

# The Carbohydrate Economy

## IN THIS REPORT

■  
A Historical  
Overview

■  
The  
Carbohydrate  
Economy:  
Present Status  
and Near Term  
Prospects

■  
The  
Current  
Use of  
Plant Matter



## Making Chemicals And Industrial Materials From Plant Matter

By David Morris and Irshad Ahmed

**ILSR**

Institute for Local  
Self-Reliance

# **The Carbohydrate Economy**

**Making Chemicals  
And Industrial Materials  
From Plant Matter**

By David Morris and Irshad Ahmed

**Institute for Local Self-Reliance**

The Institute for Local Self-Reliance (ILSR) is a nonprofit research and educational organization that provides technical assistance and information to city and state government, citizen organizations, and industry.

Since 1974, the ILSR has researched the technical feasibility and commercial viability of environmentally sound, state-of-the-art technologies with a view to strengthening local economies. The Institute works to involve citizens, government, and private enterprise in the development of a comprehensive materials policy oriented towards efficiency, recycling, and maximum utilization of renewable energy sources.

### **Institute for Local Self-Reliance**

1313 5th Street S.E.  
Minneapolis, MN 55414  
(612) 379-3815  
(612) 379-3920 (Fax)

2425 18th Street, N.W.  
Washington, D.C. 20009-2096  
(202) 232-4108  
(202) 332-0463 (Fax)

©1992 by the Institute for Local Self-Reliance  
All Rights Reserved  
Published 1992 Reprinted 2000  
Printed in the United States of America

No part of this document may be reproduced in any form or by any electronic or mechanical means, including information storage and retrieval systems, without permission in writing from the Institute for Local Self-Reliance.

### **Library of Congress Cataloging-in-Publication Data**

Morris, David J.

The carbohydrate economy: making chemicals and industrial materials from plant matter /  
by David Morris, Irshad Ahmed.

p. cm.

"August 1992."

Includes bibliographical references and index.

ISBN 0-917582-25-X : \$25.00

1. Biomass chemicals. I. Ahmed, Irshad, 1963- . II. Title.

TP248.B55M67 1992

661'.8--dc20

92-18177  
CIP

# Acknowledgements

This report would not have been possible without the active assistance of many people. Among the staff of the Institute for Local Self-Reliance, John Decker deserves special thanks for his contribution to both research and production. We also want to thank Jodean Marks for applying her considerable editing skills to immeasurably improve an original draft, and Cynthia Aldridge for her assistance in the production of this report. Special thanks go to Ralph Bohrson and Ingrid Komar for their comments and discussions during the research phase of this project.

We also want to express our appreciation to the many companies that willingly provided information on their processes and products. A special thanks to the following people who generously gave of their time and expertise to provide invaluable suggestions during the preparation of this study:

Peter Colburn, Eco Design Co.; William Doane, U.S. Department of Agriculture; Stuart Ellis, American Soybean Association; James Hettenhaus, International Bio-Synthetics; Joel Hirschhorn, Hirschhorn & Associates; Kenlon Johannes, Missouri Soybean Association; Donna Johnson, Interchem Industries; Jerry Kineson, Warner-Jenkinson; William Luzier, ICI Americas; Steven Mojo, Novon Products; Keith Smith, American Soybean Association.

We would also like to thank the Rockefeller Foundation, the Florence and John Schumann Foundation and the Veatch Program of the North Shore Unitarian Universalist Society for the support they have given this endeavor.



# Table of Contents

Table of contents .....	i
Index of Tables and Charts .....	iii
Index of Figures .....	iv
Introduction .....	1

## PART One

<b>A Brief Historical Overview .....</b>	<b>3</b>
Plant Matter-Based Markets: 1830-1914 .....	3
Cellulosic Crops .....	3
Cotton .....	3
Wood .....	4
Starch Crops .....	4
Oil Crops .....	5
Plant Matter-Based Processes: 1914-1945 .....	5
Cellulosic Crops .....	5
Cotton .....	5
Wood .....	6
Starch Crops .....	7
Oil Crops .....	7
Coal, Iron, and The Rise of the Coal Tar Industry .....	7
Age of Oil .....	9

## PART TWO

### The Carbohydrate Economy:

<b>Present Status and Near Term Prospects .....</b>	<b>11</b>
The U.S. Materials Economy: A Statistical Snapshot .....	11
The New Economics of Plant Matter .....	11
Technological Advances .....	11
Environmental Changes .....	13
Strategies for Displacing Minerals with Plant Matter .....	14
The Current Comparative Economics of Plant Matter-Derived Industrial Products .....	20

