperators
3. Evaluate Mill
Processes
4. Materials balance
studies
5. Preliminary report
6. Final Report, Task

1977

1978

1979

1950

1921

MILESTONES, FUEL PLANTATION RESEARCH

TASK IV

Key: ▽ Complete
○ Report

Task I: Paraquat Treatment of Test Plots

(Proof of Concept Experimentation)

This task loomed largest when we began this research with ERDA, and the unusual requirements for these studies -- copious acreage of uniform plantations of three species, of pulpwood size and age, and under very good administrative control -- are the reasons the SRP seemed ideal for these tests. Planning for these tests began in October 1975, the Prospectus was written in December 1975 (see Appendix H), and actual field work began in January 1976.

Stand Selection and Inventory

Although the first priority job for this task was to secure at least one industrial cooperator, because they were an integral part of the research plan and obviously absolutely necessary, in the meantime while contacting prospective cooperators it was essential to choose and inventory experimental plantations. To select from the thousands of acres of loblolly, slash and longleaf pines on the Savannah River Plant, we first used the computer bank of stand data compiled by and available from R-8, SRP. Promising stand areas were noted but in general the printout of stand information was not sufficiently detailed for experimental uses. The Supervisory Technician and I then narrowed candidate areas through use of the detailed maps and text of R-8, SRP stand prescriptions. Much assistance was also given by R-8 personnel that knew the plant site very well. However, all candidate plantation stands had to be checked on the ground for homogeneity and size

of homogeneous areas, stocking density, site index, and age. Based on these criteria, stands were selected or rejected beginning first with loblolly pine, then proceeding to slash pine, and finally to longleaf pine. After selections had been made, Site Use Permits (SRO 189 forms) were prepared and submitted to ERDA, SRP for this acreage, and these were approved virtually as submitted.

After approval of the Site Use Permits, loblolly plantations that were best suited to large-scale tests were inventoried by a 100-percent cruise; i.e. the diameter of each tree was measured, and heights were determined for every tenth tree in each plantation row. For each plantation the rows were numbered, individual trees in the rows were also numbered, and tree data was recorded accordingly. Slash and longleaf stands were also cruised after loblolly pine.

On the face of it this appears to be a tedious and inefficient procedure, but it was highly useful and indeed necessary to us for two reasons: 1) Until we had a cooperator, we had of course no knowledge of the amount of timber volume they would require; this row and tree numbering system allowed us to select and know the location of any quantity of volume we desired from a stand; 2) With all trees in effect numbered, the random selection and actual locating of sample trees was much simplified.

For volume determinations of each tree, a computer-derived volume table based on bole taper curves was used. This volume table was produced with the kind cooperation of the SEFES Biometry Group.

Because of this preliminary work in selecting stands and collecting volume data in detail, when cooperators were signed and we ascertained the wood requirements of each (and they varied markedly), no time was lost in promptly installing a study tailored to the individual needs of each cooperator.

Obtaining Industrial Cooperators

Finding suitable cooperators was a slow and painstaking affair, demanding much travel, discussion, and persuasion. By natural selection, pulpmill managers are conservative people; down-time at a mill amounts to tens of thousands of dollars an hour, and they are paid a bonus based on paper or pulp produced, not by-product recovery (the class in which oleoresin recovery falls). Thus business was slow at first, but by gaining influential friends and allies through the Lightwood Research Coordinating Council and the Pulp Chemicals Association (see the "Research Cooperators" section), the pace picked up remarkably. Several corporations have sought me out. In total we have had discussions with 14 companies regarding the possibility of trial runs in their various plants. Most of these showed, sooner or later, willingness to cooperate. However, logistical considerations -- costs of hauling SRP wood to several rather distant plants -- stymied negotiations several otherwise eager companies. To date we have agreements with four cooperators, three of them pulp and paper companies (Westvaco, Continental Group, and Union-Camp) and one wood naval stores operation (part of Reichhold Chemical Co.). Cooperative agreements between SEFES and the company were drawn up for each. An example of these

agreements, that with Reichhold Chemical Co. is given in Appendix G.

It must be mentioned that the original plan of obtaining just one cooperator was unsound. During my rapid education process in matters concerning this research assignment, I was quite surprised to learn that even kraft pulp mills, using virtually the same raw material, differ significantly. One mill would not have been enough, results are needed from several. Wood naval stores plants are considerably more similar at least in ways that concern this research. In all three of our pulp mill test batch digesters will be used. This was intentional because they generally show much higher oleoresin recovery than do continuous digesters. However, continuous digesters are common in the South and may become more so in the future. If funding permits another large-scale test, I would like to locate a cooperator willing to test their continuous digester with lightered wood. It would also be a good idea to secure a second wood naval stores cooperator. We are wary of samples of one.

Achievements, Task I Studies

We have completed paraquat treatment of all trees required to furnish lightwood to the four companies mentioned above. All these trees are in plantation stands 22-23 years old. A total of 71,228 trees received one of five different treatments, not including controls. This amounts to a volume of 10,580 cords and an area of approximately 530 acres. The value of these

trees as stumpage (standing in the woods) without paraquat treatment is at least \$158,000. Paraquat treatments of the four studies began in September 1976 and continued until July of this year.

Reichhold Chemical Company Test. -- Because they are a wood naval stores company geared to using natural lightwood from virgin pine stumps with an oleoresin content of about 20%, Reichhold requires wood with an oleoresin content of at least 15 percent on a green weight basis. In an attempt to achieve this we treated each tree with two paraquat containing dowels, will harvest only the lower 11 feet of bole for Reichhold (the rest used as pulpwood), and plan on a treatment duration of two years or more. Provided the 15 percent oleoresin concentration can be attained, Reichhold plans a 5-day run using 600 cords at their plant in Telogia, Florida. To obtain this volume exclusively from 11 foot butt sections we had to treat about 1500 cords of total merchantable volume. We treated an extra 100 cord for use as samples, etc.

Treatments involve loblolly pine trees 22 years of age and 9.5 inches in average diameter (range 5 to 15 inches). Three blocks totaling 10,102 trees were treated beginning in November 4, 1976, and ending February 16, 1977. These trees were treated by drilling 2 holes into the trunk on opposite sides of the tree, each hole spanning approximately 1/3 of the circumference of the tree, and inserting 1/2" birch dowels impregnated with 2.04 lbs. of paraquat cation per cubic foot. The lower 6 feet of each tree was sprayed immediately after treatment with an aqueous solution of 1/10% BHC to deter bark beetle attacks.

This is rather a drastic paraquat treatment, chosen because of the high oleoresin concentration specified by Reichhold.. Compared to a 1/3 circumference bark streak and use of 5% paraquat solution, a tree receiving two dowels gets about six times as much paraquat. However, it was thought that the double dowel method was not biologically equivalent to a 30% paraquat solution because of slow release of paraquat from the dowel. We have tested this method on slash pine trees in Florida with no untoward results.

However, it is a good thing that we tested this treatment in South Carolina, on loblolly pines during a drought year. We periodically inspect all studies for evidence of insect attack, and through March of this year saw no cause for concern in the Reichhold study. Then came three months with virtually no rain, and tree crowns began turning brown in the Reichhold plots, but with no exterior evidence of bark beetles. The trees were evidently too desiccated to form the usual pitch tubes. In May 1977, inspection by removing bark revealed that these trees were well stocked with Ips beetles. A spraying treatment was immediately started using a 1/2% solution of BHC in water, to a height of 35 feet on the tree boles. A survey in June showed that most of the trees were attacked by Ips beetles; of a total of 10,102 trees, 2,417 trees were dead and 1,677 more were in a comatose condition. Mortality at present is about 50% of the treated trees, and we will probably lose a few more. Salvage of dead timber is now underway.

While this is not the sort of thing one desires in a study, the information is far from negative. If we had had a wet spring and little--

loss from beetles, an erroneous conclusion would have been drawn. On our advice several of our cooperators might have treated some thousands of acres with this method, with a high risk of disastrous results. Also, as part of our sampling for oleoresin buildup (see Task II below), we are sampling both dead and living trees. From these bark samples have been taken (360 total) for more information on insect emergence from paraquat treated trees. At present there is some evidence that insect broods in paraquat treated trees have a poor emergence ratio; i.e. a few adults are produced. It is critical to obtain more data on this question.

According to our cost records, direct costs of this treatment was about \$7.90 per cord, and \$1.15 per tree. The total research costs for this experiment were about \$46,200.

Information pertaining to this study is summarized on the next page.

PULP CHEMICALS ASSOCIATION

CON	<u>Reichhold Chemical</u>	SITE LOCATION	<u>Savannah River Plant</u>
WOUNDING METHOD	<u>Drill Hole</u>	SIZE, TYPE OF WOUND	<u>Two 9/16" holes thru tree at 1/3 circumference on either side</u>
HOW APPLIED	<u>Elect. Drill</u>	LOCATION ON TREE	<u>1 ft. from ground level</u>
DATE TREATED	<u>Nov. 4, 1976 to Feb. 16, 1977</u>	HARVESTED	<u>July 27, 1977 to Aug. 16, 1977</u>
NO. TREES	<u>10-103</u>	NO. MONTHS	<u>8-9</u>
		NO. TREES	<u>180</u>

SPECIES Loblolly Pine AGE 22 DBH AVERAGE 9.5 DBH RANGE 5.0"-15.0"
DENSITY/ACRE 175 PLANTATION OR NATURAL Plantation SITE INDEX 85
SOIL/MOISTURE CONDITIONS Moist under normal conditions
OTHER All trees were sprayed with 1/10% BHC and H₂O up to 6" after treatment. After beetle attack, they were sprayed with 1/2% BHC and H₂O up to 35 ft. from ground

CONCENTRATION	QUANT./TREE	HOW APPLIED
2.04 lbs.of Active Ion	Two 1/2" dowels	Paraquat-impregnated
per cu. ft. of dowel	(length of 1/3 circumference at wound on either side)	wooden dowels

SUMMARY OF ANALYSES

SUMMARY OF ANALYSES					PERCENT						
BASIS		NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL	BASIS		NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL
BOLTS (LENGTH/LOCATION):					DISCS (SIZE, LOCATION):						
WHOLE TREE					OTHER						

ANALYTICAL METHOD USED (REFERENCE OR BRIEF DESCRIPTION):

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

This study plot was attacked by black turpentine beetles at a rate of 7% but no mortality from them. On May 10, 1977, we noticed a few stems were dying. A mortality survey was conducted on June 17, 20, 23, and we found that Ips beetles had killed 2,417 trees and 1 were dying, as of 8/17/77, we probably have a 50% loss to mortality.

Westvaco Pulp and Paper Company Test. -- Westvaco has agreed to make a run at their Charleston, S. C. mill, with paraquat treated loblolly pine comprising 100 percent of the furnish. They are able to isolate a line and digester and only require 400 cords from each of three paraquat treatments, and 400 cords of control wood. However, to allow for harvest of trees for wood samples, and for possible losses, we treated a total of 1,380 cords and not 1,200 cords. A total of 9,282 trees were treated on about 55 acres.

These loblolly pines are in a plantation 22 years old, and average 9.0 inches in diameter (range 5 to 14 inches). The three treatments are as follows: 1) 1/3 circumference bark streak using a power chipper, 5 percent paraquat sprayed on the wound in 3 ml increments up to 9 ml depending on tree size; 2) a drilled hole joining points at 1/3 circumference, paraquat concentration and amounts as above placed in the hole, drill exit and entrance holes corked; 3) a drill hole as in two above with a paraquat impregnated birch dowel driven into the hole (dowels contained 2.04 lbs. of paraquat cation per cubic foot of wood). All treated trees were sprayed soon after treatment to a height of 6 feet with an aqueous 1/10 % BHC solution. Treatment of these trees began in September 1976 and was finished in November 1976. Treatment duration will be 14 months.

Initial surveys for insect attack and mortality indicated that approximately 7% of the trees were under attack by beetles but no mortality had occurred. In August of 1977 there was still no mortality in the two groups of trees treated with the bark streak treatment or

the bore hole plus paraquat solution. However, in the group treated with a paraquat impregnated dowel there is approximately 15% mortality.

Our cost data show that the direct costs for the three treatments are as follows:

1. Power chipper, 5% paraquat: \$3.00 per cord, \$0.45 per tree.
2. Paraquat impregnated dowel: \$6.36 per cord, \$0.93 per tree.
3. Drill hole with 5% paraquat: \$4.40 per cord, \$0.66 per tree.

The total research costs for this experiment were about \$23,400.

On the next three pages are summaries for the three treatment methods employed in this study.

PULP CHEMICALS ASSOCIATION

OLEORESIN FORMATION AS RELATED TO PARAQUAT TREATMENT METHOD

COMI Westvaco SITE LOCATION Savannah River Plant
 WOUNDING METHOD streak SIZE, TYPE OF WOUND 1" x 1/3 circumference
 HOW APPLIED Chipper saw LOCATION ON TREE 1 ft. from ground level
 DATE TREATED Sept. 22, 1976 to Oct. 19, 1976 NO. TREES 3,055 HARVESTED Mar. 23, 1977 to May 5, 1977 NO. MONTHS 6-7 NO. TREES 90

TREE DATA

SPECIES Loblolly Pine AGE 22 DBH AVERAGE 9.3" DBH RANGE 5.0" - 15.0"
 DENSITY/ACRE 150 PLANTATION OR NATURAL Plantation SITE INDEX 85
 SOIL/MOISTURE CONDITIONS Moist under normal conditions
 OTHER All trees were sprayed with 1/10% BHC and H²O up to 6 ft. from ground

PARAQUAT USED

CONCENTRATION 5% QUANT./TREE 3 to 12 ml per tree depending on size HOW APPLIED Calibrated Man-o-Stat. Volume dispenser.

