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RENEWABLE RESOURCES FOR INDUSTRIAL MATERIALS

Extractives as a Renewable Resource for Industrial Materials

A Panel Report for

the Committee on Renewable Resources for Industrial Materials
Board on Agriculture and Renewable Resources
Commission on Natural Resources
National Research Council

Prepared by an ad hoc advisory panel as a background paper for consideration of the Committee on Renewable Resources for Industrial Materials. The information in this Report was reviewed by the Committee and was incorporated in part in the recommendations and discussions in its Report "Renewable Resources For Industrial Materials." This report does not necessarily reflect the Committee's opinions nor those of the National Academy of Sciences/National Research Council.

National Academy of Sciences
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FOREWORD

Potential problems from changes in patterns of materials supply or use are causing concern: the current emphasis is on mineral or nonrenewable resources. The Science and Technology Policy Office (STPO), in support of Dr. H. Guyford Stever, the Science Advisor to the President, requested the National Academy of Sciences (NAS) to reexamine the role of renewable resources, as the other major component of natural resources, in helping to better meet needs for materials in the future. Important factors to be taken into account in assessing the desirable balance between these different classes of resources for materials are 1) the increasing variety of technological options available for choice of material for a required performance in a given application, and 2) the increasing concern to minimize both consumption of energy and environmental impact. In addition, the usual economic factors apply in the use of materials.

While the concept of renewable resources is useful, it lacks the coherence of statistical information on resources and use, and the scientific perspective that has developed for "Materials from minerals" (including metals, ceramics, electronic solids, and synthetic organic polymers derived from fossil fuels). Strong specialization exists in forest sciences and wood products on the one hand, and agricultural sciences and associated natural materials (such as fibers and leathers) on the other. We require both a broader view of the science and technology of natural products and, correspondingly, more integrated statistical information on resources, and on materials flows and use (including aspects associated with energy and the environment).

The above considerations led to this analysis of renewable materials in the United States economy as a basis for identifying both the optimum use of such resources and the role of science and technology in helping overcome barriers to their use. The following are the principal items addressed in the study at the request of STPO:

1. Quantitative analysis of current materials flows for renewable resources as the basis for assessing the impact of potential future changes (compared with nonrenewable flows). Definition of the limitations (cost and technical) of renewable resources for meeting expanded demands for materials based on them. Delineation of the energy, environmental, and social consequences of such increases. International aspects.

CHAPTER 1

INTRODUCTION

Extractives from plants and animals are used to varying degrees in manufacturing processes of industrial goods. While they were major raw materials of chemical industries in centuries past, more recently their market shares have been declining. Their disappearance was gradual and coincided with the transition from wooden to metal ships, and from natural to synthetic pharmaceuticals, adhesives, dyes, fragrances, and flavors. The downward trend has continued steadily throughout this industry for the past 100 years, and experts of the field are disputing whether the extractives-depression will ever "bottom out," whether we are in the bottom, or whether we are already on the incline again.

There are several indications that extractives are on the upswing, indeed. However, it is unclear whether this represents a reversion of the general trend, or whether this is a short-lived phenomenon with the valley still to come.

Reference to a recent article in the Wall Street Journal (Friday, February 7, 1975, p. 28) may illustrate the situation:

> A new word, silvichemicals, has been coined as a name for pulp chemicals. There are many of them. Wood wastes yield ammonia, alcohol, formaldehyde and even crude oil, though its synthesis is prohibitively costly now. Silvichemicals and their derivatives have hundreds of applications. They are used in solvents, deodorants, detergents, paint removers, adhesives, metal cleaners, drilling fluids and printing inks. Some Champion International by-products go into soil conditioners; some of Westvaco's into football helmets.
>
> Union Camp Corp. turns mill wastes worth about eight cents a pound into flavors and fragrances worth more than $1 a pound. St. Regis Paper Co. sells a black, oily waste from its pulp-making operation for as much as $300 a ton, more than many grades of paper. Georgia Pacific Corp. recovers some of the costs of pollution control by using its wastes to produce energy

and chemical by-products: "We make money on materials we used to dump," a spokesman says. "The return from chemicals is higher than from the paper industry as a whole," says David L. Luke, III, president of Westvaco, a pioneer in by-product recovery.

Westvaco's chemical sales, which have doubled in the past five years, to $45 million, have helped boost its earnings fivefold over the same period. Since 1967, when Union Camp began producing the rose-smelling chemical geraniol from pine-wood turpentine its chemical sales have grown to more than $100 million a year. Analysts estimate that chemical sales gave Union Camp about $25 million of its pretax profit in 1974.

Apparently, wood extractives have undergone a change from main-products of an industry collecting oleoresin from slashed pines to waste-products of the processing of wood and they are presently recovering to become "co-products" or "by-products." That this recovery might continue until today's "main-products" become "by-products" in favor of extractives is conceived by a number of individuals in this field. Thus, paper may some day be merely a by-product of a tree-based chemical industry.

The task of the extractives panel of CORRIM borders upon other panels - fibers and lignocellulosic materials. This study also borders upon a recent National Academy of Sciences study "Enhancement of Food Production for the United States" (NRC, 1975). Such chemical plant-constituents as starch, rubber, chitin, gums, protein, casein and gelatine were found to share more common grounds with the panel report on lignocellulosic materials than with this study, and were therefore excluded from the present report; so were extractive materials used exclusively for human or animal nutrition. In contrast, bark, oleoresin, waxes, oils and fats, and tallow are covered in this report. These products are derived from forest, agricultural and marine sources.

The oleoresin field illustrates the variety of products and properties obtainable from renewable resources. A list of terms used in the oleoresin field and their definition is given in Table 1. These are representatives of the compounds obtainable from renewable resources.

TABLE 1

Explanation of Terms Used in the Oleoresin Field

Canada Balsam:	The (cortex) pocket oleoresin of balsam fir; Canada balsam is not a true balsam. True balsams are characterized by fragrant aroma and pungent taste due to cinnaminc and benzoic acids and their esters (e.g., storax).
Essential Oil:	A liquid mixture of volatile organic compounds which are derived from plants, and which are largely insoluble in water. The essential oils are usually responsible for the characteristic odors of plants.
Gum:	A viscid, water-soluble mixture of polymeric carbohydrates. Although it is technically incorrect to designate the oleoresinous exudate from pine as a gum, such definition is in wide usage.
Induced Lightwood:	Lightwood formed as a result of treating certain oleoresin-containing trees with bipyridinium aqueous herbicides such as paraquat and diquat.
Lightwood:	Oleoresin-soaked pine wood used at one time for torches (light) and kindling.
Naval Stores:	Resins, pitches, tars, oils, and other products derived from the oleoresin exuded by or extracted from trees chiefly of the pine species.
Oleoresin:	Any natural mixture of essential oil and resin from pine which is: 1. Contained in or exuded from resin ducts. 2. Accumulated in dead wood such as knots and stumps.
Resin:	A mixture of nonvolatile, hydrophobic, solid organic compounds. Natural resins are usually terpenoid in character.
Resin Acids:	The resin acids of pine are monocarboxylic diterpenes. They consist mainly of

	the tricyclic abietic and pimaric (including isopimaric) types and often contain small amounts of bicyclic labdane acids. Mixtures of resin acids are the primary constituent of rosin.
Rosin:	A specific kind of natural resin obtained from pine oleoresin by removal of the volatile essential oil, or from tall oil by the removal of the fatty acid components. It consists primarily of tricyclic, monocarboxylic diterpene acids known as resin acids having the general empirical formula $C_{20}H_{30}O_2$, with small quantities of nonacidic (neutral or nonsaponifiable) materials.
Tall Oil:	A generic name of Swedish origin for by-products obtained by acidifying the soap skimmings of the concentrated black liquor resulting from the manufacture of wood pulp by the kraft (sulfate) process. To provide some distinction between the various products, designations are often applied in accordance with the process or composition, some of which are: crude tall oil, distilled tall oil, tall oil fatty acids, and tall oil rosin.
Turpentine:	The essential oil of pine oleoresin. For most pine species, it consists primarily of monoterpenes.

REFERENCE

National Research Council (1975) Enhancement of Food Production for the United States. Board on Agricultural and Renewable Resources, Commission on Natural Resources, National Academy of Sciences, Washington, D.C.

CHAPTER 2

USE OF EXTRACTIVES

CURRENT USE AND FLOW OF MATERIALS

The extractives that this report is concerned with can be divided into five distinctly different groups; they are bark, naval stores, vegetable oils, tallow and fats, and oils from aquatic sources. 1972 figures concerning the production and consumption for industrial materials of these extractives are compiled in Table 2.

Among the five extractive classes, bark is by far the predominating one with respect to production or growth. Its consumption for industrial purposes, however, is small, and cannot even be determined with accuracy.

While approximately 50 percent of bark residues is used as fuel, it is expected that more unused bark residues will be allocated for production of process steam and electricity at forest products plants (Grantham and Ellis 1974).

Even with greatly anticipated expanded use of bark as fuel and in agriculture, this need not discourage the use of bark as a potential source of extractive chemicals, since a bark chemical processing plant would leave a residue amounting to about 75 percent of original weight, which could be used as fuel and/or in agriculture. The objective of any system using residues is to develop these materials to their highest product value.

Bark is converted into soil amendments, used as fuel, or used in structural materials--mainly particleboard--as admixture with wood. One plant in Eugene, Oregon (BOHEMIA, Inc.), has recently started to solvent extract Douglas fir bark, and manufactures a number of wax, cork, and phenolic extender products. ITT Rayoniers's operations in Washington market a sulfonated extract of western hemlock bark. Some pulpmills tolerate bark in their digester furnish in the form of whole tree chips; in this case, most of the bark is dissolved and appears in the black liquor recovery cycle. Precise figures on the current use of bark for other purposes are not available, but it can be assumed that they represent minor quantities.

Table 2

U.S. Production from Domestic and Imported Materials, and Disappearances for Nonfood Uses of Extractives in 1972 (In 1,000 lbs.)

Material		Production	Disappearance for Nonfood Products	Tot Nonfoc
I.	Bark	45,000,000		
II.	Turpentine, total	203,900		
	Gum	9,500		
	Wood	27,400		
	Sulfate	167,000		
	Rosin, total	846,200		
	Gum	46,200		
	Wood	364,000		
	Sulfate	436,000		
	Tall Oil Fatty Acids	428,874		
	Citrus Peel-Limonene	10,457[1]		1,489,
III.	Vegetable Oils			
	Soybean Oil	8,084,000	446,000	
	Cottonseed Oil	1,355,000	110,000	
	Coconut Oil[2]	215,000	434,000	
	Corn Oil	507,000	38,000	
	Linseed Oil	440,000	223,000	
	Peanut Oil	258,000	12,000	
	Castor Oil	-	140,000	
	Others	5,187,000[3]	174,000	1,577,
IV.	Inedible Animal Fats	5,076,000	1,650,700[4]	1,650,
V.	Fish Oils	188,000	100,000	
	Seaweeds	2,205		102,

[1] Includes approximately 1 million lbs. estimated for California; rest Florida; 19
72 growing season.

[2] Oil produced from imported copra.

[3] Includes oil equivalent of exported domestic oil seeds.

[4] From "Current Industrial Reports, Fats and Oils" Series M20K (72)-13 U.S. Bureau
the Census, 1973, excludes animal feed.

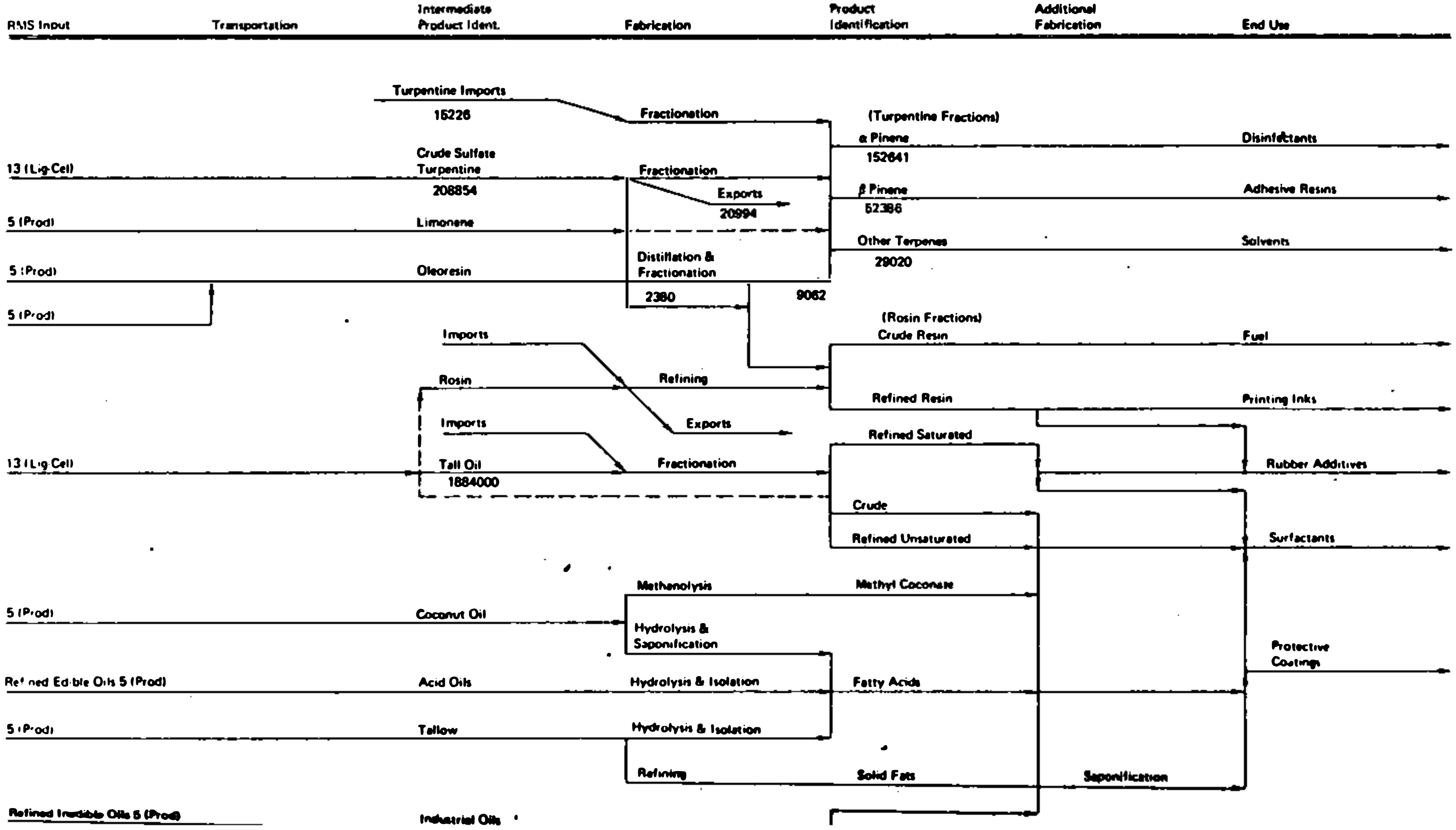
Sources: Navel Stores Annual Report, USDA, April 1973 - March 1974; Statistical R
porting Service, USDA (1974); Florida Canners Association Statistical Summary 19
Kromer, G. W. 1974 "Economic Aspects of the Vegetable Oils and Fats Industry in
U.S.," paper presented at the International Trade and Development Conference, U.
Economic Commission for Asia and the Far East, Seattle, Washington, June 10, 197