**PART THREE**

**A Detailed Examination of the Current Use of Plant Matter** .....23

- End Products .....23
  - Surface Coatings Industry .....23
  - Pigments and Dyes Industry .....27
  - Printing Inks Industry .....30
  - Soaps and Detergents Industry .....34
  - Adhesives and Glues Industry .....39
  - Plastics and Resins .....43
    - General Survey of Uses of Plant Matter in Plastics .....45
      - Plasticizers .....50
      - Copolymers with Bio-Components .....51
    - Bioplastics .....52
      - NOVON .....52
      - PHBV .....53
      - Lactic Acid-Based Plastics .....53
- Intermediate and Specialty Chemicals .....54
  - Biosources .....54
    - Vegetable Oils .....54
    - Tree Oils .....56
    - Lignin .....56
- Chemicals from Plant Matter .....56
  - Surfactants .....56
  - Fatty Acids .....57
  - Acetic Acid .....57
  - Activated Carbon and Phenolics .....58
  - Methyl Aryl Ethers .....60
  - Polyol .....60
  - Glycerol .....61
  - Furfural .....61

**NOTES** .....62

# Index of Tables

1. Production Trend of Natural and Synthetic Fibers .....	9
2. Industrial and Energy Uses of Fossil Fuels .....	10
3. Trend in Material Use, by Material Type .....	12
4. Trend in Uses of Plant Matter .....	12
5. Trend in Per Capita Material Use, by End Use .....	12
6. Trend in Industrial Materials Use, by Material Type .....	12
7. U.S. Use of Plant Matter in Industrial Products: 1989 .....	14
8. Total 1990 Organic Chemicals Production in the U.S. ....	16
9. Total 1990 Inorganic Chemicals Production in the U.S. ....	16
10. Annual Availability of Waste Bioresources for Fuels, Chemicals, and Biomaterials in the U.S. ....	17
11. Projection of Plant Matter Potential and Its Current Utilization in the Production of Industrial Materials and Important Intermediate Chemicals in the U.S. ....	18
12. Projected Increase in the Industrial Products Derived from Plant Matter by 1996 .....	20
13. Normalized Price Comparison of Plant Matter-Based with Petrochemical-Based Wall Paints.....	26
14. Cost Comparison of Inorganic, Synthetic Organic, and Natural Plant-Based Coloring Pigments and Dyes .....	28
15. Price Comparison of Natural, Extracted Colorings with Food, Drug and Cosmetic Grade Synthetic Dyes .....	29
16. Typical Range of Composition of Soy Oil-Based Inks and Water-Based Inks.....	31
17. Typical Composition of the Latest Powdered and Liquid Detergent Formulations Replacing STPP/TSP with Enzymes and Zeolites .....	35
18. Average Composition of Conventional Dry Phosphate-Based Powdered and Liquid Detergents Produced in the U.S. ....	37
19. Comparative Cost Differential Analysis of Powdered and Liquid Laundry Detergents Derived from Petrochemicals and Bio-Based Components .....	38
20. Cost Comparison of Petrochemical and Bio-Based All-Purpose Cleaners.....	39
21. Total Production of Natural and Synthetic Adhesives in the U.S. ....	40
22. Production of Major Product Categories of Plastics in the U.S. ....	44
23. Comparison of Typical Property Ranges for Plastics Derived from Petrochemical and Plant Matter Sources by Polymer Type and Applications .....	46
24. Plasticizer Production from Plant Oils and Petrochemical Feedstocks in the U.S. ....	50
25. Industrial Applications Breakdown of Soybean Oil Consumption in the U.S. ....	54
26. Yields and Prices of Potential and Conventional Oil Crop Raw Materials for Fuels and Industrial Products Manufacturing in the U.S. ....	55
27. Estimated Vegetable Oil Contributions to Specialty and Intermediate Chemicals Production in the U.S. ....	56
28. Market Trends of Fatty Acids (C8-C14) Production from Synthetic and Plant Oil Hydrolysis Routes in the U.S. ....	58
29. Comparative Economic Crossover Analysis for the Production of Fatty Acids (C8-C14) from Synthetic vs. Plant Oil Hydrolysis .....	59