SUMMARY OF ANALYSES

BASIS	PERCENT				BASIS	PERCENT			
	NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL		NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL
BOLT LENGTH/LOCATION):					DISCS (SIZE, LOCATION):				
WHOLE TREE					OTHER				

ANALYTICAL METHOD USED (REFERENCE OR BRIEF DESCRIPTION):

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

This study was infested with black turpentine beetles to 9% but no mortality, as of August 17, 1977.

PULP CHEMICALS ASSOCIATION

COM	<u>Westvaco</u>	SITE LOCATION	<u>Savannah River Plant</u>
WOUNDING METHOD	<u>Drill Hole</u>	SIZE, TYPE OF WOUND	<u>9/16" hole thru tree at 1/3 circumference</u>
HOW APPLIED	<u>Electric drill</u>	LOCATION ON TREE	<u>1 ft. from ground level</u>
DATE TREATED	<u>Oct. 21, 1976 to</u> <u>Nov. 9, 1976</u>	NO. TREES	<u>3,236</u>
HARVESTED	<u>May 18, 1977</u>	NO. MONTHS	<u>6-7</u>
		NO. TREES	<u>90</u>

SPECIES Loblolly Pine AGE 22 DBH AVERAGE 9.0" DBH RANGE 5.0" to 14.0"
DENSITY/ACRE 150 PLANTATION OR NATURAL Plantation SITE INDEX 85
SOIL/MOISTURE CONDITIONS Moist under normal conditions
OTHER All trees were sprayed with 1/10% BHC and H²O up to 6 ft. from ground

CONCENTRATION 2.04 lbs. of active QUANT./TREE One 1/3" Birch dowe HOW APPLIED Paraquat impregnated
Ion per cu.ft. of dowel (Length of 1/3 circumference wooden dowel
at wound)
 SUMMARY OF ANALYSES

SUMMARY OF ANALYSES									
BASIS	PERCENT				BASIS	PERCENT			
	NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL		NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL
BOL LENGTH/LOCATION):					DISCS (SIZE, LOCATION):				
WHOLE TREE					OTHER				

ANALYTICAL METHOD USED (REFERENCE OR BRIEF DESCRIPTION): _____

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

This study plot was attacked by black turpentine beetles at a rate of 6%, but no mortality from them.

On May 10, 1976, we noticed a few stems were dying. A mortality survey was conducted on 5/77, and it was found that Ips beetles had attacked and killed 72 trees and 81 more were dying from the total 3,236 trees.

As of 8/17/77, we probably have a 15% mortality in this study.

PULP CHEMICALS ASSOCIATION

CON Westvaco SITE LOCATION Savannah River Plant

WOUNDING METHOD Bore Hole . SIZE, TYPE OF WOUND 9/16" hole through tree at 1/3

HOW APPLIED electric drill LOCATION ON TREE 1 ft. from ground level

DATE TREATED Sept. 23, 1976 to Mar. 29, 1977
Nov. 8, 1976 NO. TREES 2,991 HARVESTED May 4, 1977 NO. MONTHS 6-7 NO. TREES 90

SPECIES Loblolly Pine AGE 22 DBH AVERAGE 9.0" DBH RANGE 5.0"-14.0"

DENSITY/ACRE 150 PLANTATION OR NATURAL Plantation SITE INDEX 85

SOIL/MOISTURE CONDITIONS Moist under normal conditions

OTHER All trees were sprayed with 1/10% BHC and H²O up to 6 feet from ground

CONCENTRATION 5% QUANT./TREE 3 - 12 ml per tree HOW APPLIED Calibrated Man-O-Stat.
(depending on size) Volume dispenser

BOL		PERCENT				BOL		PERCENT			
		NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL			NON-VOL. RESIN	TURPS	OLEO-RESIN	TALL OIL
BOL LENGTH/LOCATION):						DISCS (SIZE, LOCATION):					
WHOLE TREE						OTHER					

ANALYTICAL METHOD USED (REFERENCE OR BRIEF DESCRIPTION): _____

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

This study plot was attacked by black turpentine beetles, at 6%, but no mortality has been observed as of 8/17/77

Continental Forest Industries Test. -- Continental Group, Inc. will accomplish a mill trial with 6000 cords of treated loblolly pine. This wood representing about 15 percent of the mill's monthly pulpwood requirements, will be uniformly added to the pulping process over a one month period. Trees will be treated with a 1/3 circumference bark streak sprayed with a 5 percent paraquat solution as was used in one of the Westvaco treatments. Treatment duration will be one year.

These loblolly pines are plantation trees presently 23 years old, and have an average diameter of 9.5 inches (range 5 to 15 inches). A total of 6,060 cords was treated, comprised of 39,251 trees on about 300 acres. Paraquat treatment of this rather large experiment began in late October 1976 and continued until March 1977. As with the experiments previously described, this one also received an aqueous 1/10% BHC spray to a height of 6 feet immediately after paraquat treatment.

Approximately 3 months after treatment began, some black turpentine beetles were found in treated trees but no other insects have been observed through August 1977. A survey of the trees in June 1977 found that 10 trees of approximately 40,000 were dead. This mortality ratio of 0.025 percent is much less than normally expected in stands without paraquat treatment.

Our cost records show that the direct costs for this paraquat treatment were \$2.96 per cord, \$0.46 per tree. It is of interest to compare these data with costs given previously for an identical treatment in the Westvaco study; these were \$3.00 per cord, \$0.45 per tree, rather close.

agreement.

The total research costs for this experiment were about \$65,800.

Data Pertaining to this large-scale test are summarized on the next page.

cc Continental Group, Inc.

SITE LOCATION Savannah River Plant

WOUNDING METHOD Streak

SIZE, TYPE OF WOUND 1" x 1/3 circumference

HOW APPLIED Chipper saw

LOCATION ON TREE 1 ft. from ground level

DATE TREATED Oct. 21, 1976 to
Mar. 31, 1977 NO. TREES 39,251

HARVESTED none

NO. MONTHS

NO. TREES

TREE DATA

SPECIES Loblolly pine

AGE 23

DBH AVERAGE 9.5

DBH RANGE 5.0"-15.0"

DENSITY/ACRE 190

PLANTATION OR NATURAL Plantation

SITE INDEX 90

SOIL/MOISTURE CONDITIONS Moist to wet under normal conditions

OTHER All trees were sprayed with 1/10% BHC and H²O up to 6 ft. from ground

PARAQUAT USED

CONCENTRATION 5%

QUANT./TREE 3-12 ml per tree
(depending on size)

HOW APPLIED Calibrated man-o-stat.
volume dispenser

SUMMARY OF ANALYSES

[illegible]

ANALYTICAL METHOD USED (REFERENCE OR BRIEF DESCRIPTION):

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

A few black-turpentine beetles entered this study approximately 3 months after treatment.

began. No other insects have been observed as of 8/17/77. However, we counted a total

of -- trees dead on a mortality survey that was made in June 1977.

Union-Camp Corporation Test. -- This mill trial will utilize 1,200 cords of slash pine. Treated wood will furnish 100 percent of the intake of a single isolated batch digester and skim tank. These slash pines are in several 23-year-old plantations, and were treated between April 25 and July 18, 1977. This was an injection treatment; "Jim-Gem" tree injectors were used, metering 1 ml of 2 percent paraquat solution per injection. These injections (1½ inches wide) were spaced on 5-inch centers around the base of each tree. A total of 1,544 cords was treated, demanding 12,593 trees and about 63 acres. Treatment duration will be 18 months.

Insect attack and mortality have not yet been formally surveyed, but preliminary inspections of these stands indicate there are some black turpentine beetles present but no mortality at this time. All trees in this stand were sprayed with 1% mixture of BHC in diesel fuel to 5 feet above the ground. Use of diesel fuel is much more costly than water, but this spray method was selected because our cooperator, Union-Camp, has used this in their proprietary studies with paraquat and have been remarkably free of the insect pests that have plagued virtually every other experimenter in lightering.

Our data show that the direct costs of this paraquat treatment, including the diesel fuel spray method, are \$7.86 per cord, \$0.96 per tree.

The total research costs for this experiment have been about \$44,400.

Data of the experiment are summarized on the next page.

OLEORESIN FORMATION AS RELATED TO PARAQUAT TREATMENT METHOD

TREE DATA

PARAQUAT USED

SUMMARY OF ANALYSES

OTHER PERTINENT INFORMATION (MORTALITY, BEETLE ATTACK, ETC.):

Task II: Determination of Oleoresin Yields

At the time we signed our agreement with ERDA we had a backlog of approximately 10,000 wood samples at our laboratory in Olustee, Florida. These came from a series of experiments in chemical inducement of light-wood, some wholly ours and others in cooperation with various industries. By January 1976, through hard work and judicious compositing my group at Olustee, under Dr. Donald R. Roberts, had reduced this to 4,000 samples. In mutual agreement with ERDA, about \$50,000 of the FY-76 operating funds, were informally earmarked for analysis of these samples.

We would have preferred to have these analyses done here at the SRP site by DuPont. After long and detailed negotiations we thought that a suitable agreement had been reached with DuPont, but this fell through for several reasons. However, in order to have alternatives if needed, we also concurrently checked several other possibilities. Of these by far the best bid was received from John Drew, Director, Forest Chemicals Department, Glidden-Durkee Division, SCM Corp. in Jacksonville, Florida. He has given us a firm quote of \$20 a sample, which includes sample preparation (disk grinding), computer calculations to put results on a bolt and whole tree basis, etc. We wrote up a contract with the necessary stipulations and specifications, but because of the large sum of money involved, it had to be advertised nation-wide for closed bidding. To our amazement a firm near Boston won the contract, bidding \$14.90 per sample analysis. We know what these analyses cost and they were obviously going to lose money. To verify that they understood what was required, and to investigate their capabilities and reputation

in general, we visited them for several days in Boston and found no reason for prejudice against them. So far they have received nearly 4,000 samples from us, all but 700 from the SRP studies.

Our wood sample collection here at the Savannah River Plant was delayed over 3 months because of lack of freezer space (samples must be kept frozen to avoid loss of the turpentine which is quite volatile). An outdoor, walk-in freezer was purchased and delivered to the site but it was nearly 6 months before it was supplied with electrical power. No suitable commercial freezer space was available in this area.

We have collected one series of samples from the Westvaco plots (360 trees sampled) and one from the Reichhold test (also 360 trees). As mentioned earlier, by sampling both dead and living trees in the Reichhold test we doubled the originally planned number of samples. In general, due to the delay mentioned above, each study is scheduled for sampling 6 months after treatment and every 3 months thereafter until they are harvested for a mill run. Samples are analysed for resin acid content (rosin), turpentine, and turpentine components. We have in hand most of the analysis data for the Westvaco samples, but not all of it. Resin acid and turpentine yields for all paraquat treatments are greater than those of controls (Table 6). When all these data are received we will perform statistical analyses.

Table 6.--Oleoresin Content of Westvaco Study Trees
Six Months After Treatment

Treatment	Resin Acids	Turpentine
(On a percent dry wood weight basis)		
Bark streak	4.38	0.74
Drill hole	4.02	0.51
Dowel	4.21	0.61
Control	3.32	0.32

Task III: Evaluation of Mill Trials

As briefly discussed earlier, one might suppose that it would be preferable to have all these test runs accomplished at one plant. Not only is this impracticable -- there is a limit to what one may request of any one cooperator -- but it would not be desirable. No two kraft pulp mills, for instance, are alike and some differ a great deal. This is relevantly illustrated by variation in oleoresin by-product recovery from mill to mill, which ranges from ca. 60 to over 90 percent. Consequently, oleoresin-yield data from one or even two mills would be insufficient, and no practical test would have been made of possible technical problems within the array of mills. The wood naval stores plants present much less difficulty in this regard; with them two cooperators should suffice.

Pulping tests with lightwood of paraquat origin have shown that it pulps as well as normal wood, with no reduction in either quantity or quality of the pulp. Some minor modifications of the process are indicated, particularly the need for more active alkali in the digester liquor. The industry people are fairly confident no untoward problems will arise; but we all are aware that production runs in digesters of 3000-plus cubic feet capacity are quite a different thing than runs in laboratory digesters of 1 or 2 cubic feet. There is a good deal of art along with science in making such a complex and gigantic apparatus as a pulp mill run properly. Problems in scale, laboratory to mill, are

almost certain to occur. Other possible sources of trouble include excessive foaming at the pulp washers, because of more "soap" in the black liquor, and difficulties at the evaporators and skim tanks for the same reason. In short, the pulp and paper companies are taking some risks, and the costs of even a few hours shut-down time in a mill are really quite high. In a wood naval stores extraction plant the possibilities for technical problems seem to be much less. Fresh wood, however, unlike old lightwood stumps, contain fatty acids and there is some concern that these may react on copper and bronze valves, etc. of the fractionating tower, with several undesirable results one of which might be production of rosin with weird green color.

To serve as a model of the type of extractive parameters that will be collected at a pulp mill, an outline of Continental Group's mill procedure follows. Procedures for a wood naval stores extraction plant will be similar but obviously need not be as complex.