The rest of the extractive categories are used to the extent of about 5.0 billion pounds for industrial materials. Assuming an average value of about 8 cents per pound, this amounts to a total of $400 million of extractive raw materials consumed for industrial purposes annually. annually. Roughly 34 percent of these materials stem from tallow, and about 31-33 percent each from naval stores and vegetable oils.

In terms of annual production, vegetable oils far outweigh naval stores. Soybean oil, cottonseed oil, coconut oil (imported) and lard are the major contributors to this category. However, only small fractions of these oils are used industrially; most are converted into margarine, salad dressing and other food products, or are exported. The prominent vegetable oils used for industrial products are coconut oil, soybean oil and linseed oil. Tall oil fatty acids almost match the use of coconut as an industrial raw material. Resources from marine origin amount to only a minor portion of the entire extractives raw material base of industry.

Extractives are used for many end products, some of which are manufactured in very small quantities. The materials flow of renewable extractives into major end products is shown in the trajectory, Figure 1.

The turpentine part of the trajectory is shown with three main sources. The first is from the fractional distillation of crude sulfate turpentine obtained as a by-product of the pulping of softwoods, mostly southern pine. The second is from the fractional distillation of turpentine obtained from oleoresin by distillation. Oleoresin can be obtained directly by wounding a pine tree ("gum"), or by extraction of natural lightwood from stumps (technically a nonrenewable resource) or of induced lightwood (1985 and 2000 only). The third source is limonene extracted from citrus peel. The turpentine fractions can be divided into three major groups: alpha-pinene, beta-pinene, and other terpenes which includes the limonene and other monoterpene fractions. The major significant use for alpha-pinene that competes with nonrenewable resource (NRR)-derived products is conversion with mineral acids to terpineol (synthetic pine oil). The competitive NRR-based materials are phenols. Pine oil is also widely used for ore flotation and textile processing. The major significant use for beta-pinene that competes with NRR-derived products is polymerization to polyterpene resins which find uses in pressure sensitive adhesive. The competitive NRR-based materials are derived from paraffins and isoprene. The major single use of all the other monoterpenes that compete with NRR-derived products is as a solvent (additional fabrication not required). The competitive NRR-based material is mineral spirits.


RMS Input
Transportation
Intermediate Product Ident.
Fabrication
Product Identification
Additional Fabrication
End Use
Turpentine Imports
15226
Fractionation
(Turpentine Fractions)
α Pinene
152641
Disinfectants
13 (Lig-Cel)
Crude Sulfate Turpentine
208854
Fractionation
β Pinene
52386
Adhesive Resins
Exports
20994
5 (Prod)
Limonene
Other Terpenes
29020
Solvents
5 (Prod)
Oleoresin
Distillation & Fractionation
2380
9062
5 (Prod)
(Rosin Fractions)
Crude Resin
Fuel
Imports
Rosin
Refining
Refined Resin
Printing Inks
Imports
Exports
Refined Saturated
13 (Lig-Cel)
Tall Oil
1884000
Fractionation
Rubber Additives
Crude
Refined Unsaturated
Surfactants
Methanolysis
Methyl Coconate
5 (Prod)
Coconut Oil
Hydrolysis & Saponification
Protective Coatings
Refined Edible Oils 5 (Prod)
Acid Oils
Hydrolysis & Isolation
Fatty Acids
5 (Prod)
Tallow
Hydrolysis & Isolation
Refining
Solid Fats
Saponification
Refined Inedible Oils 5 (Prod)
Industrial Oils

The terpene insecticides (16%) are based on camphene, which is obtained either from wood turpentine or by isomerization of alpha-pinene. The toxaphene-type insecticides are prepared by chlorinating camphene and camphene-alpha-pinene. The future of these chlorinated insecticides, however, is uncertain.

Perhaps the most interesting area of turpentine utilization is in the small, but growing, production of flavor and fragrance chemicals (9%). Synthesized products such as lemon, lime, peppermint, spearmint, and nutmeg essential oils are being marketed along with a wide range of fine chemicals for the flavor and fragrance industry.

Rosin fractions may be obtained from two sources, by distillation of oleoresin (however derived) followed by refining, or by fractionation of tall oil obtained on pulping conifer pulpwood, and collecting (including acidification) the tall oil soap skimmings. The products of this refining or fractionation are a refined rosin fraction, and a crude rosin fraction which includes tall oil heads and bottoms, distilled tall oil, and the residue from refining of wood rosin. Crude rosin's major single use that competes with NRR-derived products is as a fuel where it competes with No. 6 bunker fuel oil. Refined rosin's major uses that compete with NRR-derived products are in printing inks and rubber additives and as paper size where it competes with petrochemical waxes, acrylics, and other synthetic sizes.

Rosin uses in the U.S. are summarized in Table 3. They are mostly in some modified form: hydrogenated, dehydrogenated, disproportionated, esterified, polymerized, as salts, or reacted with formaldehyde or maleic anhydride, for example. The largest use is in the sizing of paper to control water absorptivity. A rosin soap or emulsion is added to the pulp and is precipitated onto the paper fibers with aluminum sulfate.

Although rosin found considerable use at one time in the old yellow bar laundry soaps (38% of rosin was used for this purpose in 1938), this use is almost negligible now. Rosin soaps, however, find important use as emulsifying and tackifying agents in synthetic rubber manufacture. Other uses for rosin are in adhesives, surface coatings, printing inks, and chewing gum.

Tall oil fatty acids are in the other major fraction collected from the distillation of tall oil and these will be discussed later.

Of the over 1 billion lb. of fatty acids produced in this country, about 30 percent comes from tall oil. Major uses for tall oil fatty acids include protective coatings

Table 3

Utilization of Rosin in the U.S. by Categories, in Percent of Total

	1971	1972	1973	1974
Paper Size	38.5	36	33	27
Chemical Intermediates and Rubber	43	40	42	44
Rosins and Ester Gums	15	15	17.7	21
Coatings	3.9	5.0	3.9	4.0
Others	3.0	3.5	3.1	4.1
Total Reported (1)	760	743	706	661

(1) In million lbs.

Source: Naval Annual Report, USDA (1974).

(31%), intermediate chemicals (35%)--(a catch-all category, of which the major uses are for epoxy tallates, and for dimer acids, that in turn, are used in polyamide resins for inks, adhesives, and coatings), soaps and detergents (11%), and as flotation agents (6%).

Natural fats and oils from agricultural sources -- vegetable oils, lard, and tallow -- and from aquatic origin are being used for a variety of industrial products (Table 4).

Total consumption for industrial uses (including animal feeds) in terms of pounds per capita remains at a high level, even though consumption in food products has increased by 19 percent over the past 25 years:

	All Industrial Products (lbs/capita)	All Food Products (lbs/capita)
1935-39 aver.	22.2	45.4
1950-59 aver.	24.0	44.9
1960-69 aver.	25.8	48.0
1970-74	25.6	53.3

Major industrial markets for fats and oils include drying oils (529 million pounds in 1972, or 40 percent of the total paint binder market), surface active agents (1,547 million pounds of fatty acid-based products, or 38 percent of the total market), and plasticizers (258 million pounds of fatty acid-based products, or 15 percent of the total market). The fats and oils share of these markets is being maintained because of their unique and desirable properties, in spite of the inroads made by lower cost petrochemicals.

Protective coatings is one of the largest industrial outlets for vegetable oils. Alkyd paints consumed a high of 155 million pounds of soybean oil in 1955, and 80-90 million pounds in 1972. Linseed oil is used to the extent of 83 percent for paints and varnishes, and its consumption has declined from 483 million pounds in 1951 to the present low of about 200 million pounds. Linoleum and oil cloth are other outlets for linseed oil of declining importance. A growing market for linseed oil appears to be concrete treatment, which consumed an estimated 10-12 million pounds in 1973. A rapidly growing market for soybean oil is epoxidized soybean oil as a plasticizer/stabilizer for plastics. This use, a development of the Agricultural Research

Table 4

Fats and Oils Use in Industrial Products for Civilian Consumption, Total and Per Capita, United States, 1935-39 Average, Annual 1950-74

	SOAP		DRY OIL PRODUCTS		FATTY ACIDS		ANIMAL FEEDS		OTHER INDUSTRIAL PRODUCTS		ALL INDUSTRIAL PRODUCTS	
	TOTAL	PER CAPITA	TOTAL	PER CAPITA	TOTAL	PER CAPITA	TOTAL	PER CAPITA	TOTAL	PER CAPITA	TOTAL	PER CAPITA
	MTL LB.	LB.	MTL LB.	LB.	MTL LB.	LB.	MTL LB.	LB.	MTL LB.	LB.	MTL LB.	LB.
AVERAGE 1935-39	1,638	12.8	774	6.0	---	---	---	---	440	3.4	2,852	22.2
1950	1,804	12.0	1,182	7.9	501	3.4	---	---	653	4.3	4,140	27.6
1951	1,505	10.0	1,129	7.5	453	3.0	---	---	763	5.0	3,850	25.5
1952	1,352	8.8	1,010	6.6	412	2.7	---	---	819	5.3	3,593	23.4
1953	1,291	8.3	1,064	6.8	577	3.7	---	---	699	4.5	3,631	23.3
1954	1,177	7.4	1,001	6.3	521	3.3	111	.7	717	4.5	3,527	22.2
1955	1,115	6.9	1,104	6.8	606	3.8	181	1.1	834	5.1	3,840	23.7
1956	1,038	6.3	1,089	6.6	645	3.9	296	1.8	894	5.4	3,962	24.0
1957	994	5.9	1,015	6.0	737	4.4	425	2.5	783	4.7	3,959	23.5
1958	914	5.3	920	5.4	722	4.2	550	3.2	883	5.2	3,989	23.3
1959	862	4.9	910	5.2	1,150	6.6	505	2.9	808	4.7	4,235	24.3
1960	860	4.8	821	4.6	1,245	7.0	504	2.8	841	4.7	4,271	24.0
1961	830	4.6	846	4.7	1,226	6.8	502	2.8	819	4.5	4,223	23.3
1962	774	4.2	879	4.8	1,319	7.2	876	4.8	878	4.8	4,726	25.7
1963	775	4.2	866	4.6	1,408	7.6	827	4.5	920	4.9	4,796	25.7
1964	773	4.1	889	4.7	1,598	8.5	838	4.5	885	4.7	4,983	26.4
1965	706	3.7	895	4.7	1,735	9.1	717	3.8	763	4.0	4,816	25.1
1966	719	3.7	908	4.7	1,957	10.1	893	4.6	852	4.4	5,329	27.6
1967	706	3.6	844	4.3	1,893	9.7	972	5.0	819	4.2	5,234	26.8
1968	659	3.5	850	4.3	1,907	9.7	1,011	5.1	788	4.0	5,245	26.6
1969	673	3.4	728	3.7	1,943	9.8	1,078	5.4	988	5.0	5,410	27.2
1970	679	3.4	620	3.1	2,004	9.9	1,098	5.4	872	4.3	5,272	26.2
1971	677	3.3	619	3.0	1,779	8.8	1,143	5.7	1,062	5.2	5,240	25.7
1972	802	3.9	529	2.6	1,992	8.6	1,100	5.3	1,108	4.9	5,430	26.3
1973	722	3.5	679	3.3	1,958	9.4	945	4.5	844	4.1	5,149	24.7
1974	779	3.7	558	2.7	2,051	9.8	1,137	5.4	692	3.3	5,216	24.9

Source: U.S. Fats and Oils Statistics, 1950-1974, Economic Research Service, USDA.

Service, U.S. Department of Agriculture, has grown from a 16 million pound market in 1961 to 85 million pounds in 1972 and 117 million pounds in 1973.