# Index of Figures

1. Average Composition of Lignocellulosic Feedstocks by Type .....	6
2. Elemental Breakdown of Fossil Fuels and Plant Matter by Carbon, Oxygen, and Hydrogen Content .....	8
3. Trend in Total Material Usage in the U.S. ....	13
4. Industrial Material Use, by Material Type .....	13
5. Interrelationship of Major Precursor Chemicals Derived from Fossil Fuels for the Manufacture of Consumer End-Products in the U.S. ....	15
6. Market Share of Plant Matter-Derived Chemicals and Industrial Materials in the U.S. ....	19
7. Cost Premium of Plant Matter-Derived Chemicals and Industrial Materials in the U.S. ....	19
8. Representative Product Spectrum of Biomass Processing .....	21
9. Conceptual Diagram of Biomass Conversion Processes and Products .....	22
10. Production of Surface Coating Products in the U.S. by Application Type in 1990 .....	23
11. Typical Liquid Paint Composition .....	24
12. Ink Market Breakdown by Application Type in the U.S. ....	32
13. Annual Demand for Phosphates in the U.S. ....	36
14. Adhesives and Sealants Market, by Use .....	41
15. Adhesives and Sealants Market, by Type of Adhesive .....	42
16. Total Annual Production of Plastics and Resins in the U.S. ....	45
17. Price Comparison Between Coconut Oil and Ethylene: Raw Materials for the Manufacture of Surfactants .....	57

# THE CARBOHYDRATE ECONOMY

## Making Chemicals and Industrial Materials from Plant Matter

### Introduction

One hundred fifty years ago most of our non-food consumer products and industrial raw materials were derived from plant matter in all its forms – fruits, vegetables, grains, grasses, bushes, and trees. The rest came from animal matter, and from inorganic (noncarbon-based) minerals like sand, iron, and other metal ores.

Then came the discovery of fossil fuels, whose name derives from the fact that they are the fossilized remains of living matter. Like living matter, fossil fuels are organic (carbon-based) materials; they are composed primarily of hydrocarbons. But because they are dead matter, fossil fuels are called minerals: organic minerals.

In the mid-nineteenth century, hydrocarbons began to vie with carbohydrates for materials supremacy. Coal, and later to a much greater extent petroleum, became the basic raw material of industrial economics. Industrial uses of plant matter stagnated. Research and development in the carbohydrate economy tapered off and, after World War II, virtually ceased.

Fossil fuels replaced plant matter because they offered definite advantages. As fuels, they contain much more energy by weight and volume, making them easier to transport and store. The liquid nature of petroleum, and the ease of liquefying natural gas, allow them to be transported cheaply over long distances via pipelines, and to be more easily converted into by-product chemicals. The large-scale nature of petroleum refineries, and the attendant size of their parent corporations, enables them to afford vastly larger research and development budgets than their much smaller and more dispersed agriculture- and forestry-based counterparts.

By 1970, petroleum had routed carbohydrates in virtually every product category, except for paper manufacturing. Oil accounted for 70 percent of our fuels and more than 95-percent of our organic chemicals.

Now, just 20 years after the age of oil reached its apogee, we may be seeing the pendulum swing back in favor of a carbohydrate economy. In the 1980s and 1990s we discovered the disadvantages of relying on fossil fuels.

From an environmental perspective, all kinds of pollution, from acid rain to global warming, from smog to ground water pollution have been linked to using fossil fuels.

From a political perspective, relying on distant lands for our energy needs imposes very high national security costs.

From an economic perspective, relying on imported raw materials when local alternatives are available weakens local and regional economies.

The 1990s may be witnessing a historic turnaround in the fortunes of plant matter. The comparative economics of carbohydrates and hydrocarbons is changing. Advances in the materials and biological sciences are reducing the cost of manufacturing plant matter-derived products while environmental regulations are increasing the cost of hydrocarbon-based products. Moreover, the growing environmental consciousness has prompted many customers to pay willingly a "green" premium for carbohydrate-derived, environmentally benign products.

The potential industrial market for plant matter consists of both fuels and chemicals. The energy market is by far the larger. In 1989, Americans used 1.8 billion tons of materials for fuel: triple the ton-

nage of all plant matter consumed that year for food and nonfood purposes combined.

Yet the very size of the energy market raises important environmental and social questions. If we were to substitute plant matter for a majority of our fossil fuels, what would be the impact on the U.S. and the global food supply? What would be the effect on soil erosion, on biodiversity, on water quality resulting from the increased use of fertilizers and pesticides?

The potential scale of the energy market, and the need to address environmental effects in detail, convinced us to address the issue of biofuels in a separate, upcoming study.

This report focuses on industrial applications for plant matter in the form of cellulose, starches, and vegetable or plant oils. It is not an analysis of the long-term potential, but rather of the current status of an emerging economy. Its focus is restricted to those plant matter-derived products already in the marketplace.

A few intermediate chemicals derived from plant matter have been in the marketplace since the beginning of this century (e.g. carbon black, adhesives). These are making new inroads into petrochemical markets. But the appearance of carbohydrate-based consumer products is a very recent phenomenon. The vast majority of these products, such as enzyme-based detergents or vegetable oil-based inks and paints or starch-based plastics, were unavailable only a decade ago. While most are still more expensive than their hydrocarbon-derived counterparts, they have already found a share of the market due to green consumerism and environmental regulations. Moreover, their price has dropped significantly in the past 5 years and promises to continue to drop in the near future.