PULP MILL PROCEDURE

I. Chips to Digesters

- A. Record weight/day
- B. On daily composite sample test:
 - 1. Percent moisture
 - 2. Available turpentine volume/unit weight oven-dry chips
 - 3. Available tall oil weight/unit weight oven-dry chips

II. Turpentine System

- A. Daily measure=decanter and storage tank levels
- B. Alternate days measure:
 - 1. Underflow turpentine loss
 - 2. Recovered turpentine composition

III. Pulp Washers

- A. Measure (indirectly) daily pulp production
- B. Alternate days measure residual tall oil in pulp

IV. Black Liquor

- A. Measure flow daily
- B. Measure alternate days:
 - 1. Percent black liquor solids to evaporators
 - 2. Tall oil weight/unit weight black liquor solids
 - 3. Percent black liquor solids to soap skimmers
 - 4. Tall oil weight/unit weight black liquor solids from skimmers

V. Soap Storage

- A. Measure tank levels daily
- B. Measure soap density, available tall oil

VI. Tall Oil Plant

- A. Determine daily production by tank inventory
- B. Measure tall oil composition alternate days
- C. Measure use-rate of sulfuric acid
- D. Sample spent acid daily for:
 - 1. Flow
 - 2. Tall oil content
 - 3. Lignin content
 - 4. Saltcake equivalent

VII. Paper Production

- A. Measure production rate periodically
- B. Determine paper quality periodically

Our cooperator Reichhold Chemical Co. will make a wood naval stores run at their stump wood extraction plant at Telogia, Florida. They will perform measurements and analyses to determine:

- 1. Weight loss in storage and handling.
- 2. Chip size.
- 3. Bulk density.
- 4. Packing capacity (amount that can be placed in a retort).

5. Moisture and Rosin content of prepared wood and spent wood.
6. Terpene content of samples from the solvent stream.
7. Rosin content of the liquor.
8. Terpene content of samples from the distillation units.
9. Fuel value of spent wood.
10. Color grade, acid number and melting point of rosin.
11. Alpha- and beta-pinene and pine oil contents of the volatile oils.

The first pulp mill test, that with Continental Industries, will begin in January 1978. We have written a first draft of a research contract, ERDA-SRP and Continental, and sent it for review to both parties. A copy is enclosed in Appendix F.

Task IV: Exploratory and Complementary Studies

Here at the Savannah River Plant we have not yet installed studies of this task (see Milestone Plan, pages 18 and 19). The experimental variables which we plan to investigate are given under Task IV, pages 16 and 17. However, this sort of research has been and continues to be done by our team at Olustee, Florida, a part of the Research Work Unit headed by the principal investigator, Jack Stubbs. As tables 2, 3, and 4 show, some funds have been used for Task IV; these represent costs in connection with this Olustee team, primarily review of study plans, reports, and manuscripts, and also general research guidance. Olustee has dealt primarily with slash and longleaf pines, while here at SRP we will concentrate on loblolly pine.

Research Conducted by Team #2 of Our Work Unit (Olustee, Florida)

This research team, headed by Dr. Donald R. Roberts, is engaged in several studies designed to better define: 1) the most effective chemical concentrations; 2) best method of application; 3) optimization of the concentration and amount of paraquat for each combination of species and method of treatment. The following are summaries of these studies:

1501-1.--Paraquat lightwood tests in four southern pines

Slash, longleaf, loblolly and sand pine trees were treated by applying 0.5 ml of either 10.5, 1.0, or 2.5 percent paraquat to ax chops spanning 1/3 the tree circumference. All species formed lightwood in response to

paraquat treatment but sand pine did not yield as much turpentine and rosin as the other three species. Results for slash, longleaf and loblolly were reported in an oral presentation to the Forest Products Research Society in July 1975 and in a paper published in the Forest Products Journal, Vol. 27(6). June 1977. Sand pine results are in manuscript form.

1501-4.--Response of Pinaceae genera to paraquat

Trees of 19 conifer species were treated at four locations near the following cities: Fort Collins, Colorado; Rhinelander, Wisconsin; Asheville, North Carolina; and Lake City, Florida, to determine whether they would produce increased amounts of oleoresin in response to paraquat treatment. In each species, 15 trees were selected and five trees each were treated with either 0.25, 1.0, or 5.0 percent solution in a 4-inch ax frill wound.

Material from these species has been collected and the analytical work has been completed at Olustee, Florida and the Forest Products Laboratory at Madison, Wisconsin. Only the pines and spruces showed an extractive increase of potential commercial value. The hard pines appear to be better suited for lightwood production than the white pines and all pines produce more extractives than the spruces. The FPL should complete analytical work on the remaining species this next year. Two papers were published this past year, 2 more have been submitted for publication and 2 or 3 more should be completed this next year to finish this study.

A more detailed account of work at the Forest Products Laboratory" appears later in this report.

1501-2.--Lightwood Induction in Slash Pine.

In cooperation with Buckeye Cellulose Corp., trees in 15-, 16-, 17-, 18-, and 20-year-old slash pine stands were treated with 8-percent paraquat on a single bark streak, or with 4-percent paraquat on 2 bark streaks 4 feet apart on the same side of the tree.

The trees have been cut and analyzed. The results are not yet tabulated.

1501-6.--Intensive lightwood for solvent extraction.

Most of a large acreage of slash and longleaf pine trees was treated with 4 treatments designed to induce large quantities of rosin in the basal 10 feet of the trees. Other small areas were used to study specific problems: optimum wound depth, methods of application, and intensity of wounding.

The depth of wound experiment indicated that wounds to the live phloem, the cambium, or 1/4 inch into the xylem gave the same result. The method of application experiment indicated that injections 3 inches apart gave better results than single to 1/3 circumference bark streaks, drill holes, or injections 1 inch apart spanning 1/3 circumference.

The intensity of wounding experiment showed that insect activity increased as wound size and paraquat concentration increased. Ax chop wounds attracted more insects than bark streaks. Samples have been analyzed for rosin and turpentine content.

1501-12.--Methods of application of paraquat to young planted slash pines.

In cooperation with Buckeye Cellulose Corporation, we established a study involving 10 treatments on 400 slash pine trees in a 19-year-old plantation. All except the control methods of application used a 4 percent paraquat solution. The methods were as follows:

1. Open hole 4 inches deep
2. Hole with cellulose plug 4 inches deep
3. Pressure injector, .4 ml, 4 inches apart around the tree
4. Tree injector, .4 ml, 4 inches apart around the tree
5. Vertical bark streaks 1 inch wide, 4 inches apart around the tree
6. 1/3 circumference bark streak, 1 inch high, liquid spray
7. 1/3 circumference bark streak, 4 inches high, liquid spray
8. 1/3 circumference bark streak, 1 inch high, organic gel
9. 1/3 circumference bark streak, 1 inch high, silica gel
10. Control- no wound and no paraquat

Wood samples were collected in April, 1977 but the laboratory analyses are not complete. Insect attack and tree mortality were quite heavy.

1501-10.--Application of paraquat to multiple small wounds for production of lightwood with high resin content.

High resin concentration is necessary for economical solvent extraction of lightwood. This study was designed to test paraquat treatment of multiple small wounds in an effort to produce lightwood with 15 percent

resin content in the basal 10 feet. Small vertically oriented bark streaks and tree injector incisions will be compared to the standard 1/3 circumference bark streak, both using 5 percent paraquat.

1501-7.-- High pressure injection of paraquat

This study in cooperation with Glidden-Durkee Division of SCM involved treatment of slash pine trees in a 20-year-old plantation. All combinations were tested of 2 and 8 percent paraquat concentrations, three application procedures, and an untreated control.

Based on the results obtained in this study the following conclusions are drawn:

1. The best whole-tree enhancement was produced by 8% paraquat streaks followed by 8% paraquat injected with the Med-E-Jet 3 inches apart all around the circumference. The treatments ranked as follows for whole-tree enhancement:
 - a. 8% streaked
 - b. 8% - 3 inches apart, all around
 - c. 8% - 1 inch apart, 1/3 circumference
 - d. 2% streaked
 - e. 2% - 1 inch apart, 1/3 circumference
 - f. 2% - 3 inches apart, all around
2. The most effective treatment (8% paraquat streaked) caused the turpentine content to double at 4.9 months and resin acids to double at 7.2 months after treatment.

1501-8.-- Paraquat induced lightwood field tests in pine plantations.

Cooperating companies treated two 250-tree groups in plantations of both slash and loblolly pines with 8% paraquat applied to a single 1/3 circumference bark streak, or 4% paraquat applied to two bark streaks, 4 feet apart. Results of these treatments will be compared in the same plantations.

Insects caused heavy damage in both treatments. Most companies have sampled trees and reported results. These results must be summarized and reported.

1501-13.--Standard experiment for lightwood induction in southern pines.

Each of the 20 cooperators selected 50 trees, 5 to 9 inches d.b.h., in a slash or loblolly pine plantation, treated half with 2% paraquat applied to a single 1/3 circumference bark streak and left half untreated. Approximately 8 months after treatment all trees were cut and sampled. Analyses showed that rosin and turpentine contents were greatly increased by paraquat treatment. Yield increases for slash pine were 128% for rosin and 172% for turpentine. In loblolly the increases were 96% for rosin and 159% for turpentine. Insect attacks were a problem in some stands but only 3 of the 500 paraquat-treated trees died before harvest at 8 months. (A detailed report of this study is given in Appendix D)

Our work unit lists research attainments in an annual report. Several of the people who will receive copies of this progress report, especially ERDA staff, have expressed interest in receiving a copy of this Research Attainment Report. Consequently, a copy may be found in Appendix E.

INSECT CONTROL RESEARCH

Screening of insecticides at the Savannah River Plant began in the Summer of 1976 at about the same time as trials of paraquat for lightwood induction. Not only was the climate different than in Olustee, Florida, where earlier paraquat and insecticide studies were done, but the complex of beetle species and their attraction to paraquat-treated trees was also possibly quite different.

Three insecticides, BHC, Dowco 214 (Reldan--the methyl ester of Dursban), and Dursban were tested in three 23-year-old loblolly pine (Pinus taeda L.) plantations. Each was applied at concentrations of 0.5 and 1%. BHC was the standard of comparison because of its past use, and because another compound was needed that would protect trees as well as BHC. If Dowco 214 and Dursban are equally effective, Dowco 214 is preferable because of its lower mammalian toxicity (LD₅₀ 2140 mg/kg to the rat, as opposed to 163 mg/kg for Dursban).

Within treatment blocks, one row was assigned to each of the following treatments: (1) 5% paraquat on wound, insecticide applied; (2) 2% paraquat on wound, insecticide applied; (3) 5% paraquat on wound, no insecticide; (4) wounded, no insecticide applied; and (5) control (no wound or paraquat, insecticide applied).

Trees were prepared for paraquat treatment by removing a 1-inch-wide strip of bark from 1/3 of the tree's circumference with a rotary bark hack. Five ml of paraquat (2% or 5%) were applied to the wound. Paraquat was applied with a steel and plastic syringe that controlled the dosage to the nearest 0.5 ml. Trees were treated with paraquat and sprayed with insecticide on the same day. A similar group of trees were treated in the Winter of 1976 and in the Spring of 1977.

Trees were examined after 1 week and then monthly through 6 months. At each inspection the newly infested trees per row were counted.

In the Summer treatment all three insecticides at both concentrations protected the treated trees quite well. There was little difference between the 0.5% and 1% concentrations in number of trees attacks. The 0.5% concentration of Dowco 214 which had the least mammalian toxicity was thus adequate according to the summer test. (See Moore Appendix A)

In the Fall treatment all chemicals greatly decreased insect attacks but Reldan and BHC appear to be superior to Dursban. In the Spring treatment all insecticides were effective with little difference in chemicals 3 months after treatment.

The total number of trees attacked by insects 3 months after treatment was least for the Winter treatment (27 trees) and greatest for the Summer treatment (378) trees and intermediate for the Spring treatment (138 trees).

Insect infestation in the Winter treatment increased rapidly 5 months after treatment but 6 months after treatment the total insect infestation was still greater for the Summer treatment (419 trees) than for the Winter treatment (288 trees). Data for 6 months after treatment are not yet available for the Spring treatment.

The study is still in progress.

EFFECT OF TREATING NORTHERN AND
WESTERN CONIFERS WITH PARAQUAT TO INDUCE LIGHTERING

(FPL STUDY NO. 2-74-2)

This research was performed by the Forest Products Laboratory (FPL) in cooperation with the Southeastern Forest Experiment Station who treated most of the trees (Study No. 1501-4 reported under Task IV of this report). The work was supported in part by a grant of \$25,000 from ERDA via the Southeastern Forest Experiment Station awarded December 23, 1975. Receipt of this grant enabled FPL to hire additional staff to accelerate progress of this study. It also helped provide justification for FPL to give a \$21,000 extra-mural grant to the University of California Forest Products Laboratory, on September 8, 1976, to extend the species range of the study to include western white, jeffrey and sugar pines.

Analyses were performed on samples of 10 northern species and 7 western species as presented in Table 7. In summary, the sapwood of all the pines becomes enriched in oleoresin of normal composition subsequent to paraquat treatment. However, none of the other Pinaceae species responded to an extent that holds commercial potential. Of conifers aside from Pinus, the spruces respond best. Results have been published in the following publications, some of which predate the grant:

Zinkel, D. F. 1975. Research in progress at the Forest Products Laboratory in induced lightwood formation. Proceedings of the Lightwood Research Coordinating Council Annual Meeting. 1/22-23/1975. pp 25-29.

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European conifers--Scotch Pine and Norway Spruce. Wood Sci.
(In Press).

The cooperative phase of the research is finished. Future papers on the Northern and Western conifers will deal mainly with the oleoresin in normal trees although they will usually incorporate the data already presented and published at the Lightwood Research Coordinating Council meetings.

Table 7.--Northern and Western Species treated with
paraquat to test for lightwood formation

<u>Northern Species</u>	<u>Western Species</u>
Jack pine	Limber pine
Red pine	Lodgepole pine
Eastern White pine	Ponderosa pine
Scotch pine	Douglas-Fir
Eastern hemlock	Western white pine
Tamarack	Jeffrey pine
Balsam fir	Sugar pine
Norway spruce	
Black spruce	
White spruce	

THE BATTELLE REPORT: FEASIBILITY OF OLEORESIN

SUBSTITUTION FOR PETROCHEMICALS

Early in the planning stages of this cooperative venture with ERDA, our Station Director, Dr. J. B. Hilmon, and the representative of ERDA-DBER, Dr. J. B. Hanson, agreed that funds should be used in an investigation to determine the technical feasibility of substituting oleoresin-derived chemical feed stocks for certain uses now wholly dominated by petrochemical sources. This study was not to be an economic analysis. To pursue this, SEFES entered into a research contract with the Battelle Memorial Institute effective January 15, 1976. ERDA-DBER funds in the amount of \$43,427 financed this Battelle study. Dr. Duane F. Zinkel of the Forest Products Laboratory acted as SEFES representative for this grant, and the principal investigator for Battelle was Dr. Theodore J. Collier.