Tallow is derived from the rendering of beef fat, whereas lard is obtained from the fat of hogs. Edible tallow originates from fat of certain parts of the animal body, and from federally inspected processing plants, exclusively; all other tallow is classified as inedible. About half of the tallow production of this country is exported, mostly to Japan and Western Europe, for use in food products. The domestically consumed, inedible tallow finds its major uses in animal feeds (38 percent), in fatty acids (30 percent) and in soaps (22 percent). Fatty acids and their chemical derivatives are used in almost every segment of today's industry in a wide array of products. Fatty acids are usually intermediates used in the further manufacture of everyday products in which they lose their identity, and they are generally unknown to the ultimate consumer. Fatty acids and derivatives are used in soap and detergents, protective coatings, textile processing, rubber manufacture, lubricants, pharmaceuticals, cosmetics and toiletries, plastics, metallic driers, cutting oils, lubricants, napalm (jellied gasoline) and many chemical intermediates. Table 5 shows the production of fatty acids by source in the U.S. for the years 1950 to 1971. Tallow and grease supply about 60 percent, and tall oil about 30 percent of the total market; and the rest (10 percent) comes from vegetable oil foots and soap stocks.

Coconut oil, an imported oil, is another important industrial oil. Of the 825 million pounds consumed in 1972, 434 million pounds or about one-half was used industrially, mainly in the manufacture of surface active agents. Coconut oil, with its high proportion of C_{12} and lower fatty acids, has no counterpart in U.S.-grown crops and so must be imported.

Glycerol is a co-product of many of the schemes used for the production of surface active agents and other compounds, mainly from tallow and coconut oil. Glycerol from agricultural sources constitutes about 32 percent of total U.S. capacity, the major portion being produced from petrochemical sources. Glycerol consumption is distributed as follows: Drugs and cosmetics (19%), exports (18%), alkyds (17%), tobacco (12%), foods and beverages (10%), cellophane (10%), others (14%).

Very considerable quantities of oils and fats of aquatic origin go into the manufacture of food (especially in Japan); this use is outside present consideration, but it is not possible at the moment to separate the food and non-food components. But substantial quantities of marine fats and

Table 5

Fatty Acid Production and Fats and Oils Used in Manufacture, 1950-71

Year	Fatty acid production (all grades)	Fat and oils used in producing fatty acids						Fatty acid production as % of total fats and oil used
		Inedible tallow and grease	Tall oil 1/	Coconut oil	Vegetable foots	Other	Total	
	---Million pounds---							Percent
1950	651	229	---	52	147	73	501	130
1951	595	243	---	55	101	54	453	131
1952	548	187	---	48	143	34	412	133
1953	512	252	2/	45	130	150	577	89
1954	500	242	2/	54	116	109	521	96
1955	517	278	2/	40	116	172	606	85
1956	545	286	161	45	99	54	645	84
1957	505	284	264	45	89	55	737	69
1958	462	256	293	39	83	51	722	64
1959	681	373	557	98	94	28	1,150	59
1960	708	386	674	83	77	24	1,245	57
1961	706	356	676	74	82	37	1,226	58
1962	785	411	720	56	92	41	1,319	59
1963	836	449	779	51	89	39	1,406	59
1964	936	489	925	54	79	55	1,598	59
1965	1,041	540	1,023	54	72	46	1,735	60
1966	1,134	583	1,171	60	79	64	1,957	58
1967	1,089	545	1,167	56	81	43	1,892	58
1968	1,108	573	1,144	64	82	44	1,907	58
1969	1,138	608	1,154	56	79	46	1,943	59
1970	1,123	585	1,230	60	81	49	2,004	56
1971 3/	1,096	585	1,017	60	80	37	1,779	62

1/ The use of whole or crude tall oil in the distillation or fractionation process is reported by Census as consumed in fatty acids. This overstates the amount of tall oil going into fatty acids as the fractionation process also yields rosin acids, and secondary products. 2/ Included in "other secondary products" not shown separately to avoid disclosure of figures for individual companies. 3/ Preliminary.

Source: U.S. Fats and Oils Statistics 1950-71 Statistical Bulletin No. 489 Economic Research Service, U.S.

oils go into commerce, for a variety of uses: paints, varnishes, linoleum, insecticide, compounding, lipstick, soap, ink, leather treatment, core oils (iron and steel casting), lubricants and greases, ore flotation, fungicides. Algin, alginic acid, and soluble metallic alginates serve in many roles as food additives. Industrially they have a small market in the disappearing fiber technique of weaving. Seaweeds are used as fertilizers in coastal areas in light, sandy soils. The most significant advance in the use of seaweeds in recent years is the development of liquid seaweed fertilizers. Their chief virtues are in the efficient use of nutrients and the ease of storage and transport.

In Figures 2 and 3 are given simplified schematic flow diagrams of various industrial processes operating on bark and tall oil. These schemes contain information pertaining to materials flows, and requirements for capital investments (at 1972 erection costs), manpower, and energy of mills typical for their respective processes and products.

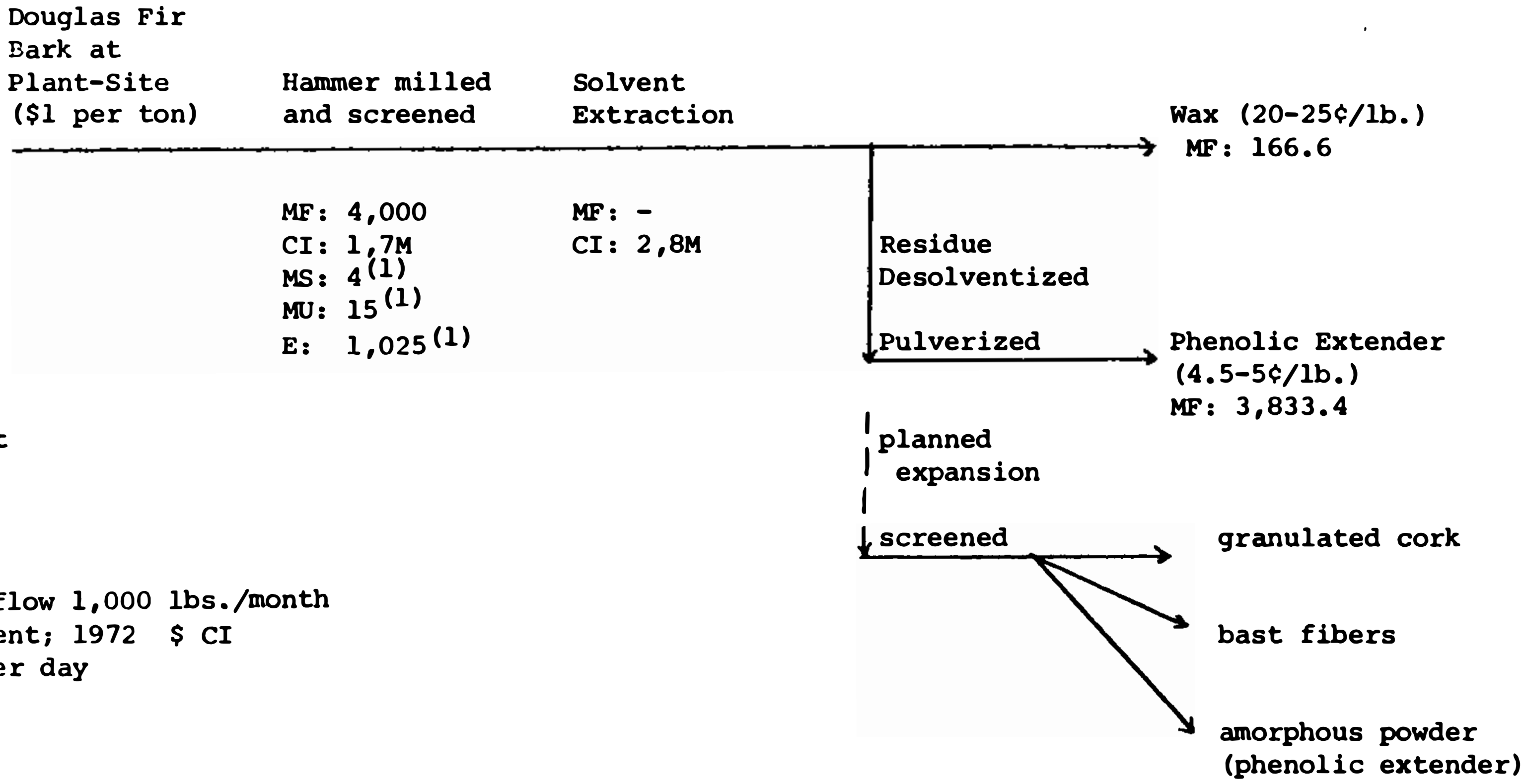
Linseed oil is one of the most important vegetable oils used in this country for industrial materials. Consumption of linseed oil in paints has steadily declined from a high of 483 million pounds in 1951 to 162 million pounds in 1972 and 126 million pounds in 1973, largely as the result of introduction and consumer acceptance of latex paints. Use of linseed oil continues, even though at a low rate, because of better adhesion resulting from its use in latex paints. Production of linseed oil at one time (1951) was 760 million pounds, from about 4 million acres, so there appears to be no problem in availability of linseed oil should linseed oil once again become the main source for paint binders. However, there are at least four major problems that need to be overcome before linseed oil could resume its dominant position for solvent based paints. These are:

- price of linseed oil,
- pollution from solvents,
- yellowing of interior coatings, and
- consumer acceptance of the convenience of latex paints.

The price of crude linseed oil stayed for many years in the range of 12 to 15 cents per pound, and then dropped to 8.9 cents per pound in 1971. In 1973 and 1974, the price rose rapidly to a high of 49 cents per pound, and in June 1975, the price fell to 39 cents per pound. If production increases to alleviate the shortage, the price may drop to the 20 to 30 cent per pound range but probably will never

Figure 2

Simplified Schematic Flow Diagram of Douglas Fir-Bark Extraction Plant



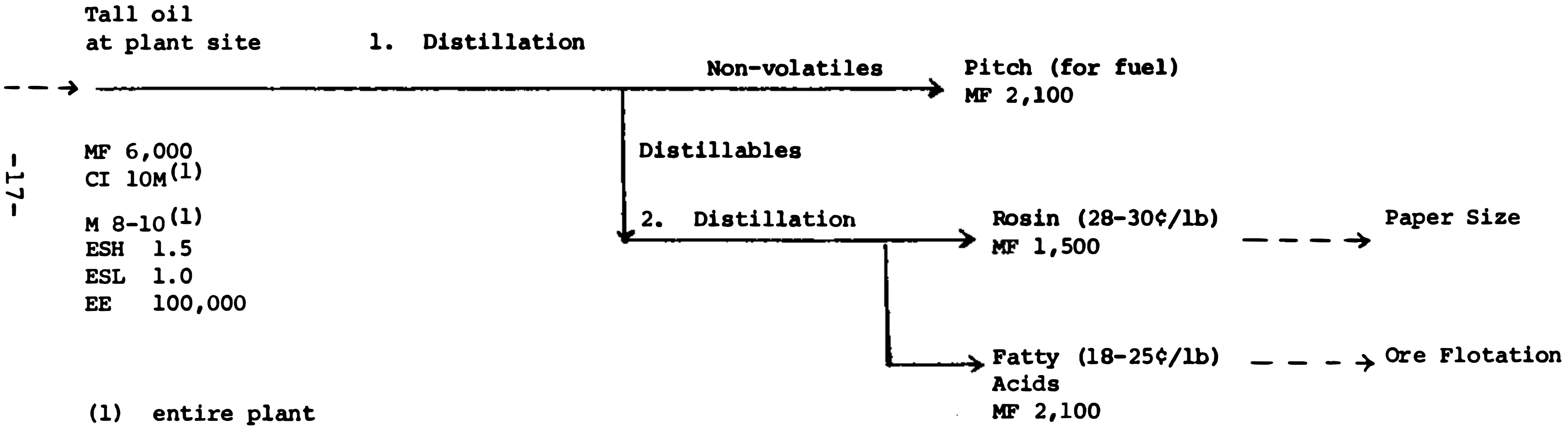
(1) entire plant

Explanation:

MF - Materials flow 1,000 lbs./month
Capital Investment; 1972 $ CI
Manpower; no. per day
MS - skilled
MU - unskilled
E - Energy; HP

Figure 3

Simplified Schematic Flow Diagram of Tall Oil Distillation Plant



(1) entire plant

Explanation:

MF - Materials Flow; 1000 lbs/month
CI - Capital Investment; 1972-$
M - Manpower; no. per day;
skilled only
Energy
ESH - 230 psi steam, lb/lb of tall oil
ESL - 40 psi steam, lb/lb of tall oil
EE - electricity; bwh, total

again reach the 15 cent per pound level. A major problem here is the development of higher yielding, rust-resistant varieties to permit lower prices for the oil with no loss in income to the farmer, and this problem is being worked on by the Agricultural Research Service. In the past, many farmers have planted flax as a second choice crop, if weather or other factors precluded planting of a first choice crop. As a result, yield has fluctuated between 7 and 13 bushels of flaxseed per acre. Yields would undoubtedly improve if flax became a first choice crop at all times.

Cobia (1974) has estimated costs for producing flax expected for the crop year 1975 as follows:

Projected yield, bu/acre		11.2
Production costs, $/acre		54.69
Marketing costs, $/acre		5.13
Elevator margin @ 15¢/bu	$1.68	
Transportation @ 31¢/bu	$3.47	
Total cost, $/acre		59.82
Break-even price (zero profit), $/bu		5.34

The following statistics pertain to the production of flax and linseed oil for the base year 1972.