The carbohydrate economy is still very much in its infancy, but our research indicates that it has clearly moved beyond the birthing stage. Plant matter-derived products now have footholds in markets from which they previously were excluded. And they have captured significant portions of other markets in which they previously had only a marginal presence.

A renaissance of a carbohydrate economy holds great promise not only for environmental protection but also for rural economies. Increasing the demand for plant matter will raise its price, thereby increasing farmers' revenue. Moreover, plant matter, unlike petroleum, is expensive to transport. This encourages processors to locate plant matter-based

manufacturing jobs in rural areas, strengthening area economies, expanding jobs, and increasing tax revenues. Policies that promote a carbohydrate economy can thus fulfill both environmental and economic development objectives.

The struggle between carbohydrates and hydrocarbons is more than 150 years old. In the 1990s, this competition is simply moving into another stage – a stage in which the prospects of the carbohydrate economy are brighter than ever.

---

This report consists of three sections.

Part I contains a historical overview of the materials economy. It briefly traces the comparative developments of products and technologies based on various kinds of plant matter and hydrocarbons.

Plant matter contains several key substances: carbohydrates, plant oils, proteins. By weight, carbohydrates constitute the largest component of plant matter. That led us to use this component in the title of this report. Carbohydrates can be divided into three major commercial categories: starches, sugars, and cellulose. This report will not examine protein as an industrial material, even though protein-based lacquers and plastics were produced in the early part of this century. Protein's value as a food makes it an unlikely and inappropriate industrial material. This report also focuses on starch rather than sugar because in the United States starch is by far the most abundant industrial material produced by plants.

In Part I, the cellulosic crops described are cotton and wood; the starch crops are grains; and the oil crops include grains and other oilseeds. The hydrocarbons include coal, oil, and natural gas.

Part II provides an overview of our use of materials, broken out by raw material category (plant matter, organic minerals, and inorganic minerals) and by end-use category (food, construction, industrial, and fuel). This section also presents the conclusions from our research on the current comparative economics of plant matter-derived industrial products.

Part III contains an extended evaluation of the new carbohydrate economy, this time broken out by product categories (e.g., paints, detergents, plastics). Since this is a dynamic economy, with new companies and products entering the marketplace monthly, the products discussed may be viewed as exemplary, but do not represent the universe of all available products in each category.

# PART ONE

## A Brief Historical Overview

In 1830, by one estimate, Americans used two tons of plant matter for every ton of organic and inorganic minerals.<sup>1</sup>

Most of our clothes were made of plant fibers – cotton, flax, hemp. The rest came from animal sources – wool, leather, fur, silk. Industrial solvents were made from grain or wood alcohol, dyes from various parts of plants, paints from vegetable oils. As late as 1870, wood fuel contributed 70 percent of our total energy. Wood also served as our primary construction material, used to make everything from handles and fences to houses, bridges, and even car bodies.

### Plant Matter-Based Markets: 1830-1914

#### Cellulosic Crops

The cell walls of all living plants are composed of cellulose. "The sturdy oak and stately palm, the grass that covers the good earth, the lichens that clothe the rocks, even the minute algae that flourish in the sea, all are manufacturing cellulose. It is the great primary substance of the whole vegetable kingdom."<sup>2</sup>

The two primary cellulosic materials used for industrial purposes in the last 150 years have been cotton, which is more than 90 percent cellulose, and wood, which consists of 50 percent cellulose.

#### Cotton

The cellulosic fibers of cotton provided the basis for the first global industry – textiles. In the nineteenth century, textiles was the world's largest manufactured goods industry. Chemistry, still an infant discipline, grew up by developing new ways to weave, treat, color, and protect fibers and fabrics.

In the 1840s, for example, Thomas Kingsford devised a method for producing large quantities of

cornstarch, which could be applied to cotton fibers to make them easier to manage. In the 1780s, Claude Berhollet discovered that chlorine could whiten cloth in minutes. The traditional bleaching process involved laying the cloth out in the sun and took several days. By the mid-nineteenth century, chlorine had become a major industrial chemical, with the textile industry its biggest customer.

Scientists did not limit themselves to developing new ways to process and protect natural fibers. They also learned to use cellulose as a chemical feedstock. They altered the underlying chemical structure of the cotton fiber, enabling the manufacture of new products with entirely different properties and markets. The new material they produced has sometimes been called "chemical cotton."