A copy of the Battelle report constitutes Appendix 6 of this progress report. The following summary is abstracted from that of Dr. Collier's:

This study was undertaken by Battelle's Columbus Laboratories (BCL) to determine the feasibility of substituting oleoresin for petrochemicals. Sources of information were the USDA Forest Service SEFES and Forest Products Laboratory, published literature, BCL files, BCL staff specialists, industry and trade associations.

During the course of the investigation, several compounds or areas came to light that appeared promising for rosin. They are as follows:

Terephthalic and trimellitic acids--attractive if crude oil goes to \$35 to \$40 per barrel

Alkyd and polyester resins
Polyamide and polyimide resins
Polyurethane foams and coatings
Synthetic lubricants.

Polyurethane foams can be made with formulations of rosins or tall oil. These formulations yield foams of reasonably good properties. However, further work would have to be done to perfect them. The market for urethane foams is large and would present a logical place for oleoresin material.

Of the items listed, synthetic lubricants is the one that is most theoretical, but market size, price of final product (\$3.50 to \$5.00 per quart) and a definite petroleum substitution make the concept attractive.

Turpentine, the other major component of the oleoresin, would be brought into a more stable supply situation with the use of paraquat. The increased and reliable quantity would make use of turpentine and its derivatives in some markets, such as pressure-sensitive adhesives, more certain: erratic supplies and prices have caused pressure-sensitive adhesive manufacturers to use petrochemical substitutes.

Areas of applicability for turpentine use are as follows:

Motor fuel--a small but incremental substitution for petroleum

Adhesives--a growing market. Turpentine could have a larger share if supply and price were steady

Terephthalic acid--an old idea that is becoming more attractive with new technology and higher petroleum prices

Isoprene--demand is increasing. Turpentine could supply incremental amounts of isoprene, substituting for petroleum.

This concludes Collier's summary.

We had planned to follow up this work with more research at the Forest Products Laboratory. It is most important to find new and/or expanded uses for the greatly increased oleoresin production that we may reasonably expect will result from the induced lightwood discovery. Toward financing this and other critical research we had asked for \$500,000 for fiscal year 1977.

RESEARCH COOPERATORS

Deserving foremost mention among cooperators is the Forest Management Group (U. S. Forest Service, R-8, SRP) at the Savannah River Plant. They have given support in ways too numerous to mention; without their wholehearted assistance our research program would have been difficult and certainly much less would have been accomplished. The Forest Products Laboratory, particularly Dr. Duane F. Zinkel, Dr. John W. Rowe, and Dr. Karl E. Wolter, have done an excellent job with the Northern and Western Conifers work and also supplied assistance on many other occasions.

The ERDA Savannah River Plant Operations group, Mr. Nat Stetson and his staff, particularly Dr. Elizabeth J. Cahoon and Stephen R. Wright, have shown a continuing strong interest in our research goals and have given unstinted help and support. We have had a similar gratifying response from the Savannah River Ecology Laboratory (University of Georgia) and the DuPont Savannah River Laboratory.

The Lightwood Research Coordinating Council (LRCC) was a Forest Service invention. It was organized in 1974 as an organization to encourage rapid development of lightwood research. All the officers past and present are from private industry; we act as ex officio members of the executive committee. Their primary interests are in field treatment techniques, investigation of problems in extractives recovery, and prompt accumulation of data to support EPA labeling of paraquat for use in lightwood production. They have organized three annual meetings at which many research papers were presented, and these

were edited by the Forest Service into Proceedings each year and published. At least 80 percent of the publications in existence pertaining to lightering are found in LRCC Proceedings. A fourth LRCC meeting is planned for January 1978. Copies of the 1977 Proceedings should be available in September. A copy of the 1976 Proceedings is included in this report as Appendix B. It is included for three reasons: 1) as an example of the sort of research we encourage through the LRCC; 2) several papers directly resulting from ERDA sponsorship are found therein (see bibliography, next section); 3) and because we have contributed data, reviews, or research information toward at least one third of these papers. By working through the LRCC, our Research Work Unit has cooperative agreements with 25 industrial corporations. They were also most helpful in locating special cooperators for our Task I research (previously discussed in this report).

The LRCC has sponsored two south-wide lightwood studies which were designed and coordinated by our work unit. One of the plots of the most recent of the two was installed by us on the Savannah River Plant. The kinds of results obtained are illustrated in the Progress Report for this study, "The Second LRCC Standard Experiment for Lightwood Induction in Southern Pines," given in total in Appendix D and summarized below:

We cooperated with 19 pulp companies and TVA to conduct a standardized lightwood induction study in pine stands dispersed through 13 Southern States. This was done to increase efficacy data of geographic range and low paraquat concentration, to support application for an EPA label for paraquat use to produce lightering. Of these 20 stands, 15 were loblolly and 5 were slash

pine. At each location, 25 trees were treated with 2 percent paraquat sprayed on a bark streak, and their yields of rosin and turpentine were compared with yields from 25 untreated trees. Nine months after treatment, treated loblolly pines yielded 96 percent more rosin and 159 percent turpentine than untreated trees, and treated slash pines yielded 128 percent more rosin and 172 percent more turpentine than did controls. Turpentine composition was altered by paraquat treatment in both species. Insect activity differed greatly among locations, but except in one stand damaged by fire, only 3 of the treated trees died.

The Pulp Chemicals Association has shown much interest in our lightwood research and has helped on several occasions to further this research by encouraging member companies to cooperate with us in specific studies. Cooperative pilot scale studies on the Savannah River Plant are partly the result of their efforts. The Association has invited Principal Investigator Jack Stubbs and Donald Roberts (leader of our Olustee team) to present papers at three technical committee meetings and encourages their attendance at all technical committee meetings. Last year they organized a lightwood subcommittee of the technical committee to more effectively follow progress in lightwood research and development.

Paraquat treatment application ought to be very amenable to mechanization, especially in the orderly tree rows of plantation stands. Toward this end we have dealt with the Research Work Unit "Engineering Systems for Intensive Forest Management" of the Southern Forest Experiment Station (USDA Forest Service). A tractor-mounted device for applying bark streaks was developed

and a prototype was constructed. Cuts in personnel and funding have halted this work.

We have also worked closely with Dr. Edward A. Brass, Director of Research and Development, Homelite Division of Textron, Inc. toward developing a gasoline powered, light weight tool for paraquat injection. Homelite is one of the largest chainsaw manufacturers in the world; they have long experience in light weight engines and have a broad array of them in production. Their design of this injection tool incorporates some very ingenious features. We are continuing to cooperate with them, and hope to be able to test prototype models by January 1978.

Recently we have contacted the USDA Agricultural Research Service Equipment Development Center at Athens, Georgia. They have an interesting prototype machine for harvesting peaches that has features of interest toward developing a machine for certain paraquat application techniques. We have had informal discussions of the funding required, and plan to further pursue this idea.

RESEARCH DISSEMINATION

This, the final section of our progress report, is in the opinion of the author the most important. Research progress must appear in the literature. In the Bibliography below are listed 22 published papers that were made possible either wholly or partially by ERDA funds. The Bibliography also shows where reprints of each are to be found, i.e. in Appendices A or B. Of these 22 publications, two relate to Task I, six to Task IV, seven to Northern and Western Conifers, one to the Battelle Report, two to Insect Control Research, and four others are of a more general nature.

Following the Bibliography is a list of six papers presented but not published. As the footnote there indicates, many of the publications of the Bibliography were also presented as papers to various groups.

Our general paraquat research discoveries have also been reported in six or eight newspapers, including the Christian Science Monitor and the Wall Street Journal. Specific mention of ERDA involvement in this research has appeared in at least three newspapers and in a local television interview of Jack Stubbs. Also, paraquat research tied with ERDA has appeared as news items in the Chemical Engineering Journal, the Naval Stores Review, and according to hearsay in several trade journals (the source of these news items is somewhat mysterious; apparently reporters or audience members where papers were presented are responsible). Battelle has recently prepared a news release of their study for us, and in it ERDA is given proper recognition.

Finally, on November 15, 1976 we assembled and sent to ERDA, Division of Biomedical and Environmental Research, a group of 8 color slides and 4 prints of pictures to be used in preparation of an information booklet on major programs of the Environmental group. These showed methods of paraquat and BHC application, lightwood produced and methods of laboratory analysis for rosin and turpentine.

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APPENDIX A

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FEASIBILITY OF PETROCHEMICAL SUBSTITUTION BY OLEORESIN^(a)

Theodore J. Collier^(b)

Abstract--Paraquat causes an increase in the formation of oleoresin in pine trees. The total quantities of oleoresin capable of being produced by this means are small as compared to petrochemical usage. At present, the cost of petroleum does not permit widespread expansion of oleoresin substitution. However, with the possible increase in oleoresin yield combined with increasing petroleum prices, substitute chemicals made from oleoresin could become more attractive. Since oleoresin is a hydrocarbon, it is technically feasible to derive compounds from it that are identical with those derived from petroleum.

The eventual depletion of petroleum reserves in the United States has prompted searches for other sources of material for both energy and chemical uses. Oleoresin represents a natural resource of renewable nature which might be a potential source of chemicals that could substitute for chemicals now derived from petroleum. There still exist substantial markets for oleoresin derivatives. Rosin and turpentines, whether derived from oleoresin, paper pulping (tall oil and sulfate turpentine), or extraction (wood rosin and turpentine) have found uses in industry. Of these three sources, kraft pulping of southern pines is now the major one for rosin and turpentine in the United States.

Rising petroleum costs coupled with the recent discovery of methods of stimulating the production of oleoresin in the living tree caused a reconsideration of the use of oleoresin as a broader base for chemical materials.

METHODS

During the course of this study, numerous sources of information were used. Literature was studied that included texts, published articles, patents, abstracts, and current news. Personal interviews were held with selected members of industry, trade associations, a consultant, and the United States Department of Agriculture's Forest Service Laboratories. Additionally, BCL files were examined and pertinent information included. Staff specialists of BCL were used in the course of the study to help develop possible uses for oleoresin as a petrochemical substitute. Although rosin and turpentine have been around for many years, and industry and the United States Government have done much work to find uses for these materials, much thought was put into the area of new uses and petrochemical substitutes. No laboratory work was done by BCL to prove or disprove concepts taken from literature and records.

(a) This is based on a study performed under a grant to Battelle from Forest Products Laboratories, USDA.

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By comparison with the gum collecting operation, the paraquat treatment procedure should be less costly overall. The herbicide treatment requires essentially two trips to the tree. One to treat the tree, and the other to cut the tree. The gum collecting operation requires multiple visits to each tree.

The paraquat herbicide is a highly toxic material and proper precautions must be used to protect workers during application. A recent listing, in the June 14, 1976 issue of Chemical & Engineering News, of 45 compounds, that may be too dangerous to use, included paraquat. Although the list is tentative, EPA was scheduled to issue rebuttal presumptions against the first compounds starting in August, 1976.

Rosin and turpentine are obtained from three sources, oleoresin from the living tree (gum), stump wood (wood), and wood pulping (tall oil rosin and sulfate turpentine). In the United States, the major source is the pulping operation.

The decline in gum rosin and turpentine has been due to the shortage of the kind of labor required to cut the faces on pines and gather the gum drippings. The decline of wood rosin and turpentine is due largely to economics of the recovery of stumps. The farther away the stumps are from the extraction plant, the less attractive they become economically. While these two sources of rosin and turpentine have been declining, the pulp and paper industry has been increasing the output of rosin and turpentine as a result of increased pulping capacity, increased demand, and improved recovery methods. In order for rosin and turpentine output in the U.S. to increase greatly, a method of increasing the available oleoresin will have to be put into use.

Paraquat treatment of pine trees increases the yield of oleoresin in pine trees by 2 to 5 times the untreated tree yield. If the tree treatment program grows to its practical limit, it is felt that about 30 percent of the tree population may eventually be treated.

To make a conservative estimate of the increased rosin that would be available, let us consider yields of the three rosins for the crop year 1975-1976 to be as follows:

Gum	37,130,940 pounds
Wood	186,196,400 pounds
Tall oil	<u>343,714,800 pounds</u>
Total	567,042,140 pounds

If the rosin were extracted in the pulping operation, which it probably would be at first, then the initial increase would be based on the larger yield of tall oil from the pulp and paper industry.

Assume a level of increase of twofold above normal with paraquat treatment. This twofold increase above normal coupled with a 30 percent limit on tree treatment would yield the following:

Yield of 343,714,800 pounds tall oil rosin from 100% untreated trees.
Yield from 70% of untreated trees: $0.7 \times 343,714,800 = 240,600,360$ lb
Yield from 30% of treated trees: $0.3 \times 3 \times 343,714,800 = 309,343,320$ lb
Total of tall oil rosin 549,943,680 lb

549,943,680 lb - 343,714,800 lb = 206,228,880 lb increase in tall oil rosin yield.

The total yield for 1975-1976 crop year for gum and wood rosin, indicated above, was 223,327,340 pounds. The increase of 206,228,880 pounds from the 30 percent paraquat treatment is nearly equal to these two sources. Except for specialty resin, produced in small quantities from gum and stumpwood sources, it is believed that the gum and wood rosin industries as we know them today would cease to exist.