Resource: Flaxseed - 1972

Total supply (July 1, 1972)	34,041,000	bushels
	864,687	metric tons
	1,906,000,000	pounds
Total domestic disappearance	22,941,000	bushels
	582,732	metric tons
	1,285,000,000	pounds
Exports	8,775,000	bushels
	222,897	metric tons
	491,400,000	pounds
Land Use:		
Acreage planted	1,191,000	acres
Acreage harvested	1,151,000	acres
Yield/acre harvested	12.1	bushels
Price: season average, per bushel	$3.10	
Flaxseed crushed	19,944,000	bushels
	506,604	metric tons
	1,117,000,000	pounds
Linseed Oil:		
Production, pounds	439,700,000	
Consumption, pounds	243,700,000	
Stocks at end of period, pounds	253,700,000	
Exports, pounds	185,200,000	
Consumption in paint or varnish, pounds	162,200,000	
Price, cents/pound, Minneapolis	10.1	
Price, cents/pound, New York	11.5	

Sources: U.S. Department of Agriculture (1974), Agricultural Statistics 1974, U.S. Government Printing Office, Stock No. 0100-03335.

U.S. Bureau of the Census (1973), Current Industrial Reports, Fats and Oils, Production, Consumption, and Factory and Warehouse Stocks, Series M20K(72)-13, Washington, D.C.

HISTORICAL PERSPECTIVE AND CHANGING PATTERNS

Bark

The annual volume of bark products manufactured in the United States in 1963 was estimated at 50,000 tons, having a wholesale value of about $4 to $5 million. The principal uses developed for bark, other than fuel and soil amendment, mulch, or ground cover were (1) filler or extender for plastics and adhesives, (2) insulation, (3) oil well drilling mud additives, and (4) dispersants, resin ingredients, and complexing agents. Three companies were involved in the manufacture of chemicals from bark. Two companies have now discontinued the bark chemical plants. One pioneer company has been expanding its western hemlock bark chemical production and a new Douglas fir bark plant has been installed to recover wax and other products.

In 1968, one company sold 56.7 million lbs of bark chemicals valued at about $6 million. And a new plant was installed to produce 40,000 tons of bark chemicals per year.

In some localities, as much as 10 percent of the bark is used in agriculture. About 100,000 tons per year was used in agriculture in the Pacific Northwest. Transportation costs appear to limit the use of bark as soil amendment and is most successful within a reasonable distance of the bark source (Bratt 1965; Bollen 1969).

Naval Stores

In the early 1930s, tall oil (a pulping by-product consisting primarily of resin and fatty acids) was first introduced as a commodity in this country. However, it made little impact on the American naval stores market until World War II when substitutes were needed for inedible fats and oils. Today, naval stores production is from three principal sources: gum naval stores, steam distilled naval stores, and sulfate naval stores. The production statistics for naval stores are given in Table 2.

Rosin is a commodity product produced over the whole world. World production of rosin has been increasing slowly over the past 15 to 20 years. At the same time there has been very little change in rosin production in the U.S., at least as far back as 1900. The reported production in the U.S. was 859 million pounds of rosin in 1900 and in 1971 was 848 million pounds. Production has fluctuated during the period as high as a reported production of 1,111 million pounds in 1950 and as low as 518 million pounds in 1918. Thus, there has been very little increase through the years.

The changes in U.S. production have been in the source of rosin, generally shifting from gum to steam-distilled wood, and then to the present with tall oil as the major source of rosin in the U.S. It should also be emphasized that consumption of rosin in the U.S. has not exceeded production, and in fact, the U.S. has always been a net major exporter of rosin.

In the world, gum rosin continues to be the major source and probably in those countries where labor is readily available and not drained off by other industries or programs, will continue and could increase. Wood rosin, which is obtained from stumps of first-growth pine has been decreasing slowly.

The important point, however, is that the production of rosin, worldwide, has remained in balance with consumption. Furthermore, since the development of the use of rosin in production of SBR rubber during World War II, no significant new use of rosin has appeared despite considerable work in both government and industrial laboratories. Rosin currently has three main uses: (1) rubber, (2) paper size, and (3) resins for adhesives, coatings, and printing inks. Much effort has been expended in attempting to use rosin as a raw material for higher molecular weight plastic resins such as polystyrene where usage runs in the billions of pounds. Suffice it to say such efforts have been singularly unsuccessful, and, in our best technical judgment, cannot be expected to be more successful regardless of the effort expended. One can, of course, project routes which would crack rosin back to more elementary building blocks such as benzene or ethylene but not in competition with petroleum based products at any time in the foreseeable future.

For the past decade world production of turpentine has ranged between 70 and 80 million gallons yearly, with U.S. production being nearly half of this amount.

Recovery of kraft pulping by-products has increased dramatically until 1969 when it levelled off. These increases have not been able to compensate completely for the loss in production from the other sources. Output of these by-products is correlated, obviously, with production of kraft pulp from pine and is further influenced by wood sources, wood storage, pulping, recovery efficiency, and by-product processing. Drastic changes in the output of pine chemicals from pulping by-products appear feasible in the immediate years ahead. These changes may result from a general technical acceptance of the treatment of pine trees with a herbicide such as paraquat, which was recently developed by USDA scientists. However, at this point it does not appear possible to make precise estimates as to the likely impact of this treatment on existing markets as there exist too many diverging opinions on it among representatives of the scientific and industrial communities.

Agricultural and Marine Fats and Oils

Sources of fatty materials for industrial, nonfood purposes are many and varied and include

1. oils grown specifically for such uses (e.g. linseed oil).
2. oils that are grown mainly for edible purposes but that have industrial uses as well (e.g. soybean oil).
3. fats that are by-products of food processing (e.g. tallow).
4. fatty acid soaps that are by-products of food refining (e.g. soybean soapstock).
5. fatty acids that are isolated by industrial product refining (e.g. tall oil fatty acids).

Table 6 shows the percentages of vegetable oils used for industrial purposes relative to total consumption. The percentages refer only to the amount of oil per se used directly in non-food uses. For example, cottonseed oil had (in 1972) 24 million pounds of oil going into non-food use out of a total supply of 1739 million pounds. However, there were 104 million pounds of foots and loss in the same year, most of which was available for conversion to fatty acids. The decline in percentage for some of the oils is better ascribed to the rising per capita consumption of edible oils than to any decline in industrial use. Indeed, the per capita consumption of fats and oils in industrial products has remained fairly constant for the past 15 years, as discussed earlier. Accordingly, industrial use of fats and oils can be expected to increase gradually in direct proportion to increases in population. Deviations from this expectation may result if petrochemical prices continue to rise at a rate greater than for fats and oils prices, or if more emphasis is given to the concept of renewable vs. nonrenewable resources.

Table 7 reviews the industrial consumption for individual fats and oils. The most striking increase is in tallow, and the most drastic reduction is in marine oils and fats, which are down to 1/3 of the 1960 consumption. This reduction probably reflects reduced availability of source material rather than loss of applications.

Table 6

Percentage of Selected Oils for Inedible Uses, 1964-68

	1964	1965	1966	1967	1968
Cottonseed oil	.9	1.1	.8	.9	.8
Soybean oil	5.4	5.8	5.3	4.8	4.6
Coconut	67.0	64.2	57.5	54.0	56.3
Corn oil	.3	-	-	-	.1
Linseed oil	100	100	100	100	100
Peanut	5.5	5.6	3.0	2.5	2.3
Castor	100	100	100	100	100
V.O. Foots	100	100	100	100	100
Others (V.O.)	21.2	21.7	20.0	14.8	12.1
Edible tallow	2.1	2.1	2.2	1.3	1.5
Inedible tallow	100	100	100	100	100
Marine oils[1]	100	100	100	100	100

[1] According to National Cotton Council statistics, all marine oils go into inedible uses.

Source: National Cotton Council

Table 7

Fats and Oils Used for Industrial Purposes, 1960 - 1974

Extractive[1]	Used for Industrial Purposes (million pounds)					
	1960	1965	1970	1972	1973	1974
Cottonseed oil	122	121	77	110.0	120	103
Soybean Oil	360	421	299	446.0	457	506
Coconut oil	460	493	441	434.0	469	450
Corn oil	30	33	38	38.0	49	41
Linseed oil	364	340	246	223.0	225	203
Peanut oil	9	7	10	12.0	12	10
Castor oil	131	150	139	140.0	119	118
Others				174.0		
Tallow[2]	1,832	2,210	2,622	2,762.0	2,540	3,029
Marine oils and fats	153	125	84	100.0	37	58

[1] Includes foots and losses.

[2] Total domestic disappearance, including use in animal feeds.

Source: U. S. Department of Agriculture (1975), Commodity Economics Division, Economic Research Service.

PROJECTION OF USE

Most renewable resources considered by this panel are by-products or products which are recovered from disposed wastes in the course of a general clean-up required by environmental laws. Many of these products are used because of their low price, often in products that can tolerate the inferior quantity of low-cost extenders. An exception to this rule is turpentine which finds more and more uses in high price, though low quantity, products such as flavors and fragrances.

The potential use of natural extractives for industrial materials is often burdened by heterogeneity (many similar but different chemicals intimately mixed with each other) where separation of individual components is difficult and costly, and where use in combinations impairs product quality or process performance.

In projecting future use of renewable extractives one recognizes several requirements for intensive utilization. Good prospects require:

1. an extractive which is not in competition with higher valued food or feed applications, since cost of food will most likely increase more rapidly -- at least on a worldwide scale -- than that of materials; this penalizes those materials that are raised on potentially food-productive lands with intensive, agricultural cultivation methods (e.g. linseed and castor oil);

2. extractives that have constant supply bases, free of detrimental fluctuations in price, quantity or quality; bark, inedible tallow, and, citrus peel-limonene belong to this category;

3. extractives which can replace nonrenewable and non-biodegradable raw materials or those products foreign to the environment to a particularly high degree (halogenated and some N-containing materials), for example certain resins, plasticizers, surfactants, and insecticides;

4. extractives which are either relatively homogeneous or pure upon recovery, or that are easily purified on a technical scale; Westvaco (Registered) DiAcid belongs to the latter group;

5. extractives with properties that can be matched only by high-price nonrenewable materials requiring difficult, multiple-step processes; alginic acids are examples for this category;

6. extractives that are assigned functions that are similar to those assigned to them in their natural environment; examples are turpentine in fragrances and flavors.

With these considerations in mind the use of renewable extractives for industrial materials was projected by the committee, and the results are shown in Table 8. Overall, it must be stated that extractive utilization cannot be projected with any degree of accuracy. Total amounts may remain constant to the year 2000, or they may increase by as much as five times their present levels. Major increases could occur in the naval stores and tallow markets if demands and economic incentives are adequate.

Tallow production is directly related to the total number of cattle raised, their average weight per head, and their feeding habits. Corn prices determine whether cattle will be feedlot-fed or grazed, and this impacts the average tallow yield per head. Table 9 summarizes the data which have been used to arrive at the projections for tallow listed in Table 8. However, it must be mentioned that projections of beef consumption are highly speculative and that many experts predict a decline of present per capita levels.

Major increases are also projected for turpentine, tall oil fatty acids, seaweeds and citrus peel. Losses should not occur with annual crop industrial oils and for oils and fats from aquatic origin. By 1985, increased imports of coconut and palm oil, can be expected as well as increased production of inedible tallow, of tall oil fatty acids, and of vegetable oil foots and soapstocks, by-products of the refining of oils for food consumption. Naval store gains -- lower ones due to improved recovery techniques and more extractive-conscious storage practices, and higher ones due mainly to successful paraquat treatments -- will be readily absorbed by industries with the exception of rosin for which new outlets will have to be developed. Limonene extraction from citrus peel will follow closely the trend of turpentine.

Bark will see some increases for specialty products such as extractives (waxes, adhesives, etc.), but most of these gains will be due to increased use of undebarked wood and whole tree conversion (foremost in the Eastern U.S.). The committee's projection of bark use for the years 1985 and 2000, in percent, is given in Table 10. According to these projections, most of the bark will be used in some way by 2000, with the bulk going into fuel.

Table 8

Projected Use of Extractives for Industrial Materials in the U.S. for the Years 1985 and 2000

(In million pounds)

	Used for Industrial Purposes 1972[4]	Projection for 1985		Projection for 2000	
		high	low	high	low
Turpentine	203.9	1070.0[1]	255.0	5090.0[1]	30.0
Rosin	846.2	3210.0	555.0	15270.0[1]	44.0
T.O. Fatty Acids	428.9	515.0	450.0	550.0	480.0
Cottonseed Oil	110.0	150.0	135.0	200.0	150.0
Soybean Oil	446.0	600.0	500.0	700.0	560.0
Coconut	434.0	600.0	510.0	700.0	575.0
Corn Oil	38.0	45.0	43.0	50.0	48.0
Linseed Oil	223.0	260.0	250.0	300.0	280.0
Peanut Oil	12.0	15.0	13.0	17.0	15.0
Castor Oil	140.0	175.0	157.0	200.0	176.0
Others	174.0	200.0	195.0	225.0	219.0
Citrus Peel Limonene	10.5	25.0	15.0	60.0	30.0
Tallow	1650.7[2]	3500.0[3]	1900.0[2]	4300.0	2100.0[2]
Marine Oils and Fats	42.0	50.0	35.0	35.0	7.0
Seaweed	1.0	4.0	2.0	8.0	4.0
Total	4767.1	10000.0	5000.0	27000.0	5000.0

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[1] In case paraquat treatment is approved and widely applied.