Chemical cotton was the basis for the first synthetic fiber. Count Hilaire de Chardonnet imitated the action of silkworms, which extrude a gum in the form of a fine continuous filament. After converting cotton fibers to soluble form, Chardonnet pressed the dissolved or digested cellulose through a small opening and produced a strong, durable fiber called rayon. The first commercial rayon factory opened in France in 1889. By the start of World War I, more than 100 factories were producing rayon.

Cotton was the source of the very first plastics as well. Nitrocellulose, also called cellulose nitrate, was first developed in the 1820s when Christian Schoenbein, looking for a way to strengthen fibers, coated cotton with nitric acid and sulfuric acid, demonstrating its polymeric properties.

Chemists learned that if nitration is complete – that is, if each of the possible nitrogen atoms is combined with a cellulose molecule – the product is explosive and almost insoluble. If nitration is incomplete in varying degrees, the product, while it will burn, will not actually explode. As the degree of nitration decreases, these products are increasingly soluble in a mixture of alcohol and ether. This allowed even further latitude for developing new products.

In 1832 Henri Bracconet modified the proportion of nitric acid and produced a water-resistant, moldable product which he called xyloidine.

Xyloidine found its first commercial application as a liquid court plaster, a waterproof, protective coating for cut or abraded skin tissue. The material contracted significantly on drying; the resulting film was brittle, prone to cracking and peeling. In 1850, wood-derived turpentine was added to make it flexible.

In the 1870s, printer John Wesley Hyatt and his brother and partner, Isaiah, modified the process of making cellulose nitrate and developed the world's first commercially successful plastic. Because of its cellulosic feedstock, Isaiah called the new plastic "celluloid." Celluloid was the basis for checkers, dominoes, and molded dental blanks.

Still another modification of nitrocellulose was used to make photographic film. To this day, many in Hollywood still call their movies "celluloids."

## Wood

Scientists discovered and classified the cellulosic content of wood in the 1820s. In the 1840s, mechanical processes were developed for producing wood pulp; later, chemical processes were also developed. The modern paper industry was born. Since an enormous amount of cellulose is available in an acre of trees, wood quickly displaced the traditional cellulosic sources of paper, such as rags and straw. Wood pulp became the raw material of choice, and production rose from 1,000 tons in 1869 to 1.2 million tons in 1899.

Wood traditionally has been used as a construction material. For centuries it has also been converted into charcoal for the smelting of iron. That conversion process, called destructive distillation, involves burning wood in the absence of oxygen. In the late nineteenth century destructive distillation was used to produce industrial chemicals such as methanol or wood alcohol. Methanol was used as an industrial solvent and also, at the turn of the century, as an intermediate chemical in the production of plastics and other products.

## Starch Crops

Pure cellulose, whether it comes from cotton or hemp or wood, consists of 44.4 percent carbon, 6.2 percent hydrogen, and 49.4 percent oxygen. Translating these percentages of gross weight into the

atomic weights of these three elements gives the chemical formula for cellulose as  $C_6H_{10}O_5$ . This combination of carbon, water, and oxygen is called a carbohydrate.<sup>3</sup>

Starch has the same chemical formula as cellulose, but its atoms are arranged quite differently within the molecule. This gives it properties very different from those of cellulose. Starch has a key advantage over cellulose. It can easily be broken down into its simpler component sugars by the action of microbes in a process called fermentation. Cellulose is harder to break down because it is protected by a covering made of another chemical, lignin. Indeed, woody crops are often called lignocellulosics because lignin is a significant component.

The first industrial product derived from sugars and starches was drinking alcohol. Fruits and grains were the primary feedstocks. In the early nineteenth century, alcohols began to be used not only as liquor but also as industrial materials and fuels. In the 1850s about 80 million gallons of grain alcohol, or ethanol, were produced in the United States annually. Ethanol was used as a solvent and as a lighting fuel for lamps.

The growing use of grain alcohol as an industrial material or fuel ceased in the U.S. in 1862. That year the federal government imposed a \$2.08 per gallon tax on liquor to pay for the Civil War. Industrial alcohol was subject to the tax, but poisonous materials like petroleum-derived kerosene or wood-derived methanol were not. A generation passed before Congress lifted this tax in 1906. Research and development in grain alcohols came to a halt for almost 50 years.

The understanding of fermentation, however, did expand, albeit slowly. It was not until the 1870s that Louis Pasteur proved his theory that yeast cells were responsible for fermenting sugars into alcohols and carbon dioxide. Enzymes, protein substances produced by microbes which are the actual keys to fermentation, were not identified until later, and were isolated and produced commercially only after World War I.