If it is assumed that the petroleum supply were cut off, depleted, or became prohibitively expensive, paraquat treatment of all available trees as a means of bolstering chemical material supplies might be accomplished. The yield of rosin, based on the same method of calculation as above would yield 1,031,144,000 pounds through the current pulping processes. This is a conservative estimate.

The gum naval stores has been declining for many years and is even now a minor part of the total rosin production. This industry would certainly disappear earlier with the advent of paraquat treatment. The wood naval stores, on the other hand, can adapt to the use of paraquat as a means of increasing rosin formation. This transition would have to be anticipated, however, with sufficient lead time to permit the wood naval stores companies to acquire forested areas, either by lease or tree purchase and to treat the trees with paraquat. With paraquat treated wood available to the stumpwood processor, it will become uneconomical to seek out and pull stumps. Additionally, the quality of rosin and turpentine extracted from the treated wood should be equal to gum rosin and turpentine in many ways.

ROSIN

The production of rosin in the U.S. has been declining for several years. The use has also been declining. One of the largest declines in rosin usage has taken place in its use as a paper sizing agent. The decline started in the late 1940's when maleic anhydride or fumaric acid modified rosins were used as fortified paper sizes, which were more efficient than rosin. In the 1960's and 1970's neutral pH sizing and surface sizing caused a growth in synthetic substitutes. Recently, rosin emulsions, rather than the traditional paste rosin soaps, have been used with some promise, and have shown to be more efficient under certain conditions. The first year the use of rosin for paper sizing showed a significant drop was 1973, perhaps due to all of the above factors. The reversal of the trend of reduced consumption of rosin by the paper industry is not indicated⁽⁸⁾.

Rosin Utilization

The use of rosin in some areas has been well investigated and in spite of the encroachment of petroleum resins, resins based on rosin remain the mainstay in inks, hot-melt and certain pressure-sensitive adhesives, various coating formulations, and paper sizes.

In searching the area of oleoresin substitutes for petrochemicals, it is quickly concluded that, although it is technically possible to derive the simpler compounds such as benzene and phenanthrene from rosin, it is not economical to do so unless the cost of petroleum is multiplied many times its current level.

There are areas in which rosin has not been replaced by petroleum derivatives. Two of these are paper sizing and emulsion aids and tackifiers for rubber. The rosin maintains its position in areas like these because of the chemical characteristics at reasonable cost.

If, on the other hand, petroleum prices rose high enough, it might be conceivable that rosin could find uses that are now claimed by petrochemicals. With the current price of crude oil at \$11 to \$12 per barrel, there is little or no incentive to use oleoresin materials for petrochemical substitutes. Company sources indicate current rosin prices to range from \$0.17 per pound for tall oil rosin to \$0.25 per pound for gum rosin. The price of crude tall oil is \$125 per ton or \$0.0625 per pound. Compared to these prices, a pound of crude petroleum costs about \$0.034 to \$0.036 per pound.

Let us assume that the price of petroleum rose drastically to, say, \$35 to \$40 per barrel. This would mean \$0.10 to \$0.13 per pound crude oil. Assuming the same ratio for the prices of petrochemicals such as terephthalic acid and trimellitic anhydride, we would find the prices of these materials advanced from the current \$0.21 per pound and \$0.45 per pound⁽⁹⁾ to \$0.64 to \$0.73 per pound and \$1.37 to \$1.56 per pound, respectively. At these price levels, it might become economically feasible to produce these, or similar materials from rosin. Other compounds produced from rosin become more attractive as the price of crude oil rises.

Resins

The use of fumaric acid or maleic anhydride have been noted to prepare oil modified alkyd type surface coating vehicles from oleoresin⁽¹⁰⁾. Although the fumaric or maleic adduct is not obtained in pure form, it nevertheless functioned in a satisfactory manner. With the correct choice of tree as the source of the oleoresin, good yields of the rosin suitable for the Diels-Alder reaction can be obtained.

Loblolly pine, the major pine tree to be considered for treatment with paraquat, yields nearly 80 percent⁽¹¹⁾ of the Diels-Alder reactive rosin in the total rosin content. If the pure or nearly pure forms of the fumaric or maleic adduct is of importance, then perhaps the separation and purification of these materials should be considered as a research program.

Rosin acids can be incorporated into polyesters. One method is by decarboxylation with a variety of catalytic agents, including orthophosphoric acid. The rosin oils, as they are called, have been reacted with fumaric acid and also maleic anhydride to yield dicarboxylic acids. These acid components, when reacted with glycols, yield polyesters. Styrene dilution of the polyesters produce combinations that can be cast in a mold and cured with heat and benzoyl peroxide as the catalyst⁽¹²⁾.

Other uses of rosin are indicated from patents and literature. Poly (amide-imides) can be prepared from maleopimaric and diamines for use in ink manufacture^(13,14). Also, maleopimaric and amino alcohols yield poly (ester-imides) suitable for use in inks⁽¹⁵⁾.

Urethane Foams

Crude tall oil has been evaluated in rigid polyurethane foams⁽¹⁶⁾. The foams derived from the use of crude tall oil, along with other components such as an ethylene diamine derivative and diphenyl methane diisocyanate, showed promise of yielding formulations with reduced raw material costs. Although the foams have shown good strength and density characteristics, dimensional properties under storage at room temperature conditions have been inconsistent. Further research in improving this property would have to be performed before the foams would be commercially acceptable.

Rosin derivatives have been shown to function in both rigid polyurethane foams and polyurethane coatings. The rigid foams were formulated to include rosin acid derivatives with increased functionality^(17,18). The alkoxylation of the hydroxymethylated rosin acids were used to make both one-step and two-step rigid urethane foams⁽¹⁸⁾. Formulations were evaluated that yielded rigid foams of good quality when judged for density, compressive strength, thermal conductivity, porosity, water absorption and friability. The comparison between foams, one produced from commercially available materials, and one produced using a rosin derivative, is shown below⁽¹⁸⁾.

Glycol Component	Density lb/ft ³	Compressive Strength PSI; Yield %	Thermal Conductivity BTU in/hr ft ² F	Friability % wt loss/10 min	Water Absorption lb/ft ²
Hexol LS 490 ^(a)	2.09	12.2; 7.6	0.163	3.08	0.0421
Rosin VI b ^(b)	1.97	12.3; 8.4	0.183	2.18	0.0364

(a) Commercial glycol manufactured by Union Carbide Corporation.

(b) Ethylene glycol ester of formaldehyde-modified rosin.

This formulation is a one-step foam preparation. The experimental "Rosin VI b" produced a foam with properties equal to the foam produced from Hexol LS 490.

Methods of producing diols from rosin acids are outlined in several publications^(19,20). These diols have not only been demonstrated to function in polyurethane foams but in polyurethane coatings as well. The coatings produced did not represent the best obtainable, but they were sufficient to prove the utility of rosin derivatives in polyurethanes.

The importance of urethane foams is pointed out by the fact that in 1975, flexible urethane foams markets used 1044 million pounds, and 340 million pounds were placed in the rigid foam markets⁽²¹⁾. This is a total of 1.384 billion pounds. For 1976, the total consumption of polyurethanes is estimated at 1.68 billion pounds. By 1980, the requirements for the polyurethane market is estimated to be about 2.37 billion pounds.

This sizeable market is one in which oleoresin could play a role because of lower cost, as well as availability of materials. It would release petrochemical materials for other uses or fractionally decrease petrochemical demand.

More research will have to be done with oleoresin and rosin in order to produce products with specified properties. There should be time to achieve this since it will be several years before the paraquat treatment program will be producing increased, harvestable yields of oleoresin.

Synthetic Lubricants

An area that could open a new use for oleoresinous materials is in the field of lubrication. The new synthetic oils are lubricants made up of compounds that are not the conventional mineral oils. The use of crankcase oils in 1975 totaled 5.37 billion pounds. By 1985, this is expected to increase to 5.50 billion pounds. The synthetic lubes will have chemical requirements of 360 million pounds by 1985⁽²²⁾.

When considering a suitably sized market or product demand into which oleoresin materials could fit, synthetic "oils" or lubes could be considered of the right size. The market is not so large as to require all of the rosin produced by paraquat treatment, but it is sufficiently large to require a considerable portion of the output.

Conventional mineral oils range in price from \$0.50/quart to \$1.00 quart. Synthetic automotive lubricants range in price from \$3.50/quart to \$5.00/quart and up⁽²³⁾. Increasing operating temperatures of newer automobile engines cause greater demands on lubricating oils. The synthetics are capable of withstanding greater engine temperatures for longer periods of time than mineral oils. These capabilities allow the engineers to design more efficient engines, operating at higher temperatures. Additionally, the much longer period between oil changes, 25,000 miles for synthetic oil versus 4,000 to 7,500 miles for conventional oils, permits less raw material to be used.

The synthetic lubricants are capable of low temperature service. With pour points as low as -85 F they are serviceable under Arctic conditions, while the low temperature performance of petroleum oils is generally limited

to -15 F because of high viscosity and wax formation⁽²⁴⁾. This low temperature capability permits a broader range of use possibly including the military.

Four basic types of synthetic lubricants have been developed for automotive use. These types are esters, poly- α -olefins, alkylated benzenes, and polyalkylene glycols. The polyalkylene glycols, made by Union Carbide, were test marketed in the 1950's, but are not presently sold.

The poly- α -olefins are synthesized from simple olefins extracted from petroleum. The alkylated benzene derivatives are also constructed from petroleum. Ester type lubricants are usually produced by blending of two different esters, diesters, and polyol esters. The diesters are synthesized from dibasic fatty acids and monohydric alcohols and the polyol esters are made from short chain monobasic fatty acids and polyhydric alcohols. A wide range of properties is possible by varying the types and ratios of esters.

Esters are derived presently from natural gas. However, the base materials could come from such sources as animal fats and coal. There is no technical barrier that would prevent the development of lubricant esters from rosin acid sources. Also, it may be possible to construct an alkylated benzene type of lubricant from the turpentine portion of oleoresin.

The technical details of such developments are limited only by the imagination and ability of the organic chemist. It is believed that with the increasing rate of depletion of petroleum reserves and the rising oil prices, research done in the area of using oleoresin to produce synthetic lubricants would be timely. Additionally, the use of oleoresin materials for this purpose would decrease alternative sources of chemicals used in synthetic lubricants.

Mellitic Acids

In some previous sections rosin has been treated as a chemical material to be used in formulations in modified form. However, rosin can be considered as a raw material from which other chemicals can be made with which rosin has no identification. An example of this is the synthesis of hemimellitic and trimellitic acids according to the following scheme.

The formation of the hemi- and tri-mellitic acids has been noted in the literature⁽²⁵⁾. These tricarboxylic acids may be considered as raw materials for polyesters, polyamides, and polyimides.

The mellitic acids, being multifunctional in nature should lend themselves to the production of polyesters, polyamides, polyimides, and combinations of these. The ring structure would lend itself to rigidity and resistance to pyrolysis, and therefore temperature resistant polymers would result. A particularly resistant combination should result from trimellitic acid and paraphenylene diamine. By extension of the technology, it may be also possible to economically produce terephthalic acid from rosin.

TURPENTINE

Of the two primary components of oleoresin, rosin is produced in the larger quantity. It is realized, however, that turpentine production with the paraquat treatment also increases drastically. For instance, according to trials with paraquat, analysis of the treated trees and controls indicate an increase of about 220 percent in the turpentine level over untreated trees⁽²⁶⁾. Although

the number of trees used in the determination was limited and only one area of the country was used, it is indicative of the increase in turpentine yield possible with paraquat treatment.

The quality of the turpentine produced in the trees treated with paraquat does not appear to be jeopardized. Although there may be some minor differences in the ratios of the components such as α - and β -pinenes and camphene, there seem to be no major dislocations. It is, therefore, projected that turpentine quality will be high. This will be of particular advantage to the producers of steam distilled (wood) turpentine, since few of the constituents will be lost by oxidation or evaporation as they are in the aging of stump wood.

To estimate the increase in turpentine that would be available after paraquat treatment, let us consider the 1975-1976 crop year yields for the three types of turpentine.

Gum	1,034,500 gallons
Wood	2,071,000 gallons
Sulfate	<u>19,274,000</u> gallons
Total	22,379,500 gallons

As is projected with rosin, the first increase in turpentine yield due to paraquat treatment would probably come from the pulping of pine wood by the pulp and paper industry.

Assuming a two-fold increase above normal yield, by using paraquat treatment, and a 30 percent limit on tree treatment, the following yield might be expected.

Yield of 19,274,000 gallons sulfate turpentine from 100% untreated trees

Yield from 70% of untreated trees: $0.7 \times 19,274,000 = 13,491,800$ gal

Yield from 30% of treated trees: $0.3 \times 3 \times 19,274,000 = \underline{17,346,000}$ gal

Total Sulfate Turpentine 30,838,400 gal.

$30,838,400 \text{ gal} - 19,274,000 \text{ gal} = 11,564,400 \text{ gal}$ increase in sulfate turpentine yield.

The total yield for 1975-1976 crop year for all three types of turpentine, as indicated above was 22,379,500 gallons. The increase in yield projected for pulping of paraquat treated pine wood is 11,564,400 gallons or 51.7 percent increase as compared to total untreated production.

As sources of treated pine wood become available to the processors that use stumpwood at present, yields of steam distilled (wood) turpentine will increase rapidly. By using wood from paraquat treated trees, these processors gain turpentine usually lost in the aging of the stumps traditionally used in the steam distilling process.