[2] Does not include animal feed. Projection based on population increases.

[3] Includes animal feed. Projection based on article in <u>Fats and Oils Situation</u>, FOS-260, November 1971, p. 17, Economics Research Services, U.S. Department of Agriculture and on the assumption that 50% of tallow produced goes into industrial uses.

[4] From Table 2.

Table 9

Projected Production of Tallow in 1985 and 2000 (million lbs.)

Year	Number of Cattle	Avg. Dressed wt/head lbs/head	Avg. Yield of Tallow Per Head	Total Expected Yield of Tallow
1972	36,500,000	625	132.7	4,844
1974	37,600,000	650[1]	148.8[1]	5,350
1980	45,800,000	635	140	6,412[2]
1985	49,800,000	635	140	6,972
2000	60,700,000	635	140	8,498

[1] Exceptionally high dressed weights.

[2] G. W. Kromer's estimate of 7.0 billion lbs. of tallow in 1980 was based on a maximum of 49 million cattle and an average yield of tallow of 142.8 lbs/head.

Source: Hoffman, George (1975) Slaughter Cattle Outlook, June 30, 1975 U.S. Department of Agriculture, Economic Research Service, Washington, D.C.

Kromer, George W. (1975) Economic Aspects of the Vegetable Oils and Fats Industry in the United States, June 10, 1975. U.S. Department of Agriculture, Economic Research Service, Washington, D.C.

Table 10

Projected Use Pattern of Bark in 1985 and 2000, in Percent of Total Bark

Uses	Average[1] 1970/74	1985	2000
Unused	50	30-35	5-10
Used, total	50	65-70	90-95
fuel	85[2]	80[2]	75[2]
boards	0[2]	3[2]	5[2]
pulp	3[2]	5[2]	8[2]
silvichemicals	0[2]	2[2]	4[2]
mulch and agricultural uses	12[2]	10[2]	8[2]

[1] estimated

[2] of used total

ADDITIONAL CONSIDERATIONS

Institutional Considerations

Most extractives are generated as by-products of the manufacture of some other materials. As such, their supply and consumption depend entirely on developments in other areas. The planting, growing and harvesting of trees is regulated to suit the needs for fiber and structural materials; extractives are spin-offs of certain processes, which will most likely not affect institutional regulations. A few examples, where institutional regulations impact the supply and use of extractive materials, can be cited.

Most of the oils and fats produced from marine sources are used for nutritive purposes. Those fatty materials that do not meet domestic FDA standards will be exported unless their food or feed consumption is generally prohibited by similar standards throughout the world. It is only then that they are used for industrial materials. Thus, the establishment of a federal standard on foods or feeds may have a drastic impact on the use of agricultural and marine by-products for industrial goods.

In general, forest, agricultural and marine resources are looked upon as sources to satisfy needs for food, feed, fiber, and structural materials. Institutional regulations concerning their production will be concerned with these primary needs, and their impact on by-products can hardly be assessed to any degree of accuracy.

Environmental Considerations

The waste treatments which have been forced upon industries in recent years have had a definite and beneficial effect on the supply of by-products, as was expressed in an article in The Wall Street Journal (Chapter I, this report). In many cases waste water treatments have initiated or enabled the recovery of by-products which formerly were regarded as waste products. Obvious examples are lignin sulfonates, and also tall oil and sulfate turpentine.

Environmental considerations are also important when it comes to the marketing of new types of fragrances and flavors which need to demonstrate environmental compatibility. Natural extractives should be in a better and more competitive position to meet this requirement than synthetic materials.

Environmental restrictions might have an adverse effect on the lightwood induction of pine trees with a highly toxic herbicide (paraquat).

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CHAPTER 3

MATERIALS SUPPLY DEVELOPMENT

DEVELOPMENT UNDER UNCHANGED CONDITIONS

The future supply of renewable extractives for use in the manufacture of industrial goods is closely related to their current and future use (Chapter 2), and to the availability and cost of competing nonrenewable materials. The supply of by-product extractives will largely be determined by the supply situation of the respective main products.

Bark

The amount of unused bark residues at primary manufacturing plants in 1970, was estimated by Grantham and Ellis (1974) to be almost 10 million tons. The regional distribution of this material was as follows:

	Millions of Cubic Ft.	Tons, Million
Pacific Coast	213	3.195
Northern Rocky Mountains	66	0.990
Southern Rocky Mountains	23	0.345
South	165	2.475
North	180	2.700
Total	647	9.705

Source: Grantham, J.B. and T.H. Ellis (1974).

It is also estimated that a total of approximately 20 million tons of bark are made available annually in the U.S. Most of the used bark is consumed as fuel, while lesser quantities are used in agriculture as soil amendments. Perhaps about 1 percent of bark is used as source of silvichemicals (i.e., extractives).

In 1968, 74 percent of all bark residues in the Pacific Coast region were generated at lumber manufacturing plants, as can be seen from the following compilation:

Location and Industry Source	Unused Bark Residue Pacific Coast 1968 Tons, Thousands
California	
Veneer and Plywood	113
Lumber	1,053
Other	1
Oregon	
Veneer and Plywood	434
Lumber	908
Shake and Shingles	40
Washington	
Veneer and Lumber	104
Lumber	232
Shake and Shingles	94
	2,979

Source: Grantham (1974).

The availability of bark is related to wood production and harvesting techniques. It would be easy to predict the amount of bark produced (grown) each year in the United States. However, this may be a meaningless number, as it is unreasonable to expect that all this material will at some point be used for industrial materials. In contrast, the amount of bark separated from wood (mostly logs) at plant sites, where it is readily, continuously and inexpensively available, will say more about the future supply of bark for industrial products. Two recent technological developments seem to indicate that this quantity might not increase in the future. One is the increasing trend in the eastern U.S. of carrying out initial log breakdown on mobile chip'n-saw units in the forest; the bark is thereby scattered around, and its recovery would require costly handling and transporting equipment. The second trend that runs countercurrent to an increased supply of bark for industrial purposes is that of whole tree conversion with its associated elimination of the traditional debarking operations. However, the latter could also be considered commercial use as bark now serves as a low-grade extender of wood in particleboard or pulp. This may even open up new challenges for the recovery of new, so far unknown, bark-derived by-products from spent pulping liquors. In any event, the supply of bark will most likely exceed even the high projected use-increases for the year 2000.

Naval Stores

Domestic production of the three types of rosin and turpentine, totaling some 1.1 billion pounds, continued its decade-long decline in 1972. The downward trend in production occurring despite price advances in rosin and near-record prices for turpentine was attributed to the high cost of producing gum, a leveling off of sulfate pulp output, a drop in oleoresin content of pulp chips, and the increased cost of harvesting the dwindling and increasingly scattered old-growth pine stumps. High prices brought increasing imports of both rosin and turpentine in 1972. Reduced supplies here and abroad, and rising prices, have spurred efforts to replace rosin and have reduced rosin consumption about 10 percent below the average for the past 10 years. Substitutes, including petroleum resins, are gradually gaining a larger share of paper size and synthetic rubber markets. To make serious inroads in hydrocarbon resin use, more rosin would have to be available or hydrocarbons would have to become considerably more scare.

In 1972 turpentine consumption remained well below mid-60s levels. Industrial markets have weakened from lower utilization of synthetic pine oil in cleaners and displacement of alpha- and beta-pinene resins by hydrocarbon resins.

Overall U.S. production of rosin in the 1972 crop year was 1.63 million drums or about 21 percent below 1965. This downward trend has varied with source of production with gum and steam-distilled rosin production off 75 and 35 percent, respectively, although tall oil rosin output increased by 34 percent. Turpentine production totaled 566,000 barrels in 1972, some 19 percent below 1965. Since 1965 gum and steam-distilled turpentine production decreased 76 and 56 percent, respectively, with sulfate turpentine output higher by 10 percent.

The future "production" of naval stores by forests will parallel that of wood, mainly of pines. The commercial availability for industrial raw materials, however, will increasingly depend on the efficient recovery of sulfate turpentine and tall oil from the kraft pulping process, as gum and wood naval store supplies will continue to dwindle. Several factors can be identified that are likely to impact naval stores by-product supplies from kraft pulping. Developments that will enhance sulfate naval stores supplies in the future are:

(1) pine trees will continue to grow as the most important species for pulp papermaking in the U.S.;

(2) year-round chipping of whole trees in the forest will enable pulpmills to limit the size of their

outside chip storage piles, and enable them to cut storage times to a minimum;

(3) improved recovery systems and waste treatment facilities may result in higher yields of recovered oleoresinous by-products; and

(4) higher market values for oleoresins will add incentives to a more efficient by-product recovery.

Developments that might reduce the supply of naval stores from pulping in the future are:

(1) continued practice of month-long storage of chips in open piles;

(2) continued gains of high-yield, semi-chemical pulping processes for pulp may limit the growth of kraft pulping industry; and

(3) the replacement of sulphur as active pulping agent by oxygen.

As a result of these developments it is expected that the overall supply of naval stores will show moderate gains in the future. However, the increases may reach several times the present levels if the treatment of pines with herbicides would become a widespread practice.

In the case of rosin, there seems to be little chance of increased domestic production. Therefore the increase must come from other sources. For a variety of reasons production of tall oil rosin per se has not increased in recent years. Better technology in the recovery of tall oil soap, the precursor of tall oil rosin, from kraft pulping is possible and is being studied in both industrywide sponsored work under the auspices of the Pulp Chemicals Assocation and by producing companies. Some modest increase, possibly 100,000 tons could result. The important question is whether this modest increase could supplant most, if not all, the hydrocarbon resins obtained from nonrenewable resources. Whether this will happen will depend largely on prices.

As far as turpentine and tall oil fatty acids are concerned, increases are expected to find ready acceptance by the market.

Limonene from citrus peel is not recovered to the full extent possible at present because a firm market does not exist. Potential production could be 4 to 5 times as high as today, but it would require increased plant facilities thereby making it possible to recover limonene from all available peel. Limonene is used in the naval stores industry in place of dipentene by Hercules Inc. - Arizona Chemicals Division.

Oils and Fats

Per capita consumption of fats and oils for industrial uses has remained at a steady state for several years and probably will continue to do so. At the same time, there has been a steady increase in per capita consumption of edible oils, mainly soybean oil. Accordingly, the supply of by-products from edible oil refining will continue to be sufficient to serve many industrial uses.

Direct use of an edible oil in a non-food application will depend mainly upon price relative to other resources, and the price of soybean oil may be depressed by several factors. First, as increased demand for soybean protein results in increased crop production, a corresponding increase in demand for the oil will not be likely. Secondly, there will be increasing pressure from foreign-grown soybeans and from low-cost, imported palm oil.

Linseed oil is the only significant, exclusively-industrial oil grown in the U.S. at present, and its production has been decreasing. However, production at the present level is likely to continue, as it is grown when weather conditions, type of land, or other factors preclude growing other crops. Other major oils for industrial use include soybean, coconut, and castor oils. The last two are available only as imported oils.

Tallow production may increase, but whether at a nominal rate or at a more rapid rate is a question that cannot be resolved at this time.

Marine oil production can increase only through improved management of ocean resources.

Factors limiting expansion of fats and oils as intermediates for industrial use include cost and availability of land. Farm land acreage has decreased slightly in the past, and total acreage of plants harvested may not change a great deal from the present 300 million acres. However, it has been suggested that there may be available an additional 100 million acres. Even if acreage harvested does not change, there could be a change in distribution of crop acreage. For example, the projected level for soybean demand by 1985 is 2.2 billion bushels, 66 percent over the 1972 level, requiring 20 percent of total harvested acres as compared to the present 14 percent. This increase will occur at the expense of corn plantings, but only if the soybean/corn price ratio is favorable.

Most of the fats and oils of marine origin come from fish (about 85 percent), the remainder from whales (see Table 11). The present sources of fish which produce oil are mostly fully exploited (menhaden) or over-exploited (whales, California sardines, Peruvian anchovies). The principal ways of increasing production are through improved management of ocean resources and through aquaculture. For example, the California sardine resource once produced 620,000 metric tons of fish, and now yields nothing. The Peruvian anchovy stock at its maximum produced 123 million metric tons; in 1974 it produced only 1.8 million tons. This decline was due to overfishing and "El Nino," a wind shift, which caused the water temperature off the Peruvian coast to drop. Peru now intends to hold down commercial anchovy fishing until the anchovy population can build up enough to sustain a catch of at least 8 million metric tons per year by 1980. Other oil fish stocks (e.g., Scando-Atlantic sardines, Japanese sardines) now produce far less than they once did. It is unrealistic to expect to get the maximum from each of these, since at their heights they were probably being considerably over-exploited, and in addition the record catches probably represent untypical high population years. Nonetheless, managed to produce near the maximum sustainable yield, the aggregate of now damaged fisheries could produce far more oil and fat than in the past. The whale stocks have been notoriously overfished, and only very recently have proper management measures been agreed upon. It will require many years of good management for them to recover, but eventually the whales could supply increased amounts of industrial fats and oils.

If appropriate research and development activities are conducted to improve aquaculture techniques, skills can be gained to raise kinds of fishes with high quantities of oil, and this could eventually be an important source of oil.