Fermentation processes were notoriously slow, expensive, and low-yielding. Scientists had to isolate and select the single most suitable organism from a bewildering number and variety of microorganisms present in nature. Fermentation conditions such as acidity, air supply, and concentration of nutrients had to be carefully adjusted for days in order to achieve the proper result.

Nevertheless, industrial fermentation of chemicals did occur, beginning in the U.S. in the mid 1880s with the production of acetic acid. Lactic acid and propionic acid followed in the early 1900s. Citric acid and gluconic acid were produced by fermentation in the 1920s and 1930s.

Starch was also used in the textile industry. Its use actually began during the Middle Ages, when it was a common stiffening agent. By the early 1800s, the English were using wheat starch in textile sizing and warp glazing. Also during that time, potato starch was introduced to supplement wheat starch in the textile industry. A fire in a textile mill in Dublin, Ireland, led to the discovery of dextrans (roasted starch) in 1821.

Starch itself is not soluble in water, but its derivative, dextrin, dissolves readily to produce adhesives, glues, pastes, and gums. By the early 1830s, both starch and dextrin were produced in the U.S. from a variety of agricultural crops, including wheat, potato, and corn.

## Oil Crops

Oil has been obtained from plants since the beginnings of recorded history. Its first industrial uses were probably for illumination. The discovery that linseed oil would mix with pigments to make an excellent artist's paint encouraged the tremendous increase in painting during the Renaissance.<sup>4</sup> Castor oil was used before the petroleum era as a lubricant for the wheels of carts and wagons.

Oils are sometimes called fats. There is no chemical distinction between the two, although oils are usually liquid at room temperatures while fats are solids. High concentrations of oils are usually found in the seeds of plants, and occasionally in the fleshy part of the fruit, as in the olive and oil palm. The oil functions as a reserve of high-energy food for use by the germinating seed. (Starch serves a similar purpose in species such as wheat and corn.)

Corn oil is obtained as a byproduct of industries that use corn for its starch. Rice oil is recovered from the bran after its removal from the seed in the production of polished rice. Oil can be taken from the seeds of grapes used in the wine industry or from the seeds of the wild radish and wild mustard. Tall oil is a byproduct of the manufacture of kraft paper.

In the late nineteenth century these vegetable oils were used to make paints, linoleum, soaps, and emulsifiers.

## Plant Matter-Based Processes: 1914-1945

### Cellulosic Crops

#### Cotton

Cellulose nitrates had several negative properties. One was their flammability. Another was their lack of flexibility in manufacturing. In the late nineteenth century scientists mixed cotton with acetic anhydride, made from plant matter-derived acetic acid, and produced cellulose acetate, a chemical with improved properties.

When a series of tragic fires in movie theaters occurred around 1920, cellulose acetate, or "safety film," quickly replaced its more flammable cousin, cellulose nitrates.

Just as they had done with cellulose nitrates, entrepreneurs learned to vary the formula and the manufacturing process to make different kinds of cellulose acetates. Nitrocellulosic lacquers remained on the market. They were used primarily in spray paints on the automobile assembly line, where consumption increased from about 500,000 gallons in 1918 to 43 million gallons in 1929. But cellulose acetate lacquers also found widespread use.

A cellulose acetate yarn, called Celanese, was introduced in the 1920s. Initially, it sold for twice the cost of rayon. In order to establish a market, the Celanese company involved itself in virtually every stage of production, from making the new fiber to weaving it into yarn and fabrics to dyeing the fabrics and selling the finished product. The textile mills finally accepted the new material. Acetate yarn rose from 3 percent of all synthetic fibers in 1925 to 33 percent in 1940.<sup>5</sup>

In 1928 a cellulose acetate plastic molding powder was developed. Rather than make the powder into finished products, the manufacturer, in an innovative marketing move, sold the chemical directly to the embryonic custom plastic molding industry. The production of cellulose acetate plastics jumped from 100 tons in 1931 to 5,000 tons in 1935 and 10,000 tons in 1939. The rise of injection molding was the impetus for this astounding increase.<sup>6</sup> Over this same period, the price of cellulose acetate dropped from 78 to 58 cents per pound.<sup>7</sup> Steering wheels, instrument panels, knobs, and levers in cars were made from these plastics. Cellulose acetate sheeting was used as an interlayer for safety glass.

**Wood**

Wood had been used in the nineteenth century to make methanol, a major industrial chemical. The first hard, durable plastic, invented by Dr. Leo Baekeland in 1909, was made from phenols derived from coal tars and methanol derived from wood. Bakelite was the key material that led to the development of automobile electric ignition systems. After World War I, it was the primary material used to manufacture millions of car radios.