Turpentine as Fuel

Turpentine is somewhat like rosin in that it has inherent chemical properties that make it useful. It is a liquid and could be easily burned for fuel, although it rarely has been. The energy from a gallon of turpentine is about 130,000 to 140,000 Btu, and the energy from a gallon of gasoline is about 120,000 to 130,000 Btu. The total amount of turpentine produced by paraquat treatment could reach or exceed 50,000,000 gallons per year. Consider that the consumption of petroleum in the United States is about 3,000,000 barrels (126,000,000 gallons) a day as gasoline and about 15,000,000 to 16,000,000 barrels a day totally. Additionally, the current wholesale price of gasoline is \$0.38 to \$0.40 per gallon, and the current price of crude sulfate turpentine is \$0.45 to \$0.50 per gallon. Under these conditions, turpentine is not attractive as fuel.

In spite of the fact that approximately 50,000,000 gallons of turpentine could be produced per year, which is about 0.1 percent of the gasoline burned each year, a private research organization has allegedly developed and applied for a patent on a process to produce a motor fuel from turpentine to replace gasoline. High road mileage is claimed for the fuel. Even though the contribution is a small percentage of the total fuel requirements, such efforts should not be overlooked.

Adhesives

An example of the growing market for turpentine products is in the adhesive area. In 1970 the terpene resins accounted for 15 percent of turpentine consumption. The growth rate was 10 percent per year⁽²⁷⁾. By 1974, the use of pressure-sensitive adhesives had reached 250,000,000 pounds per year. This included all resin components, tackifiers, and modifiers⁽²⁸⁾. The growth trend, according to industry sources, continues today. Adhesive coated roll label stock is currently growing about 24 percent per year, and sheet label stock is growing at about 15 percent per year.

Industry sources indicate the trend is toward petroleum resins and away from turpentine derivatives because of the unsteady supply of the latter. However, the terpene resins are excellent and preferred, but the supply and price vary too widely for dependence. This trend is borne out by notations in publications on additional capacity⁽²⁹⁾ or new product lines⁽³⁰⁾ for synthetic terpene resins. The use of paraquat for increasing the amount of oleoresin could be the needed solution to the supply dependence problem in the area of terpens.

Terephthalic Acid

Terephthalic acid forms the basis for the resin from which polyester fibers and films are made. The fibers market consumes over 2.9 billion pounds of terephthalic acid per year, and the film market consumes over 200 million pounds per year.

The fibers find their way into apparel either alone or in blends with other fibers such as cotton and wool. Wrinkle resistant and permanent press types of fabrics result from the use of these man-made fibers. The polyester fibers are also used in cordage, which finds application in tire cord and tow lines. The fibers are also used in non-woven and non-spun applications such as filters and thermal insulation.

The films find use in such items as photofilms, drafting base, audio and visual magnetic tapes, electrical insulation, graphic arts and packaging.

Generally speaking, the industry prefers to work with dimethyl terephthalate rather than terephthalic acid. This is due to the fact that a very high purity is required for fiber manufacture. Terephthalic acid is more difficult to purify than dimethyl terephthalate. The polyester is produced from the dimethyl terephthalate and a glycol, usually ethylene glycol. The polyester may also be produced from terephthalic acid and glycol. However, when dimethyl terephthalate is used, methyl alcohol is recovered. This can again be used to esterify more terephthalic acid for the purification process.

Terephthalic acid may be produced by converting pinene to dipentene, thence to p-cymene and finally to the acid⁽³¹⁾. Claims of 70 percent conversion of p-cymene to terephthalic acid have been made by Russian scientists⁽³²⁾. The process includes vacuum distillation of p-cymene from the sulfate turpentine followed by oxidation of the p-cymene to terephthalic acid by use of 20 atmospheres pressure, 150°C with air in acetic acid solution containing 0.001-0.006 mole/liter cobalt naphthanate, and stirring in a titanium reactor.

It is true that the first commercial terephthalic acid was produced in England from p-cymene, but technology still advances. Terephthalic acid is now produced from petroleum derivatives. With the proper research, the technology could be advanced to make the production of terephthalic acid from turpentine economically attractive, with increasing petroleum costs. Of course, the amount of terephthalic acid produced from turpentine would be small as compared to the 3.43 billion pounds produced in 1974, but it would be an incremental saving of petroleum. Additionally, 2.34 billion pounds of terephthalic acid were produced as dimethylterephthalate in 1974.

An interesting route to terephthalic acid is by the Henkel reaction⁽³³⁾. The reaction allows a rearrangement or disproportionation to take place, producing terephthalic acid (potassium salt) as the stable product. The catalyst is cadmium oxide or a cadmium salt and potassium benzoate.

This reaction is applicable to pure or mixed benzene carboxylic acids. It could prove to be an additional source of terephthalic acid since the mellitic acids can be produced from rosin. An illustration of the reaction using mellitic acids follows.

Isoprene

Isoprene is an important building block for elastomers. Natural rubber is a natural elastomer based on isoprene. The polymerization of isoprene to synthetic rubber, polyisoprene, is of two general types, either CIS- or trans-configuration.

The largest use of polyisoprene is in tires for automobiles and trucks. Over half of the polyisoprene consumed in the U.S. goes into this use. A distant second in the usage of polyisoprene is in mechanical goods.

Isoprene is produced only in relatively small quantities in the cracking of petroleum under mild conditions. However, when harsher conditions are used, as in naphtha cracking, quantities of isoprene are produced that are economical to recover. Isoprene is then extracted directly from the product stream.

Other processes for obtaining isoprene are:

- Isoamylene extraction and dehydrogenation
- Propylene dimerization, isomerization, and pyrolysis
- Isopentane dehydrogenation
- Acetone-acetylene process
- Isobutylene-formaldehyde process.

The demand for isoprene has been increasing. With the increase in petroleum prices and depletion, it is increasingly more important to find new sources of this valuable monomer or to supplement supplies.

Isoprene is a basic building block of the terpenes. Turpentine can yield isoprene by producing dipentene from it and subsequently pyrolyzing the dipentene either directly⁽³⁴⁾ or over red hot platinum catalyst⁽³⁵⁾.

Since the reaction of converting isoprene to dipentene is reversible with the reaction of converting dipentene to isoprene, it is a logical assumption that reasonable quantities of isoprene could be produced from turpentine. Since the demand for isoprene is high, the conversion of turpentine to this material would relieve some demand on petrochemicals, even though the quantity would be comparatively small.

CONCLUSIONS

The following conclusions were reached as a result of this study.

- The amount of increase in oleoresin by paraquat treatment will represent a small fraction of the petrochemical requirements and a minuscule portion of fuel requirements
- Substitution of oleoresin components for petrochemical materials is technically feasible
- There are possible new areas for oleoresin components, such as synthetic lubricants and isoprene
- Growth regulators, with low toxicity, to develop oleoresin in pine trees are needed
- There already exist large possible markets for rosin and tall oil in urethane foams which could be realized with the refining of the chemical synthesis of the rosin foam components
- The use of turpentine in pressure-sensitive adhesives would increase if a steady supply and reasonably stable price could be established.

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DISCUSSION

General

Petroleum, being a fossil material, is limited in supply and is non-renewable within our current civilization. Depletion of fossil fuels, such as petroleum, is taking place at an ever increasing rate. Other feedstocks, for hydrocarbon sources, are being sought.

Oleoresin, a renewable resource material produced by pine trees, has been used to produce chemical materials of the hydrocarbon class for centuries. The two main chemical materials from this source have been rosin and turpentine. The amounts of material available from pine trees has not been significant enough to warrant attention as a petrochemical feedstock substitute. However, an announcement in the Naval Stores Review⁽¹⁾ gave reason to reconsider the possibility of using oleoresin as a substitute for petrochemical feedstocks.

Paraquat Treatment and Its Effect

The announcement in Naval Stores Review was followed by others^(2,3,4,5,6) of the increase in lightwood production in pine trees. The increased yield of oleoresin, causing lightwood formation was the result of treatment of pine trees with an herbicide called paraquat.

Treatment of pine trees is accomplished by treating an area from which the bark has been removed, usually about one inch wide and one third the circumference of the tree, with a dilute solution of paraquat. The herbicide can also be applied to trees wounded with axe frills, by direct injection under the bark by needle, or forced into the tree with a hammer device.

Once treatment of the tree has been accomplished, resinification or lightwood formation commences. A segment of the tree extending from the wound to the center of the tree, resulting in a pie-chaped, cross-section area, and extending up the tree for at least 15 feet⁽⁴⁾ is saturated. White pine has been found to saturate to heights of 40 to 50 feet⁽²⁾. Times for saturation are 1-1/2 to 2 years.

The oleoresin in the wood is obtained either by extraction or by pulping. The materials found to increase in quantity are turpentine and rosin. Fatty acids, removed in extraction or the pulping operation, do not appear to be increased by paraquat treatment. The amount of increase in the turpentine and rosin yields depends on the method of treatment, the extent to which the trees are treated, the length of time from treatment to harvest and other factors.⁽⁷⁾ Since paraquat is an herbicide, a balance must be found between the maximum amount of lightwood formation and tree kill. If overtreatment occurs, the tree is killed prematurely and the increased yield of oleoresin is not realized.

The development of the oleoresin within the tree is apparently linear relative to time after paraquat treatment. When the costs of labor and materials are considered for paraquat treatment, a tree will develop sufficient increased oleoresin in 3 to 5 months to pay for the treatment. The projected increase in value is \$0.50/cord/month.

EFFECTS OF PARAQUAT TREATMENT OF NORTHERN AND WESTERN CONIFERS

Anthony H. Conner, Marilyn A. Diehl, Hanna Wroblewska, and John W. Rowe^{1/}

Abstract.--Paraquat treatment induced lightwood in red, jack, Scotch, eastern white, lodgepole, ponderosa, and limber pine trees of the northern and western United States. Lightwood formation in these species could potentially increase the quantity and the quality of naval stores chemicals from these species that now provide only a small portion of the total U.S. naval stores production. Norway, black, and white spruce showed limited response to paraquat. No appreciable lightening was produced by treating eastern hemlock, balsam fir, tamarack, or Douglas-fir.

Additional keywords: Lightwood, oleoresin, tall oil, turpentine, Pinaceae, Pinus resinosa, P. banksiana, P. sylvestris, P. strobus, P. contorta, P. ponderosa, P. flexilis, Picea abies, P. mariana, P. glauca, Tsuga canadensis, Abies balsamea, Larix laricina, and Pseudotsuga menziesii.

Lightwood (oleoresin-soaked wood) that can be induced in pines by paraquat treatment (Komissarov *et al.* 1968, Roberts 1973, Roberts *et al.* 1973) is a potential source of additional naval stores chemicals. In the United States, lightwood induction in southern pines is being extensively evaluated by various laboratories. In other countries, paraquat-induced lightwood in Pinus sylvestris (Ranua 1975), P. pinaster (David *et al.* 1975), and P. radiata (Sioumis and Lau 1976) has been investigated.

Lightwood induction in conifer species growing in the northern and western United States has not been studied, although this induction could potentially increase the quantity and the quality of naval stores derived from these species. As an extension of their work on lightwood in southern species, Donald R. Roberts and William J. Peters of the U.S. Forest Service, Southeastern Forest Experiment Station, treated sets of northern and western conifers with paraquat placed into increment boreholes or ax frills (Table 1).

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Table 1.--Northern and western conifers treated with paraquat.

Species	Date	
	Treated ^{a/}	Harvested
<u>Northern species, Nicolet National Forest, Wisconsin</u>		
Jack pine (<i>Pinus banksiana</i> Lamb.)	6-21-73	5-25-76
Red pine (<i>P. resinosa</i> Ait.)	6-21-73	9-4-75
Eastern white pine (<i>P. strobus</i> L.)	6-22-73	5-26-76
Scotch pine (<i>P. sylvestris</i> L.)	6-22-73	11-18-75
Scotch pine (<i>P. sylvestris</i> L.) ^{b/}	10-19-73	11-18-75
Eastern hemlock (<i>Tsuga canadensis</i> (L.) Carr.)	6-21-73	5-29-74
Tamarack (<i>Larix laricina</i> (Du Roi) K. Koch)	6-22-73	12-10-74
Balsam fir (<i>Abies balsamea</i> (L.) Mill.)	6-21-73	9-30-74
Norway spruce (<i>Picea abies</i> (L.) Karst.)	6-22-73	11-19-75
Black spruce (<i>P. mariana</i> (Mill.) B.S.P.)	6-21-73	5-25-76
White spruce (<i>P. glauca</i> (Moench) Voss)	6-21-73	5-26-76
<u>Western species, Arapaho-Roosevelt National Forest, Colorado</u>		
Limber pine (<i>Pinus flexilis</i> James)	6-19-73	9-15-75
Lodgepole pine (<i>P. contorta</i> Dougl.)	6-19-73	9-15-75
Ponderosa pine (<i>P. ponderosa</i> Laws.) ^{b/}	6-19-73	9-15-75
Ponderosa pine (<i>P. ponderosa</i> Laws.) ^{b/}	10-17-73	9-15-75
Douglas-fir (<i>Psuedotsuga menziesii</i> (Mirb.) France)	6-19-73	9-15-75

^{a/} Treated with 5 millimeters of 1/4, 1, or 5 percent aqueous paraquat placed in a 10-centimeter ax frill. The solutions contained 0.1 percent Tween 20 wetting agent.

^{b/} Treated as described in footnote ^a except solutions were placed into an increment borehole.

Collaboration was established with the Southeastern Station to determine tall oil and turpentine contents of the paraquat-treated conifers because research on tall oil precursors in northern and western conifers was already planned at the Forest Products Laboratory.

A progress report on this research was presented at last year's Lightwood Research Coordinating Council Meeting (Rowe *et al.* 1976). The tall oil and the turpentine contents of all of the treated conifers have been determined; the final report is presented in this paper. The chemical composition of the lightwood tall oil precursors will be included in future publications on tall oil precursors from northern and western species.

EXPERIMENTAL

Species treated with paraquat, treatment methods, and dates trees were treated and harvested are given in Table 1.