There are large under-exploited stocks of herring-like fishes in the Gulf of Mexico and the South Atlantic regions of the United States, and very large under-exploited populations of anchovies off California. These could yield large amounts of oils if fisheries were established for them. The constraints against expansion of these fisheries are different in the two areas. In the Gulf and South Atlantic the fish schools are distributed and behave differently from the menhaden and the other oil-bearing fishes familiar to the American industry. It will require development of modified gear and fishing methods, and research on the distribution of the stocks, to promote this fishery. Off California the constraints are largely social and political. After the collapse of the California sardine

Table 11

Fish Body Oils, By Species
U.S. Production
1000 Metric
Tons

Year	Alewives	Atlantic Herring	Pacific Herring	Menhaden	Salmon	Mackerel and Tuna	Other	Total
1966	.5	2.8	.8	65.4	.0	1.9	2.4	73.8
1967	.8	2.6	-	46.0	.1	2.3	2.6	54.8
1968	.0	4.3	-	69.0	-	2.1	2.5	77.9
1969	-	1.6	-	67.7	-	1.9	5.0	76.2
1970	.4	2.5	-	84.5	-	1.6	4.2	93.2
1971	-	2.7	-	110.7	-	2.2	4.6	120.2
1972	-	2.3	-	75.7	-	2.3	5.2	85.5
1973	-	.8	-	91.0	-	3.3	6.2	101.9

Sources: FAO (1973) Yearbook of Fishery Statistics, Vol. 35; and
U.S. Department of Commerce (1973) Fisheries of the United States, Current Fishery Statistics No. 6400.

fishery in the 1950s, as a consequence of a cooling of the ocean waters off the coast and of overfishing, concern has been expressed that the same may happen to the anchovy stocks if fishing is allowed on them. In particular, sport fishermen object to this development, seeing the anchovies as forage for many of the fishes caught for sport. There is a small quota of anchovies allowed to be caught, but it is not large enough to encourage an industry to develop. Meanwhile, the Mexicans are carrying out a fishery on the same stock, which occupies water on both sides of the border.

It seems likely that there will be very little difference between the amount of fish oils produced in the U.S. by 1985 compared to the 1972 harvest, since the constraints are not likely to be removed by then. By 2000, there may well be an increase, since economic pressures and the results of biological and technological research may have overcome some of the constraints. But it is also likely by that time that the fish oils will be used for food rather than for paints or other industrial purposes. Indeed, the present quantity of marine oils used in paints is likely to fall, perhaps to zero, since their use as food will probably take precedence.

A possible substitute for sperm oil as an industrial raw material may be jojoba seed oil (Simmondsia chinensis). A recently completed report by an NAS committee (NRC, 1975) "found jojoba of interest on several counts." Jojoba, in the committee's view, "has extensive, useful commercial possibilities, especially as a substitute for materials more costly and difficult to match or to obtain, and ...," the committee believes, "jojoba can be exploited to economic benefit in ... hot, arid lands."

> "Jojoba oil -- in chemical structure a liquid wax -- is half the jojoba seed by weight. Evidence ... has shown conclusively that jojoba oil can duplicate sperm oil performance as a high-pressure lubricant, the principal use for sperm oil in this country prior to a 1970 ban on United States import of whale products. In comparison with ... formulated substitutes, jojoba oil is a virtual sperm-oil duplicate -- a material that is so close in chemical structure that it can probably be used as a sperm-oil substitute for the complete range of uses, without requiring major reformulations."

"Jojoba oil's development can reliably rest on its ability to substitute for existing oils and waxes such as sperm oil, carnauba wax, beeswax, and spermaceti," according to the committee. Studies are currently underway to investigate the feasibility of cultivating this wild plant on Indian reservations in the Southwest.

With these trends and developments in mind, major increases are projected only for imported oils (coconut, palm), and for by-products of the refining of oils and fats (vegetable oil foots).

Tallow

Tallow is a product of the rendering and meat packing industries, and, thus, the growth in production of inedible tallow is largely associated with livestock slaughter and meat consumption. Forecasts of tallow production are highly speculative. On the one hand, it has been estimated that the United States rendering industry will be producing approximately 7 billion pounds of inedible tallow by 1980. On the other hand, production has actually declined in the last few years. Inedible tallow will continue to be a major supplier of fatty materials for industrial goods and will continue to be one of the cheapest fatty material in the world. However, it cannot substitute for polyunsaturated vegetable oils in many of the industrial applications served by such oils.

Seaweeds

The total quantities of seaweeds available for harvest over the world are unknown, since few area surveys have been made. Except for a few species, principally Sargassum, they live attached to the bottom, so only shallow, near-shore areas will produce them. Thus they flourish only in water shallow enough for light to penetrate -- perhaps 160 feet or less in most areas, and to 500 or 600 feet in the clearest water.

It has been estimated that around Scotland there are about 180,000 tons of brown seaweeds (principally *Ascophyllum nodosum* and *Fucus vesiculosus*) available in densities sufficient to support economic exploitation. The high-density areas are mostly in the Outer Hebrides and the Orkney Islands, where annual yields have ranged from 7.8 to 18.1 tons per acre, suggesting that greater exploitation is possible here, as well as expansion to other areas not cropped at present. Standing crops of *Laminaria* in Scotland have been estimated to total 3,868,000 tons. Red seaweeds (*Gigartina* and to a lesser extent *Chondrus*) occur in much smaller amounts: 360.2 tons of marketable standing crop in Scotland and 11.5 tons in England.

Very considerable increases can take place in the exploitation of the California kelp beds. One expert has estimated that these beds could sustain an annual harvest of 3 million tons. Statements of total quantity in an area may be misleading, since the algae are often sparsely scattered, making the cost of collection high. In the Sargasso Sea it has been estimated that 4 to 10 million tons of sargassum exist, but the density is only two to five tons per acre -- too thin for profitable exploitation.

It may be economically feasible to raise some kinds of seaweeds under culture. Attempts are being made in California and elsewhere to "farm" the giant kelp, Macrocystis, the principal source of algin.

POTENTIAL IMPACT OF PARAQUAT TREATMENT ON THE FUTURE SUPPLY OF NAVAL STORES

(Prepared by Dr. Robert N. Stone, Research Project Leader, Forest Products Laboratory, Madison, Wisconsin.)

One of the most promising developments results from research at the United States Forest Service Naval Stores and Timber Production Laboratory, Olustee, Florida. Scientists at that laboratory recently discovered that treatment of pines with the herbicide paraquat stimulates extensive oleoresin soaking of the wood. The basic process has been patented by the United States Forest Service. Application of the herbicide to pulpwood trees appears to be a simple, low-cost operation that will either result in increased yields of sulfate naval stores and/or provide a new type of raw material to replace stumps in steam distillation.

Some 30 interested companies from the kraft pulping industry, the naval stores extraction industry, and several herbicide companies, universities, and government agencies have joined in a cooperative research program with the Forest Service to accelerate the commercial development of the paraquat-induced lightwood technology. Research is advancing rapidly in chemical application, harvesting techniques, and processing methodology.

On March 28, 1975, the United States Environmental Protection Agency issued a permit for conducting an experimental program testing paraquat. The permit covers 19 states. This program should develop the necessary evidence to demonstrate the efficiency of this system for producing rosin and turpentine and the environmental risks therein by mid-1977 when EPA registration for commercial application should be approved for pine in the South.

Pulpwood trees containing induced lightwood will begin moving to processors within 6 months of registration and volume should increase until virtually all stands of pine pulpwood trees are treated for 1 to 2 years prior to harvest.

PROJECTED YIELDS FOR 1985 AND 2000

The 1972 U.S. domestic production of roundwood pulpwood from softwoods was 34.2 million cords. The southern pine species comprised 24 million cords of this. Medium projections for 1985 of roundwood softwood pulpwood demand in the Forest Service's report Outlook for Timber in the United States (U.S. Department of Agriculture, 1974) amount to 53.5 million cords. If the South maintains current trends, its share will be 37.5 million cords of pine roundwood pulpwood in 1985 and 53 million cords in the year 2000.

Although projections of oleoresin production to result from a developing technology as yet untested in commercial-scale operations is risky, a scenario can be constructed to illustrate the probable dimensions of its impact.

If after EPA registration of paraquat for commercial use in the production of oleoresin from southern pine the technology proves profitable for some producers in southern pulpwood stands, its use will spread swiftly simply because price shifts will result quickly to make producers non-competitive if they do not also use it.

Yields of induced lightwood oleoresin per cord are not firm, but experimental results on slash pine, longleaf pine, and loblolly pine after 1 year of treatment of 5 to 20 pounds per tree are commonly obtained from different dosages of chemical and numerous types of single and multiple applications. These anticipated yields could double by repeat treatment and extension of the period between paraquat application and harvest to 2 or 3 years.

Estimated yields per cord in commercial application of additional oleoresin of the induced lightwood technique range from 50 to 375 pounds per cord. Estimates for 1985 and 2000 were made using two levels of yield estimates (Table 12). For 1985 level A assumes 100 additional pounds per cord and level B, 200 additional pounds. For 2000 level A assumes 200 additional pounds and level B, 400 additional pounds per cord.

Treatment of one-half of the southern pine roundwood cut projected for 1985 using 100 pounds of additional oleoresin per cord (level A) would contain 2,140 million pounds more of oleoresin or about twice current United States production (Table 12). The level B assumption indicates an increase of 4,280 million pounds.

Table 12

Estimated Yield of Oleoresin from Paraquat-Induced Lightwood in Southern Pine, 1985 and 2000

Year	Southern Pine Pulpwood Production (roundwood) Million Cords	Treated with Paraquat		Additional Oleoresin Per Cord		Additional Oleoresin[1]	
		Million Cords	Percent	Level A	Level B	Level A	Level B
1972	25.8	0	0	-	-	-	-
1985	42.8	21.4	50	100	200	2,140[2]	4,280
2000	63.6	50.9	80	200	400	10,180[2]	20,360

[1] Million pounds

[2] For comparison, production of U.S. rosin and turpentines for 1972 totaled 1.1 billion pounds.

If 80 percent of the pine pulpwood harvest projected for 2000 in the South were treated with additional oleoresin per cord of 200 pounds (level A), the additional oleoresin would amount to 10,180 million pounds -- 10 times current rosin and turpentine production. The highest assumption (level B) for the year 2000 of 400 pounds of additional oleoresin per cord would total 20,360 million pounds.

A more conservative estimate predicts that the paraquat induced increase over present production will be closer to sevenfold for turpentine and fourfold for rosin in the treated trees. This would amount to an increase of 1,000 million pounds of turpentine in 1985 and 2379 million in 2000. Rosin increases would be 2458 million pounds in 1985 and 5845 million pounds in 2000. The 1985 projection has the assumption that 50 percent of the pine roundwood timber cut for pulpwood would be treated for at least 1 year prior to harvest. This was increased to 80 percent for the year 2000 projection.

The additional 100 pounds per cord yield of oleoresin amounts to an increase of extractives of just over 2 percent of green weight; the 200-pound-per-cord assumption amounts to 4.4 percent of green weight; and the 400-pound estimate is 8.8 percent. These estimates imply a continual improvement in the induced-lightwood technology for both tree treatment and processing.

The implications of the new technology could change every aspect of southern pine management, harvesting, and processing. It may well add an enlarged dimension to the productivity and value of the South's third forest as a major supplier of industrial raw material. Only rarely in forest research does a striking new discovery offer promise of reshaping an entire industry. The patented process of inducing resin soaking in conifers by application of paraquat is just such a finding. Land owners will be able to create more valuable pine stumpage by treating trees before harvest. The product recovery can be accomplished by kraft processing or solvent extraction.

CONCLUSIONS

The materials supply situation for industrial products on renewable extractive basis will not change drastically over the next 25 years. Availability of oils and fats presently derived from annual crops and marine sources may diminish somewhat because of a greater demand for food production. Increases will be seen in the supply of seaweeds and bark, but their overall quantities will not create a major distortion of present use patterns. These will come from tallow and such kraft pulping by-products as sulfate turpentine and tall oil. Oleoresins from pines may well increase 20-fold over 1972 supplies by the year 2000 if the treatment of pines with paraquat is practiced on 80 percent of the stands. This supply would amount to 4-5 times the combined supplies of renewable extractives in 1972 and to nearly 60 percent of the projected market for extractives in 2000 (21 of 35 billion lbs.). However, a more conservative estimate is that increased rosin from pulpwood (some of which might be recovered in wood rosin extraction plants) could equal that of domestic tall oil production or about 400 to 500 million pounds.

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CHAPTER 4

EXTENSION OF MATERIALS USE

CURRENT TECHNOLOGY AND ULTIMATE POTENTIAL

Bark

Bark probably exceeds all other by-products in quantity and availability. However, it probably also exceeds the other materials in terms of it being considered a waste rather than a by-product. Only a minor fraction of the entire supply finds use as mulch, fuel, etc. The recently increased trend to use the entire chipped tree for pulping rather than only the bole may be some sort of bark utilization should this trend continue. Others are the extraction of waxes (BOHEMIA, Inc.), and the conversion of bark extracts into wood adhesives.

Bark constituents are generally examined by extracting comminuted bark samples with various solvents (Harkin and Howe 1971). Generally, the bark is extracted in sequence by these solvents and the nature of the material extracted are indicated below:

Solvent	Substance Removed
Petroleum ether, benzene	Terpenes, waxes, sterols
Water	Polyphenols, tannins, gums, sugars
Acetone, alcohol	Phlobaphenes, tannins
Aqueous alkali	Phlobaphenes, phenolic acids

Chemical processing of bark is limited and the principal chemical products produced commercially from barks are based on the bark's phenolic content (Anderson 1967; Chang and Mitchell 1955; Hergert 1962). Barks generally are much richer than wood in quantity and complexity of extractive components, the most important being (a) the monomeric polyphenols or flavonoid compounds, and (b) the polymeric phenols such as tannins, phlobaphenes and phenolic acids.