Ground wood pulp was not initially considered a suitable raw material for manufacturing synthetic fibers. Wood has only a fraction of the cellulose of cotton. The short cellulose fibers in wood have a lower mechanical strength than the fibers in cotton. Wood pulp also contains saps, resins, and other substances that had to be removed by additional processing.

Manufacturers learned to overcome these obstacles. By the year 1930, wood had replaced cotton as the favored feedstock for rayon manufacture. In that year U.S. rayon producers consumed 72,000 tons of wood pulp, accounting for 65 percent of the cellulosic materials used to manufacture rayon.

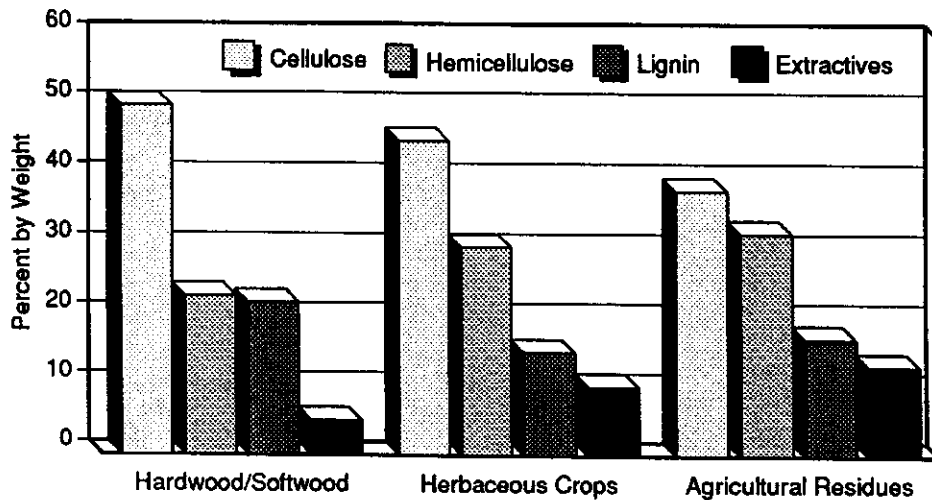
Cellulose from wood also became the basis for the first plastic film. Just as rayon was made by

forcing cellulosic syrup through tiny holes, cellophane was made by flowing wood pulp through a narrow slit. In the late 1920s, an engineer from Minnesota Mining and Manufacturing used the clear, crinkly cellophane to create an adhesive-backed tape for food packaging and labeling. He called it Scotch tape.

Wood pulp production rose from 2.5 million tons in 1910 to 4.6 million tons in 1930 and 10.4 million tons in 1941.<sup>8</sup> Along with this increase in production came a rapid expansion of the availability of one of wood pulp's important byproducts: lignin. Lignin is the third basic polymeric component of plants, along with cellulose and hemicellulose.<sup>9</sup> Figure 1 shows the composition of various plants.

One ton of southern pine made into paper by the kraft chemical process yields about 600 pounds of lignin. In 1945, the Forest Products Laboratory calculated that a ton of lignin could yield 280 pounds of phenols, suitable for making plastic, and about 140 pounds of methanol. As early as 1930, Dr. Charles A. Browne, Chief of the U.S. Bureau of Chemistry, was predicting that lignin "probably offers as many methods of utilization for the manufacture of tanning materials, dye-stuffs, and other industrial products as were offered eighty years ago by that other trade waste, coal tar."<sup>10</sup>

**Figure 1. Average Composition of Lignocellulosic Feedstocks by Type**



SOURCE: C.E. Wyman, IBIS 1992 Fuel Ethanol Workshop, Wichita, Kansas, June 9-11, 1992.

## Starch Crops

Fermentation processes received a huge boost during World War I when scientist Chaim Weizmann used certain bacterial strains to produce butyl alcohol and acetone. Weizmann's process became the basis for the first large-scale industrial fermentation facilities. Acetone, a key ingredient in the manufacture of munitions, was in high demand. The British Ministry of Munitions commandeered six whiskey distilleries and converted them to ethanol-acetone plants for the duration of the war.

Butyl alcohol also found important uses. Combining butyl alcohol made from fermentation with acetic acid made from the destructive distillation of wood, produced butyl acetate, an excellent lacquer solvent. Later, during World War II, butyl alcohol would have a far greater use in the manufacture of synthetic rubber.