After removing branches, trunks were cut into 1.5 meter sections starting 0.5 meter below the treatment site. The sections starting at the bottom were labeled A, B, C, etc. One section above any visible effect of the paraquat treatment was always studied. Pairs of adjacent 3-centimeter-thick disks were cut at 30-centimeter intervals from each section. Each pair consisted of a "research" disk used for chemical analysis and a "reference" disk used for visual observations. The reference disks were air-dried at room temperature for 10 to 14 days, sanded, and examined visually for lightwood formation, dead cambium, diminution in annual growth, and for the presence of blue stain fungi.

The research disks were immediately frozen and used for determining nonvolatile ether extractives (used as a measure of tall oil precursors) and turpentine. Wedges of lightwood and wood for use as controls were excised from each of the research disks. Where no visible lightening occurred, the wedge of wood behind the dead inner bark was taken as the lightwood area. The wedges of control wood were taken from unlighted areas 120° away from lighted areas and were free of resinous knots and other abnormalities.

The frozen wedges were chopped into 1- by 10-centimeter sticks, ground in a Wiley mill to pass an 8-millimeter mesh screen, and combined into lightwood and control wood samples from each section. For turpentine analysis a portion of this coarse sawdust was mixed with 1 percent aqueous sodium hydroxide, and the turpentine collected by steam distillation. Tall oil (nonvolatile ether extractives) was determined by extracting a portion of the sawdust with diethyl ether in a Soxhlet apparatus for 8 hours. The ether was evaporated, and the residue dried at 100° C in vacuo (15 mm Hg) and weighed. The percentages of tall oil, turpentine, and moisture were then calculated based on tall oil- and turpentine-free oven-dried wood weight.

Turpentine from lightwood and control wood was analyzed by gas-liquid chromatography (GLC) on 5 percent Carbowax 20 M using diethylcarbitol as an internal standard.

DISCUSSION

Our previous results for paraquat treatment have been published for the following species: Eastern hemlock (Kiatgrajai et al. 1976a), balsam fir and tamarack (Kiatgrajai et al. 1976b), and red pine (Rowe et al. 1976, Wroblewska et al. 1977).

The visual characterization of treated red pine, ponderosa pine, lodgepole pine, limber pine, Scotch pine, Norway spruce, and Douglas-fir was reported last year (Rowe et al. 1976). The characteristics of paraquat-treated jack pine, eastern white pine, black spruce, and white spruce are given in Table 2.

Distribution of tall oil and turpentine in red, ponderosa, and lodgepole pine was reported last year (Rowe et al. 1976). Tables 3 through 10 show these distributions for jack pine, Scotch pine, eastern white pine, limber pine, Douglas-fir, black spruce, white spruce, and Norway spruce.

Summarized in Tables 11 and 12 are the quantitative GLC analyses of turpentine from the lightwood and the control wood of the treated conifers. Detailed turpentine analyses from each of the treated trees of each species are available on request.

A zone of dead, necrotic phloem (inner bark) extended upward from the paraquat-treatment site in all of the treated trees. The cambium associated with this dead zone was also killed--no new wood growth occurred behind the dead phloem after treatment. The wood immediately behind the dead phloem was desiccated. Usually, the zone of dead phloem was associated with external resin exudation that extended up a tree. The height to which the dead zone extended increased as paraquat concentration increased. The dead phloem and the associated desiccated wood decreased in area as it extended upward and followed any spiral grain in the tree. Often, a zone of diminished wood growth extended beyond the zone of dead phloem. Blue stain fungi were usually observed within the desiccated wood, but was limited to the lower portions of a tree.

Although increases in tall oil (nonvolatile ether extractives) and in turpentine were observed in almost all of the treated species, true lightwood induction occurred in only the treated Pinus spp. In the species that did not lighter, traumatic resin ducts were often observed at the edges of the desiccated wood extending into the adjacent wood formed after paraquat treatment.

Pinus species

The control wood from the paraquat-treated pines contained ca. 3 to 8 percent tall oil and 0.2 to 2.0 percent turpentine compared to maximal contents of ca. 15 to 35 percent tall oil and 3 to 15 percent turpentine observed in the lightwood. The tall oil and the turpentine contents of the control wood were usually slightly elevated compared to those of wood from untreated trees. No significant differences in increased tall oil and turpentine were observed between the ax frill and the borehole treatment methods used with Scotch and ponderosa pine.

Scotch, red, and jack pine treated with paraquat responded with the greatest increases in tall oil and turpentine. However, this probably

Table 2.--Characteristics of paraquat-treated trees

Tree	Age	DBH ^{a/}	Paraquat concentration	Height above wound		
				Visual lightwood	Cambium kill	Diminished annual growth ^{b/}
	<u>Yr</u>	<u>Cm</u>	<u>Pct</u>	<u>Cm</u>	<u>Cm</u>	<u>Cm</u>
JACK PINE						
I	34	34	1/4	60	30	270
II	34	28	1/4	60	60	60
III	35	31	1	60	60	240
IV	34	18	1	180	90	90
V	27	20	5	540	375	570
VI	28	22	5	630	480	>690
VII	33	24	0	--	--	--
VIII	32	20	0	--	--	--
EASTERN WHITE PINE						
I ^{c/}	>68	21	1/4	30	150	150
II ^{c/}	>71	25	1/4	0	90	90
III ^{c/}	76	21	1	45	180	180
IV ^{c/}	>71	41	1	60	510	510
V ^{c/}	76	21	5	45	1,020	1,020
VI	>71	44	5	160	1,660	1,660
BLACK SPRUCE						
I	34	14	1/4	0	210	210
II	42	19	1/4	0	210	210
III	35	16	1	15	390	690
IV	39	19	1	0	360	360
V	38	21	5	0	>690	>690
VI	34	15	5	15	750	780
VII	36	21	0	--	--	--
VIII	33	14	0	--	--	--

Table 2--(Con.)

Tree	Age	DBH ^{a/}	Paraquat concentration	Height above wound		
				Visual lightwood	Cambium kill	Diminished annual growth ^{b/}
				<u>Cm</u>	<u>Cm</u>	<u>Cm</u>
WHITE SPRUCE						
I	22	16	1/4	0	210	360
II	22	19	1/4	0	270	300
III	21	17	1	0	360	360
IV	22	21	1	0	600	480
V	21	21	5	0	>600	>600
VI	21	17	5	0	>540	>540
VII	21	13	0	--	--	--
VIII	23	15	0	--	--	--

^{a/} DBH = diameter at breast height.

^{b/} Above wound in 1974-1975 growth rings.

^{c/} Heart rot in section A.

Table 3.--Tall oil, turpentine, and moisture
contents of paraquat-treated
jack pine^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	6.0	13.8	1.4	5.3	81	61
B	4.6	4.8	1.0	1.1	97	100
C	3.5	7.0	0.6	2.2	109	97
TREE 11						
A	4.4	21.7	0.6	8.2	98	40
B	3.5	3.8	0.4	0.5	103	104
C	3.9	2.9	0.6	0.4	105	112

Table 3--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE III						
A	3.3	13.2	0.4	5.1	122	62
B	3.0	3.5	0.3	0.6	121	113
C	3.3	3.4	0.5	0.7	120	108
D	2.8	2.7	0.3	0.3	127	124
TREE IV						
A	5.1	18.8	1.1	7.8	117	52
B	3.1	5.9	0.4	1.8	131	101
C	2.7	2.6	0.3	0.4	134	128
TREE V						
A	3.5	19.7	0.4	7.1	123	42
B	3.4	16.4	0.5	6.4	128	35
C	3.2	14.1	0.5	6.3	146	36
D	2.6	7.3	0.4	2.8	146	76
E	2.1	1.6	0.2	0.2	149	142
TREE VI						
A	3.9	12.1	0.6	4.6	114	63
B	2.8	13.7	0.3	5.6	107	36
C	2.3	16.2	0.2	7.3	120	41
D	2.4	14.7	0.2	6.1	131	57
E	2.5	3.1	0.2	0.3	124	109
CONTROL TREE VII						
A	3.6	--	0.4	--	101	--
B	3.4	--	0.5	--	95	--
CONTROL TREE VIII						
A	2.2	--	0.2	--	121	--
B	2.4	--	0.3	--	119	--
C	2.4	--	0.3	--	118	--

^{a/} Contents reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

Table 4.--Tall oil, turpentine, and moisture content
for paraquat-treated Scotch pine^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I ^{c/}						
A	3.8	27.3	0.3	10.8	144	88
B	4.1	6.1	0.3	1.1	155	128
C	4.1	3.4	0.3	0.3	172	147
TREE II						
A	5.4	20.1	0.6	14.0	127	74
B	4.9	6.0	0.6	1.1	127	112
C	4.6	5.2	0.5	0.8	123	115
TREE III						
A	6.1	34.7	0.8	13.3	130	46
B	5.2	14.5	0.6	4.9	124	109
C	5.6	7.0	0.6	0.9	133	145
D	5.3	4.8	0.5	0.6	152	151
TREE IV						
A	6.8	25.1	0.9	8.7	134	79
B	4.6	21.6	0.4	7.9	139	60
C	4.0	13.9	0.5	5.2	144	124
D	4.6	5.8	0.4	0.5	146	147
TREE V						
A	6.9	26.6	0.7	9.7	121	59
B	5.2	14.6	0.4	5.2	134	38
C	3.4	14.5	0.2	5.8	125	39
D	4.2	17.1	0.3	6.5	147	79
E	4.1	7.4	0.3	1.6	162	151
F	4.1	4.6	0.3	0.5	170	160

Table 4--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE VI						
A	6.0	35.3	0.9	14.0	114	57
B	5.8	22.6	0.8	8.8	141	35
C	10.1	20.4	1.4	7.7	137	35
D _{d/}	5.1	32.3	0.7	12.1	137	41
E	5.4	27.1	0.7	9.4	129	45
TREE VII						
A	5.1	31.2	0.9	15.1	140	67
B	3.9	4.7	0.5	0.9	145	153
C	4.1	4.2	0.6	0.7	150	141
TREE VIII						
A	6.9	18.6	1.0	6.5	140	98
B	5.9	6.1	0.7	1.9	143	114
C	5.4	5.2	0.6	0.5	140	134
TREE IX						
A	5.7	21.7	1.1	8.8	127	69
B	7.0	5.7	1.2	1.0	128	123
C	5.3	7.2	0.8	1.2	126	118
TREE X						
A	4.1	32.8	0.4	14.7	119	61
B	4.0	4.4	0.4	0.4	131	133
C	4.8	4.8	0.5	0.6	156	145
TREE XI						
A	5.0	17.3	0.8	7.6	121	53
B	4.6	10.9	0.8	4.6	113	37
C	3.7	11.6	0.5	4.2	121	47
D	3.7	12.3	0.5	6.0	124	48
E	4.0	10.8	0.6	3.6	129	92
F	3.6	4.6	0.4	0.6	128	138

Table 4--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE XII						
A	5.3	15.0	0.6	6.3	125	57
B	6.3	11.0	0.8	4.0	130	56
C	4.2	11.9	0.4	4.7	136	44
D	5.1	15.2	0.6	6.1	140	32
E	4.3	22.9	0.5	9.6	159	44
F	4.5	20.7	0.4	7.9	141	68
CONTROL TREE XIII ^{c/}						
A	3.9	--	0.3	--	129	--
B	3.3	--	0.2	--	138	--
C	2.9	--	0.2	--	142	--

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood. Trees I-VI treated via ax frill; trees VII-XII via borehole.

^{b/} Sections are 0.5 m long; section A begins 0.5 m below site of paraquat treatment.

^{c/} Double tree. Untreated tree is used as a control.

^{d/} Section is 90 cm long, only three disks were obtained, values are calculated for this shorter section.

Table 5.--Tall oil, turpentine, and moisture contents
for paraquat-treated eastern white pine^{a/}

Section ^{b/}	Tall Oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	7.9	11.6	0.5	2.0	149	83
B	7.1	20.4	0.4	3.4	144	89
C	6.1	9.8	0.3	0.5	133	124
TREE II						
A	8.2	11.4	0.5	1.8	134	84
B	4.9	4.9	0.3	0.4	180	164
C	4.4	4.5	0.2	0.3	166	171
TREE III						
A	5.1	8.8	0.4	1.6	165	82
B	4.3	6.5	0.3	0.9	160	97
C	4.4	3.8	0.3	0.3	143	105
TREE IV						
A	9.3	13.6	0.9	2.5	136	117
B	6.6	21.0	0.5	3.8	162	99
C	6.1	11.3	0.4	1.7	154	116
D	5.9	9.2	0.4	1.6	153	68
E	5.5	5.5	0.3	0.3	165	174
TREE V						
A	4.4	7.9	0.3	1.4	184	107
B	4.0	5.5	0.3	0.6	182	101
C	3.8	6.5	0.3	0.8	183	102
D	3.8	4.8	0.3	0.6	164	82
E	3.7	6.2	0.3	0.8	146	52
F	3.1	7.7	0.2	1.5	160	76
G	3.0	6.2	0.2	1.3	144	61
H	2.6	5.4	0.2	0.8	130	136

Table 5--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW

TREE VI						
A	7.6	15.8	0.6	3.4	154	104
B	5.9	7.2	0.4	0.8	170	62
C	4.6	8.3	0.3	1.2	96	68
D	5.5	10.5	0.4	1.4	145	73
E	5.3	9.2	0.4	1.6	134	87
F	5.4	9.9	0.4	2.0	142	73
H	5.1	10.4	0.3	2.1	143	47
J	5.9	7.2	0.3	1.5	148	32
L	4.5	5.0	0.2	0.3	157	139

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

Table 6.--Tall oil, turpentine, and moisture contents for paraquat-treated limber pine^{a/}

Section ^{b/}	Tall Oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW

TREE I ^{c/}						
A	4.4	14.6	0.3	2.6	83	49
B	3.8	5.5	0.3	0.8	86	63
C	4.1	3.7	0.3	0.3	79	77
D	3.0	3.1	0.2	0.2	79	90
TREE II						
A	8.2	12.7	0.4	1.9	66	40
B	6.9	8.4	0.3	1.0	74	52
C	4.9	8.2	0.2	0.9	69	50
D	5.8	4.9	0.3	0.2	66	57

Table 6--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE III						
A	4.8	9.9	0.5	1.8	88	46
B	5.1	8.1	0.4	0.6	85	31
C	4.9	3.1	0.2	0.7	81	52
D	2.9	7.8	0.2	0.7	79	44
TREE IV						
A	7.2	12.5	0.5	2.1	86	38
B	6.1	7.3	0.6	0.8	76	51
C	4.6	7.6	0.3	1.0	77	49
D	4.5	6.1	0.2	0.8	71	39
CONTROL TREE V ^{c/}						
A	4.1	--	0.4	--	79	--
B	3.0	--	0.2	--	83	--
C	2.9	--	0.2	--	77	--
CONTROL TREE VI						
A	6.1	--	0.4	--	100	--
B	6.9	--	0.5	--	97	--
C	3.4	--	1.0	--	94	--
CONTROL TREE VII						
A	5.6	--	0.4	--	86	--
B	4.0	--	0.3	--	95	--
C	3.7	--	0.2	--	92	--

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

^{c/} Double tree. Untreated tree used as control.