Bark tannins, such as those from western hemlock find a large market in oil-well drilling, large quantities are used to thin the muds (Hergert et al. 1965). They act as clay deflocculants, and control the viscosity and gel strength of drilling muds. Some 50,000 tons of mud thinners is used yearly. A major recent development is a commercial preparation of a chemical grout for stabilizing soils from the phenolics of western hemlock bark (Harkin and Rowe 1971).

Other uses for these polyphenolic extracts are as dispersants, binders, deflocculants in ceramic clays, antioxidants, sequestering agents in boiler feed water, flotation agents in ore beneficiation, and stabilizers in asphalt emulsions, as well as in vat dyeing of nylon and desulfurization of gasoline.

Use of the phenolic components of bark extracts in preparing adhesive components used in plywood and particleboard manufacture has been proposed from time to time (Hall 1971; Herrick and Conca 1960; Hillis 1962). Such preparations are based on the reaction of bark phenolic components with an aldehyde, usually formaldehyde.

The chemical reaction of western hemlock bark extract with formaldehyde has been proposed as a bonding agent for plywood (Herrick and Bock 1958; Maclean and Gardner 1952). Mangrove tannin-formaldehyde resin has been investigated as a strong water-resistant adhesive for plywood (Brandt 1953). Wattle tannin is being used in Australia as a waterproof adhesive in the manufacture of plywood and particleboard (Plomely 1966; Plomely and Slashevski 1969). Pinus radiata and ponderosa pine bark extracts have also been investigated as possible bonding agents for particleboard (Anderson et al., 1961).

An investigation was undertaken to evaluate the bark extracts from four West Coast species, including white fir, ponderosa pine, Douglas fir, and western hemlock as bonding agents for particleboard (Anderson et al. 1974a; 1974b; 1975).

The yield of bark extracts from the four west coast coniferous barks varied from 320 to 370 lbs of extract solids per ton of oven-dry bark. When a small amount of paraformaldehyde was added to wood particles which had been sprayed with concentrated bark extract and processed into board, formaldehyde released during the hot press cycle reacted in situ with the polyphenolic compounds present in the extract and formed a boil-proof bond.

The bark extract bonded particleboard met specifications requiring the inherent durability provided by phenolic adhesives (Lehmann 1974). These products are used for floor decking for modular homes, specialized furniture uses, home siding, garage door panels and more recently, as a wall and roof sheathing and single layer floor decking in conventional home construction. Thus, phenol and phenol-resorcinol modified resins can be replaced by a low-cost bark product. This use of bark would be a profitable outlet for bark residues and could lead to virtual independence of the wood particleboard industry from the petrochemical industry (Anon. 1974). The extracted bark residue could be used as fuel or for soil applicaton.

The particleboard industry, until recently, has enjoyed ample supplies of relatively low-cost bonding agents, including urea-formaldehyde and phenol-formaldehyde resins and hence bark extracts were not exploited as possible sources of bonding agents for particleboard. Bark extracts are a rich source of polyhydroxy phenols and the particleboard industry should be encouraged to look to their bark residues as possible source of low-cost polyphenolics to be used in the manufacture of waterproof particleboard. Development will require market research, promotion, and plant investment.

Only one company in the U.S. is producing and marketing bark extracts for its many selected uses. Other forest products plants should be encouraged to make a market research in this area. Some uses for bark extractives and a calculation of costs for bark-derived resin in particleboard are shown in Table 13 and 14.

Table 13

Selected End Uses for Bark Extractives

Bonding agent
Adhesive Plywood
Adhesive Particleboard
Grouting Agent
Tannin
Oil Well Drilling
Antioxidant
Dispersing Agent
Phenolic Replacement
Ceraminc Binder
Ore Flotation
Binder for Clay
Bark Water Additive
Carrier for Insecticides
Trace Metal Complex
Wax

Table 14

Resin Cost for M/sq ft 3/4" Particleboard

Density 0.70 or 44 lbs/cu ft
1000 sq ft - 3/4-inch particleboard = 2,740 lbs/1000 sq ft
2740 x 8 percent solids = 220 lbs solids/M sq ft

	Cost/M-3/4"
Bark extract @ 7¢/lb solids (para)	$18.82
UF @ 19¢/lb solid	41.80
PF @ 25¢/lb solid	55.00
PF modified @ 29¢/lb solid	65.00
Phenol-resorcinol @ 50¢/lb	110.00
Quebracho @ 41¢/lb	90.20

One ton of bark produces about 350 lbs extract solids per ton of dry bark, enough extract to produce 1600 sq ft of 3/4-inch particleboard or 50 - 4 ft x 8 ft panels.

Naval Stores

Turpentine

Apparently, there are plenty of uses for turpentine, and the market could absorb a greatly increased supply.

Rosin

When one considers how rosin can best be used to replace products from nonrenewable resources, one must examine rosin's major uses and the possibility of expanding them at the expense of the low molecular weight hydrocarbon resins with which they are more-or-less interchangeable and directly competitive. These petroleum resins are largely derived as by-products from the cracking of petroleum. In spite of an almost unlimited supply, the market for these products has never been as high as 50 percent of the rosin consumption.

The major use of rosin is in rubber, especially in SBR polymerization which accounts for about 200 million pounds per year. Here rosin has little competition and therefore very limited opportunity for expansion except where rosin and/or hydrocarbon resins are used as softeners or plasticizers. In paper size, the second major use, rosin consumption has been declining. To a minor degree this has been the result of replacement of rosin by synthetic sizes such as styrene-maleic anhydride resins. When this has occurred, special properties obtained from these much more expensive, but yet much more efficient, sizes has been the predominant factor. The major cause of decreasing rosin consumption has been the more efficient use of rosin size by the paper industry and the resulting great decrease in the consumption per ton of paper. Despite a great deal of effort over many years, hydrocarbon resins have not been at all successful in replacing rosin in paper size.

This leaves the general area of resins, used principally in adhesives, coatings, and inks, as opportunities for rosin to replace products from nonrenewable resources. In recent years, particularly in 1974, when rosin prices reached an all-time high, the reverse was true: the usually cheaper hydrocarbon resins were replacing the more expensive rosin-based products. With few exceptions rosin based materials could replace all the hydrocarbon resins used here. Whether they will, depends primarily on demand, supply, and price. Before the major price increases in 1974 the bulk of the hydrocarbon resins sold in the 10 to 20¢ per pound area. Rosin per se was in the same range and resins based on rosin somewhat to considerably higher. Since then the price of all resins rose sharply and recently has been declining.

One must consider that the major rosin product, i.e., tall oil rosin, is a by-product of the kraft pulping industry. Hydrocarbon resins, on the other hand, are by-products of the cracking of petroleum. The alternate use of these by-product streams is as fuel. At the current $13 per barrel price of crude, the fuel value is about 5¢ per pound--certainly not high enough to prohibit non-fuel uses.

It can be said with certainty that an increase in rosin production to replace 400,000,000 pounds of resins from non-renewable resources can be foreseen and is technically feasible.

Tall Oil Fatty Acids

The market for fatty acids is discussed under agricultural materials.

AGRICULTURAL MATERIALS - GENERAL

Historically the industrial uses of fats and oils seem to have relied on several special properties such as their chemical reactivity with oxygen, and their ability to form useful surfactants by saponification. However, drying oils use and soap manufacture seem to be declining in both absolute quantities and on a per capita basis. Research on new uses for natural fats and oils has been conducted for many years at the four USDA Utilization Laboratories. Some examples are: urethane foams from castor oil, plasticizers from animal fats, and polyamides from crambe oil.

Several important questions arise in considering renewable resources in general and fats and oils in particular. The questions considered here are:

1. What should be the "philosophy" of renewable resources?
2. What are likely to be the "best" renewable resources for various purposes?
3. What can be done to ensure that renewable resources are optimally used?
4. What are the consequences of alternative policy decisions?

The Philosophy of Renewable Resources

(Prepared by J. Peter Clark, Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.)

Among alternatives to petroleum based organics, one can consider functional substitution or chemical duplication. That is, the alternative can be a new material that provides similar properties or a new source for the same material. Examples of functional substitution are: cotton textile fiber vs. polyesters, paper vs. polyethylene film, wood vs. filled polyester, and castor oil vs. petroleum lubricating oil.

Chemical duplication is the motive for wood hydrolysis to give glucose which can be fermented to ethanol. Lignin can be processed to yield aromatics and phenolic compounds. Fatty acids can be reduced to hydrocarbons.

Perhaps a third category is the production of chemically functional substitutes. For example, crambe oil can be derivitized to give monomers which polymerize to a new polyamide. The new polymer is related to but not identical with nylon from adipic acid and hexamethylenediamine.

A key fact is that most petrochemicals are derived from some type of oxidation of hydrocarbons. In contrast, natural products are highly oxidized. This means that a chemistry based on renewable resources has a different orientation from petrochemistry. Such a chemistry is reductive and often aqueous compared with the oxidative, non-aqueous petrochemistry.

Among natural products, fats and oils are closer in many ways to hydrocarbons than are the carbohydrates or lignin. (Terpenes, of course, are even closer, but the quantities are somewhat smaller; 160 million pounds of turpentine consumed by industry in 1973.)

The challenge of using natural products is to retain, so far as possible, the useful chemical structure provided by nature. In the case of fats and oils, then, this means finding ways to exploit long chains, double bonds, and carboxylic acid groups.

Sources of Renewable Resources

The major renewable resources are grown on land. Increasingly, land that is suitable for industrial crops is also in demand for foods and animal feeds. Many candidates for industrial crops are themselves also foods and feeds.

Thus there is a competition for the resources and for the space in which to grow them.

Industries considering replacement of depleting resources by renewable resources as raw materials have certain constraints. The most critical is an assured supply. This means that many corporations will try to obtain a captive supply by ownership or contract, as paper companies do now with trees.

Chemical companies will also prefer supplies which have little waste for both environmental and business reasons.

Natural products are rarely pure. Often this impurity is useful as in fats, where a mixture of triglycerides has a lower melting point than a pure compound or in rosin, where the mix remains tacky and does not crystallize. For new chemical uses, however, purification may be more important. This puts a potential premium on sources that have high concentrations of single compounds. At the least, standardization of properties, including properties not now considered important, will be necessary. In the case of annual crop seed, such standardization is partly an agronomic problem, but it will also affect the choice of sources and the processes adapted to new sources.

The best candidates for renewable resources for industry will have these properties:

1. High yield of products per acre (or per invested resources)
2. High concentration of desirable compounds
3. Uses for all harvested material
4. Relatively few compounds or fractions
5. Agronomic flexibility, i.e., not "fragile," wide climatic range, easy to mechanize

Historically, a major by-product of oils from plants has been the meal remaining after crushing. Often the highest value for this meal has been as animal feed because the meal usually is high in protein. Many oil seeds, however, also have toxic substances which require treatment to produce useful feeds.

Some of the better oil seed meals, such as soy, are now being used as human food. This is a small use now but can be expected to grow. As traditional animal feeds are converted to food, less desirable materials will be in demand as feeds. In addition, as the U.S. becomes the granary of the world and as the country depends more heavily on agricultural exports (primarily corn, wheat, and soy) for balancing its international trade, the price of meat will rise because cheap feeds will no longer be available. This may lead to a decrease in meat consumption and hence to a decrease in meat by-products, such as tallow. (Per capita meat consumption, especially beef and pork, showed a 10 percent drop in 1973 after 10 years of steady increase.)

A decrease in U.S. meat production could make plant oils more available especially if the meals could be converted to food or feed for export. Industrial demand could be met by planting new crops where industrially less useful feed crops were grown. The decision would be purely economic, of course. For example, alfalfa and other forages might be in less demand and so crambe or castor could be grown. The forages are not generally exported, but de-toxified oil seed meal might be. There is insufficient demand at present for industrial oils to justify such a change, but the situation could change.

What Can Be Done?

1. New ways to use natural oils and fats need to be found. In particular, exploitation of chemical properties for replacement of petrochemicals should be the goal. Prior work has concentrated on the exploitation of special properties. The new emphasis should be replacement of petrochemicals. For example, electrolytic reduction and condensation of fatty acids can give long chain paraffins.

2. New crop screening should be accelerated. The present effort is quite small and slow. Only a few crops have successfully been introduced in the U.S.; soy is the most prominent example. Crambe and kenaf are close to introduction. There are a few others on the horizon:

   Lesquerella (hydroxy oil like castor),

   Vernonia (epoxy oil),

   Limnanthes (sperm oil substitute).

3. New crop introduction is a complicated business even if it were properly supported. A wild plant needs to be domesticated, which means selection for desirable characteristics that breed true. A foreign crop needs to be adapted to U.S. soils, climate and hazards. Problems include pests, poor seed handling, uneven seed maturing, and inadequate

yields. Basic research could be fruitful in finding ways to accelerate desirable genetic changes.

4. For any new crop, research is needed on all by-products. In particular, ways to remove toxins such as thioglucosides in meals are needed. The usual practice is heat treatment. Selective extraction would seem more fruitful.

5. Risks must be taken by innovators in the field. Plants will not be built until a supply is assured. Crops are not planted unless an outlet exists. Some corporations could assume the entire risk, but government may need to help if the scheme is to succeed. Perhaps a tax credit on land costs for growing raw material would be helpful.

Some Consequences of Heavier Use of Oils and Fats in Industry

1. Considerable new investment in chemical plants for new processes would probably occur.

2. Additional heavy investment in land, new farm equipment, and materials would also be needed.

3. Natural oils and fats will probably compete with the more expensive petrochemicals at first, rather than with crude petroleum. At $13 per barrel, crude oil is $.04 per pound. In 1973, soy oil was $.16 per pound and tallow was $.12 per pound. Historical prices were about 50 percent of these levels. On the other hand, ethanol (a relatively cheap petrochemical) now costs about $.17 per pound.

4. Prices of natural fats and oils grown for industry may become more stable and even drop as chemical companies become directly involved.

5. Some agricultural commodities may drop in price while others rise. For example, meat prices will probably continue to increase as cheap feeds are displaced by more expensive meals (due to more treatment required). Oils that now are used for food and industry may drop due to competition from industrial growers who may be quite efficient. Speculation in some commodities may become less volatile (so long as chemical companies have a captive supply) because the price of "floating" (uncommitted) oil will be set by corporate costs.

6. Government incentives to try new crops may cause dislocation in case of failure. This may affect food supplies by consuming resources.

Conclusion

It should be clear that some source of renewable chemical raw material will ultimately be necessary. Fats and oils will play an important role because of their desirable properties and versatility. Which oils, and how they shall be used, is still not clear.

AGRICULTURAL MATERIALS - SPECIFIC

The enhanced use of agricultural materials is possible through

(a) developing new products from commercial oils, fats, seaweeds, etc., and through

(b) developing new oilseed crops.

The following paragraphs on oilseeds are exemplary of investigations sponsored by the Agricultural Research Service, USDA; equally significant investigations have been carried out on tallow.

New Products from Commercial Oils

Unsaturated fatty acids have at least two positions on the chain where modification can be easily affected; viz., the carboxyl group and the unsaturation position. Most unsaturated fatty acids have 18 carbon atoms with unsaturation at the 9,10-position. Cleavage of the double bond in a mono-unsaturated fatty acid chain results in two 9-carbon fragments, one mono- and the other bifunctional. Polyunsaturated fatty acids will produce the same 9-carbon bifunctional fragment and a number of 3- and 6-carbon fragments depending upon the number of additional double bonds. Generally, additive reactions are more economical than cleavage reactions, but there are exceptions (e.g., production of azelaic acid where the monofunctional fragment, pelargonic acid, has value in ester lubricants).

The products formed by double bond cleavage and hydroformylation undergo the usual reaction of aldehydes. Useful and stable products made include carboxy acids by oxidation, acetals by acetalization, alcohols by reduction, and amines by reductive alkylation.

Another reaction, carboxylation, converts unsaturated fatty esters into useful derivatives. The carboxylation products and derivatives of polyunsaturated vegetable oils are finding many uses, which are being actively investigated.

Uses that have been explored include:

Plasticizers. The acetals from either the C-9 or the C-19 aldehydic esters have promise in plasticizer applications, for example, with PVC.

Polyamides. Both the C-9 and C-19 aldehydic esters have been reductively aminated to the respective amino acids. Nylon-9 is a microcrystalline polymer, and can be prepared from soy esters. Because its melting point is the highest of any of the higher nylons from nylon-8 on (190 to 195 C) and because its low moisture absorption should make it dimensionally stable under conditions of high humidity, it seems a likely candidate for engineering thermoplastics, now a 100-million-pound market.

Poly(ester-acetals) and Poly(amide-acetals). The pentaerythritol acetals of methyl azelaaldehyde and methyl formylstearate are dibasic esters and may be condensed with glycols or diamines to make the respective poly(ester-acetals) and poly(amide-acetals). These polymers have latent crosslinking ability, and when crosslinked by acid or certain metal oxides, they are bonded to glass and other siliceous surfaces. This property has been exploited in the preparation of coatings for glass and of bonded stationary phases for gas chromatography. However, this crosslinking reaction suffers from disadvantages of the high temperature (270°C) required, coupled with discoloration.

Urethane Foams. Technically satisfactory rigid foams have been made from hydroxymethylated linseed oil and its esters of glycerol, trimethylolpropane, and pentaerythritol; from hydroxymethylated soy, linseed, and safflower ethanolamides; and from hydroxymethylated castor, safflower, and high oleic safflower oils. These rigid foams are suitable material for thermal insulation.

Miscellaneous. 9(10)-Hydroxymethylstearic acid can be an intermediate in treating wool to achieve shrink resistance and a soft hand.

New Developments in Coatings

Over the past 25 years, work at the Northern Regional Research Center of the USDA has been carried out with several linseed derivatives to promote the use of linseed oil in coatings. Although they have not received commercial acceptance, as alternates to petrochemicals, they may be worth reexamining. One example is the vinyl ether, prepared by reaction of linseed alcohol with acetylene in the presence of potassium hydroxide. These vinyl ethers can be either polymerized alone or copolymerized to form new drying oil resins. The homopolymer is a somewhat viscous oil that dries rapidly in air to varnish-like, chemically resistant coatings that have excellent adhesion to glass, metal, and wood. Fatty vinyl ether copolymers with styrene can be formulated to make coatings for metals, whose properties of hardness, chemical resistance, and flexibility can be varied to meet specific end uses.

A new type of coating material is based on diethanol amides of linseed fatty acids. These are prepared in situ from linseed oil, and the mixture, composed principally of amides and monoglyceride, is heated with phthalic or other anhydrides to form polyesteramide alkyds which are generally harder, more chemically resistant, and possibly more durable than the usual alkyd. Modification of the polyesteramides with toluene diisocyanate produces even better films. Cost studies indicate that the polyesteramide films are competitive with alkyds. The polyesteramides can be modified with compounds that contain pendant carboxy or amine groups to form water-dispersible systems. Films from these formulations dry rapidly to hard films.

Often conjugated oils, such as tung or dehydrated castor, are used to make rapidly drying, hard films. A laboratory method for producing conjugated linseed or soybean oils has been developed, and these oils yield films having properties similar to those from dehydrated castor oil. Preliminary estimates to make this material on a commercial scale indicate that the process may be competitive with that for dehydrated castor oil. Further evaluation by industrial concerns is needed before pilot-plant or process studies can be carried out.

Cyclic acids are produced when linseed fatty acids are treated with alkali at 260°C. Alkyd resins modified with cyclic fatty acids have improved drying time, hardness, and chemical resistance for both air-dried and baked films compared to the original alkyd.

A number of nitrogenous derivatives of cyclized acids have been made. Mixed amides, nitriles, and amines, prepared from the hydrogenated cyclic acids, have uniquely low melting points for fat-derived substances of their molecular weight. Compatibility with synthetic resins and solubility in organic solvents of the mixed cyclic amides are high compared to common fatty-amide mixtures. The nitriles and morpholides are compatible with PVC and may have potential as plasticizers for it.

Hydroformylated linseed oil has been used to make polyacetal and poly(ester-acetal) alkyds, which when modified with toluene diisocyanate produce films having good hardness, as well as chemical and impact resistance.

Fast drying and hard films with excellent xylene and acid resistance are obtained when maleated or hydroformylated linseed oil is used with hydroxyl-bearing butadiene and acrylic resins.

Both problems of pollution and of consumer acceptance of latex paints have been resolved at least in part by development of linseed emulsion paints. These emulsion paints were available commercially in the early 60s but lost out to lower cost latex paints. Linseed emulsion paints can give coatings that have properties about equivalent to those from latex paints. It should also be noted that not all solvents have been eliminated by Rule 66 and similar legislation.

The problem of yellowing can be minimized in part by proper formulation, and research is now being carried out at the Northern Regional Research Center in efforts to further alleviate the problem.

New Oilseed Crops

The U.S. Department of Agriculture has sought to identify potential domestic sources for imported oils now filling industrial needs. Imported oils (coconut, palm, castor, olive, tung, and rapeseed) have uses that are not or cannot be satisfied entirely by current domestic oils. Needed are seed oils whose chemical compositions and properties fit existing specific industrial applications or improve and extend those areas of application.

Commercial recognition of the industrial utility of high-erucic acid oils is attested to by annual importation of more than 10 million pounds of rapeseed oil. European consumption of rapeseed oil as an industrial oil is considerably higher. However, in anticipation of sustained high volume consumption of rapeseed oil in foods, plant geneticists have introduced several low-erucic acid varieties,and since 1972, major producing areas in Canada and Europe have quickly shifted to these low-erucic acid oils to supply edible oil markets. Rapeseed production in the United States has been minimal, limited primarily to the wheat growing areas of the Pacific Northwest. A domestic source of a strictly industrial high erucic oil undoubtedly would lead to greater industrial utilization in the United States. Crambe (Crambe abyssinica) is the most promising domestic source of an oil consistently rich (55 percent) in this C_{22} acid. High erucic oils have numerous uses. One of the most important commercial derivatives of erucic acid is erucamide, among the best anti-block, slip-promoting additives for high-quality polyolefin films. Brassylic acid, from oxidative cleavage of erucic acid, can be converted to polyamides, to several types of plasticizers and to vinyl- or allyl-type monomers for thermosets or copolymers. It is likely that high erucic oils will be converted to polyol type intermediates for production of polyurethane foams, coatings, and molded items.

The new crops program at the Northern Regional Research Center also has identified Lesquerella as a source of lesquerolic (14-hydroxy-cis-11-eicosenoic) acid, possibly to replace or supplement those products now derived from imported castor oil.

Simmondsia (jojoba) is unique; its oil consists of liquid wax esters, i.e., long-chain alcohols esterified to long-chain acid. Similar esters can be obtained chemically from other triglyceride oils. Vernonia and Stokesia seeds contain epoxy oils rich in vernolic (12,13-epoxy-cis-9-octadecenoic) acid. Visualized applications include uses in resins and coatings as stabilizers and plasticizers.

Other new seed oils that are rich in C_{20}-C_{24} fatty acids have been identified as having potential applications in lubricants and waxes, but plastic and coating applications also may be visualized. Limnanthes, Lunaria, and Simmondsia are plants whose seed oils are rich in these longer chain acids.

CONCLUSIONS

Even though dangers inherent in having a single raw material base are obvious, the plastics industry depends mainly on petrochemicals. Industry has already looked at other base sources, including coal and agricultural annually renewable resources, such as starch and unsaturated vegetable oils, but costs relative to petrochemicals have been too high. The cost ratio now may be changing in favor of agricultural products, but it is premature to make a prediction at this time.

Unsaturated vegetable oils will continue to hold a minor, but significant, and growing place in plastics applications and particularly in the coatings field. In several applications, these oils are unique sources for the intermediates required. In other applications, they serve as promising starting materials capable of being alternatives to petrochemicals. Some vegetable oilseeds, particularly soybeans, are grown on a large scale for edible purposes, and as demand for protein expands, by-products from soybean processing can supply a regular base source for chemical modification. Several vegetable oils are grown specifically for nonfood, industrial uses.

In short, vegetable oils can and do provide a significant, but partial, alternate raw material base for the chemical industry, whose demands for petrochemicals increasingly conflict with energy requirements.

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CHAPTER 5

CONCLUSIONS

Extractives comprise a group of substances of relatively small volume, diverse nature, and versatile character. Their use as by-products from the production and processing of materials of forest, agricultural, and marine origin promises to contribute to the economic feasibility of technologies based on renewable resources. Their nature as chemical raw materials for the manufacture of industrial goods may be crucial to the competitiveness of an industry relying on continuous supplies of plant and animal matters.

In 1972 U.S. industries consumed approximately 5 billion pounds of extractive substances for the manufacture of industrial materials. These extractives were of agricultural (plant and animal), forest, and marine origin. Their market value was in excess of $1 billion. They were used in a great number of different products in which they typically lose their identity.

Currently, about one third of extractives for industrial products comes from tallow, and 31-33 percent each from wood and vegetable oil sources, including soapstock by-products. Oils and fats from the marine environment are processed almost exclusively into food products. Bark has not as yet achieved a sizable market as raw material except for fuel.

Per capita consumption of fats and oils for nonfood uses will probably remain at about the current level. The declining use of u.S. grown vegetable oils as such in industrial products can be attributed to past availability of lower cost petrochemical products as well as to greater demands for food products, domestically and abroad.

Declines in naval stores supplies find their explanation in reduced outputs of the gum and naval stores industries, and in a levelling off of naval stores production from kraft pulping. Gum rosin production has dwindled because of the difficulty in obtaining labor in a labor-intensive industry despite even the abnormally high prices of the recent past.

Increasing replacement of rosin in paper sizes based on nonrenewable resources contributes to an overall decrease in consumption of pulp chemicals.

The continuing decline in production and uses of linseed oil is explained by the increasing acceptance of the convenience and lower cost of latex paints.

The supply of tallow as industrial raw material would advance with beef production, but the rate of increase is not predictable at present.

The induction of light wood formation in pine trees by treatments with herbicides is in an early stage of development; the success and general application of this method could have a big impact on naval stores supplies. Increases of 5 to 20 times of present production could be feasible.

Gains in the production of turpentine and tall oil fatty acids are expected to find ready absorption by industrial raw material markets; rosin needs increased research and development efforts in order to hold its present position.

To achieve an increase in extraction for industrial materials, the Panel suggests that the following steps be taken:

1. Develop increased production of unsaturated fatty acids by a combination of improvements in tall oil recovery, chemical conversion of tallow fatty acids, and development of new oil seed crops on low quality lands.

2. Increase availability and utilization of oleoresin chemicals by development of herbicide systems, and by intensive research on improved products from resin acids and monoterpenes.

3. Demonstrate the potential of bark as a chemical raw material by establishing an integrated pilot plant which makes use of bark's resinous, waxy, polyphenolic, corky, and fibrous components.