Table 7.--Tall oil, turpentine, and moisture contents
for paraquat-treated Douglas-fir^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	2.0	2.5	0.1	0.3	69	27
B	1.9	2.5	0.1	0.2	71	27
C	1.9	2.0	0.1	0.2	78	29
TREE II						
A	2.3	2.8	0.1	0.6	63	26
B	2.0	2.2	0.2	0.3	71	29
C	1.8	2.5	0.1	0.3	79	32
D	1.8	2.0	0.1	0.2	76	71
TREE III						
A	1.8	4.1	0.1	0.7	65	35
B	1.6	2.5	0.1	0.3	70	28
C	1.7	2.7	0.1	0.4	76	28
D	1.8	2.3	0.1	0.3	87	33
E	1.7	3.7	0.1	0.5	91	48
TREE IV						
A	2.2	2.1	0.1	0.3	58	31
B	1.6	1.7	0.1	0.3	63	30
C	1.4	1.8	0.1	0.3	58	30
D	1.5	2.0	0.1	0.4	62	28
E	1.5	2.2	0.1	0.4	66	29
CONTROL TREE V						
A	1.8	--	0.1	--	78	--
B	1.7	--	0.1	--	85	--
C	1.8	--	0.2	--	96	--

Table 7--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
CONTROL TREE VI						
A	1.8	--	0.1	--	60	--
B	1.5	--	0.1	--	64	--
C	1.6	--	0.1	--	66	--

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

Table 8.--Tall oil, turpentine, and moisture contents
for paraquat-treated black spruce^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	1.5	5.0	0.2	1.6	76	34
B	1.3	4.9	0.1	1.3	75	48
C	1.5	1.5	0.2	0.2	82	73
TREE II						
A	2.0	3.1	0.2	0.9	81	36
B	1.6	2.5	0.1	0.8	83	40
C	1.4	1.4	0.2	0.2	90	78
TREE III						
A	1.1	4.3	0.1	1.5	79	33
B	1.0	3.6	0.1	2.0	71	33
C	1.0	3.5	0.1	1.6	73	33
D	1.2	0.9	0.1	0.2	91	73
E	1.1	1.0	0.1	0.1	90	93
F	1.2	1.2	0.2	0.1	90	93

Table 8--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE IV						
A	1.4	2.7	0.1	0.7	100	39
B	1.2	2.3	0.1	0.7	102	51
C	1.2	1.8	0.1	0.4	95	44
TREE V						
A	2.0	3.6	0.3	0.8	74	29
B	1.6	2.7	0.2	0.5	83	34
C	1.9	2.4	0.3	0.5	86	35
D	1.9	2.5	0.2	0.4	90	32
E	1.9	3.9	0.2	1.1	87	36
TREE VI						
A	1.1	4.8	0.2	1.8	85	29
B	1.0	2.4	0.1	0.9	87	26
C	1.0	3.0	0.1	1.1	86	27
D	1.2	3.4	0.1	1.5	101	24
E	1.5	4.3	0.2	1.8	108	30
F	1.5	1.8	0.2	0.4	110	95
CONTROL TREE VII						
A	1.2	--	0.1	--	84	--
B	1.0	--	0.1	--	84	--
C	0.9	--	0.1	--	89	--
CONTROL TREE VIII						
A	0.8	--	0.1	--	88	--
B	0.7	--	0.1	--	84	--
C	0.9	--	0.1	--	81	--

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

Table 9.--Tall oil, turpentine, and moisture contents
for paraquat-treated white spruce^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	2.3	6.9	0.4	2.3	145	35
B	1.7	3.2	0.1	0.7	163	60
C	1.7	1.9	0.1	0.2	176	169
TREE II						
A	2.7	6.4	0.2	2.5	137	43
B	2.3	4.0	0.1	0.8	164	47
C	1.9	2.6	0.1	0.2	182	175
TREE III						
A	1.8	10.5	0.1	3.3	141	33
B	1.7	3.7	0.1	1.0	145	38
C	1.7	3.5	0.1	0.6	155	99
TREE IV						
A	2.2	8.9	0.2	3.3	140	39
B	2.0	6.5	0.2	2.7	112	32
C	2.2	7.4	0.2	3.6	136	36
D	2.4	5.0	0.2	1.5	177	89
E ^{c/}	2.2	2.6	0.1	0.4	166	152
TREE V						
A	3.0	4.3	0.3	0.8	94	36
B	3.4	6.3	0.7	1.5	87	35
C	2.9	7.1	0.3	2.6	71	43
D	3.5	6.9	0.3	2.9	91	49
E ^{c/}	3.0	9.7	0.2	3.6	116	29
TREE VI						
A	2.2	3.2	0.2	0.6	97	31
B	2.1	3.7	0.2	1.0	100	28
C	2.3	3.5	0.2	0.9	104	27

Table 9--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
CONTROL TREE VII						
A	1.3	--	0.1	--	143	--
B	1.2	--	0.1	--	135	--
C	1.3	--	0.1	--	136	--
CONTROL TREE VIII						
A	1.2	--	0.1	--	159	--
B	1.2	--	0.1	--	146	--
C	1.1	--	0.1	--	146	--

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

^{c/} Section is 108 cm long; only four disks were obtained, values are calculated for this shorter section.

Table 10.--Tall oil, turpentine, and moisture contents for paraquat-treated Norway spruce^{a/}

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE I						
A	1.4	2.5	0.1	0.4	101	52
B	1.5	1.2	0.1	0.2	91	69
C	1.3	1.1	0.2	0.1	100	102
TREE II						
A	1.6	3.2	0.1	0.8	137	58
B	1.8	2.5	0.2	0.3	119	39
C	1.7	2.3	0.1	0.2	90	88
D	1.7	2.0	0.1	0.1	82	112

Table 10--(Con.)

Section ^{b/}	Tall oil		Turpentine		Moisture	
	CW	LW	CW	LW	CW	LW
TREE III						
A	1.6	4.3	0.2	0.9	89	27
B	1.4	2.5	0.2	0.5	91	28
C	1.5	4.5	0.2	0.8	121	30
D	1.4	3.2	0.2	0.8	153	37
E	1.3	2.5	0.2	0.5	162	42
F	1.6	2.2	0.2	0.3	152	103
TREE IV						
A	2.2	4.4	0.1	0.8	66	30
B	2.0	2.5	0.1	0.5	80	26
C	1.7	2.9	0.1	0.4	80	35
D	1.9	2.3	0.1	0.1	86	70
TREE V						
A	1.3	5.4	0.2	1.6	133	49
B	1.7	4.7	0.1	1.6	112	46
C	1.6	3.4	0.1	0.9	118	73
D	1.6	3.5	0.2	0.8	127	60
E	1.7	2.6	0.1	0.4	118	52
TREE VI						
A	2.5	5.4	0.2	1.4	128	35
B	1.8	2.4	0.1	1.0	107	30
C	1.8	4.7	0.2	1.4	126	28
D	2.2	5.0	0.1	1.6	115	29
E	2.1	8.7	0.1	2.8	128	37

^{a/} Contents are reported as percentages based on tall oil- and turpentine-free oven-dried wood weight. CW = control wood; LW = lightwood.

^{b/} Sections are 1.5 m long; section A begins 0.5 m below site of paraquat treatment.

Table 11.--Turpentine composition of paraquat-treated pines

Component	Turpentine composition (pct) ^{a/}													
	Red ^{b/}		Jack		Scotch ^{b/}		Lodgepole ^{b/}		Ponderosa ^{b/}		Eastern white		Limber	
	CW	LW	CW	LW	CW	LW	CW	LW	CW	LW	CW	LW	CW	LW
α -Pinene	70-77	65	49-74	51-74	18-81	20-85	3-7	8	3-7	4-7	35-60	43-59	3-11	6-16
Camphene	1-2	1	1	1	t-3	t-1	1	1	t	t	1-2	1-2	t	t
β -Pinene	14-20	25	11-31	15-42	t-56	1-59	4-8	8-11	15-27	21-34	7-24	16-27	1-4	2-8
Sabinene					0-1	0-2	t-1	1	t-1	t-1	0-1	t-4	t-4	1-6
3-Carene	2-5	4			0-58	0-57	<u>c/</u> 1-16	<u>c/</u> 1	20-40	29-36	t	t	t-29	t-31
Myrcene	1	1	1	1	1-3	1-3	1	3	3-6	4-5	t	t	1-2	1-2
Limonene			1	1	t-3	t-3	1-3	2	2-5	1-5	1-2	1-2	5-19	10-28
β -Phellandrene			1	1	0-4	0-5	21-34	57-60	1	1	t	t	t	t
Other ^{d/}	4-7	4	5-17	3-11	4-23	2-14	48-62	16-18	29-52	23-29	18-52	16-37	64-76	39-71

^{a/} t = trace, CW = control wood, LW = lightwood.

^{b/} Control wood data are from control wood areas of all trees studied; lightwood data, from trees treated with only 5 percent paraquat.

^{c/} Difference is due to inter-tree variability and is not a response to paraquat treatment. Neither turpentine from control wood nor from lightwood of 5 percent treated trees contained large percentages of 3-carene. One percent treated trees contained ca. 16 percent 3-carene in turpentine from both control wood and lightwood.

^{d/} Mostly high-boiling components not eluted under the GLC conditions used for analysis.

Table 12.--Turpentine composition for paraquat-treated conifers
exclusive of pines

Component	Composition of turpentine (pct) ^{a/}							
	Douglas-fir		White spruce		Black spruce		Norway spruce ^{b/}	
	CW	LW	CW	LW	CW	LW	CW	LW
α -Pinene	28-46	27-38	22-38	14-36	9-31	12-27	20-30	17-23
Camphene	0-3	0-2	t-1	t-1	t-3	t-3	2-3	1
β -Pinene	2-8	2-9	12-29	8-44	11-35	20-44	15-24	19-27
3-Carene	3-13	6-18	t-19	t-23	1-9	2-19	1-4	13-21
Myrcene	t-1	1-2	t-2	1-2	t-1	1-2	2-4	2
Limonene	3-8	2-9	2-14	5-20	t-3	t-2	2-3	4-8
β -Phellandrene	t-3	t-4	1-3	1-4	1-4	1-6	2-3	3-5
Other ^{c/}	33-62	27-51	25-60	10-43	35-70	15-46	39-53	26-27

^{a/} t = trace, CW = control wood, LW = lightwood.

^{b/} Control wood data are from control wood of all trees investigated; lightwood data, from trees treated with only 5 percent paraquat.

^{c/} Mostly high-boiling components not eluted under the GLC conditions used for analysis.

resulted because the other treated pines were older, slower growing trees. This conclusion is further complicated by inter- and intra-tree variability to paraquat treatment.

Conifer species exclusive of pines

Paraquat-treated eastern hemlock, tamarack, balsam fir, and Douglas-fir showed only slight increases in tall oil and turpentine. These increases are probably not commercially significant.

Paraquat treatment of the spruces produced an intermediate response. Thus, the control wood contained ca. 1 to 2 percent tall oil and 0.1 to 0.3 percent turpentine compared to maximal contents of ca. 5 to 9 percent tall oil and 2 to 4 percent turpentine observed in the lightwood areas. Thus, lightwood induction in spruce trees might be of limited commercial significance.

Turpentine

The lightwood turpentine contained less high-boiling constituents than did the control wood turpentine from the same species. Some compositional changes were observed between the turpentine from the lightwood and that from the control wood but these differences were not dramatic and were similar to inter- and intra-tree variations for that species. The two exceptions were Norway spruce with greater amounts of 3-carene in the lightwood turpentine and lodgepole pine with more β -phellandrene in the lightwood turpentine.

CONCLUSIONS

- 1) Paraquat induced lightwood in all of the pines investigated.
- 2) The height of lightwood induction upward in a tree increased as concentration of paraquat increased. Of the paraquat concentrations tested (1/4, 1, or 5 percent), 5 percent was the most effective. Borehole and ax frill applications were equally effective.
- 3) All of the spruces investigated showed an intermediate response to paraquat treatment.
- 4) All species, other than the pines and the spruces, showed only slight response to paraquat treatment.
- 5) Except for Norway spruce and lodgepole pine no dramatic compositional changes were observed for turpentine from lightwood vs. that from control wood of the same species.

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