However, industrial uses of grain alcohol continued to be impeded by beverage alcohol taxes. After the liquor tax was lifted in 1906, annual production of grain alcohol as a transportation fuel and for military purposes rose, exceeding 50 million gallons by 1918. But in 1919, the Eighteenth Amendment to the Constitution prohibited the sale of liquor. Although the prohibition did not specifically ban the sale of industrial alcohol, the difficulty of obtaining permits for production and the overall bad name given to alcohol during Prohibition discouraged manufacturers from engaging in alcohol-related commerce and research. William Hale, one of the leaders in a movement to promote the industrial uses of agricultural crops, looked back in the mid-1930s on the impact of the Eighteenth Amendment and declared, "The plague of Prohibition set back the cause of organic chemistry for 14 years."

## Oil Crops

Oil crops continued to be used as industrial materials, although petroleum oils began to make inroads into traditional vegetable oil markets as early as the 1920s. A significant development in oil crops was the rapid expansion of soybeans, a crop first introduced in the U.S. in 1840. One million bushels were grown in 1919, 7.8 million bushels in 1928, and 200 million bushels in 1940. While soybean protein and oil were used mainly for animal feed and food products, they also found industrial applications. A fire-suppressant foam was made from soy protein, as was a water-resistant glue, used in the first washable wallpaper. Fatty acids derived from

soy oil were processed into saturated palmitic acid which was used in the manufacture of soap and cosmetics.

The unsaturated portion of the fatty acids was used as a high-quality drying oil and as a base for paints, varnishes and lacquers. Soy oil-based varnishes, and lacquers resisted the yellowing action of sunlight. The Illinois Agricultural Association created a market for soy oil-based products in the 1930s by forming a cooperative to sell them, initially to the association's own members.

## Coal, Iron, and The Rise of the Coal Tar Industry

Plant matter served as the first feedstock for many product breakthroughs, but it was not the only carbon-based material to be used in industry. Since the beginning of the industrial era, living carbon in the form of carbohydrates has had to compete with fossilized carbon in the form of hydrocarbons.

The first industrial hydrocarbon was coal. The invention of the efficient steam engine by James Watt in the late eighteenth century vastly increased the demand for fuels. Europe, fearful for its timber supplies, began to shift from wood to coal in the first quarter of the nineteenth century.

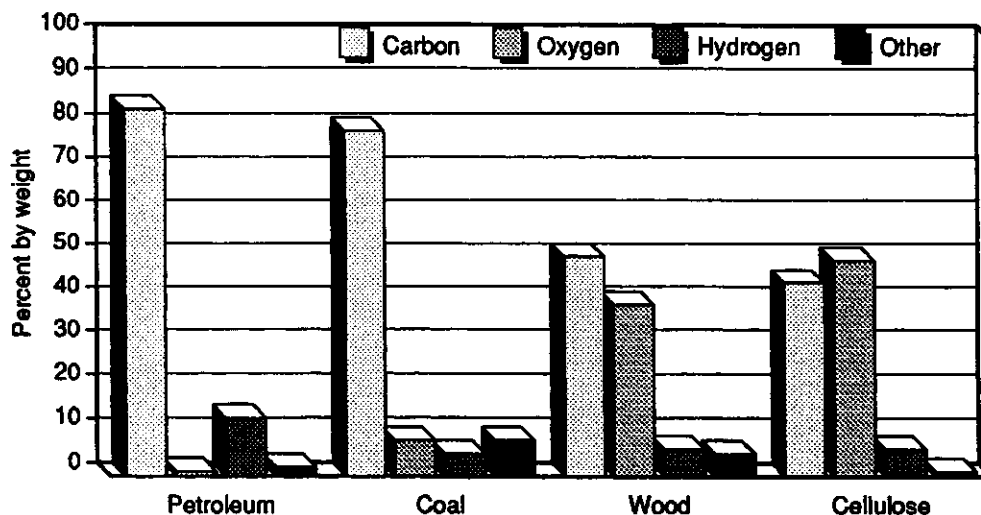
Coal was an attractive fuel because of its abundance and its energy density. Coal has almost twice the carbon density of wood and only a fraction of wood's moisture content. Half a ton of coal contains the same amount of energy as two tons of wet wood.<sup>11</sup> That compactness became especially attractive when mobile steam engines made their first appearance in railroads and steamships in the first half of the nineteenth century. See Figure 2 for an elemental breakdown of fuels.

The steam engine provided the impetus not only for coal's use as a fuel, but also for iron's use as an industrial material. Steam engine-driven bellows raised foundry temperatures, thereby improving iron's quality. Steam-driven railroads created a huge demand for iron, both for rail car bodies and for tracks. For a century, coal was the railroad's primary cargo.

Coal soon surpassed wood as our basic fuel, and iron surpassed wood as our basic industrial material. In 1860 Americans consumed about 15 million tons of wood and 4 million tons of coal. By 1900



**Figure 2. Elemental Breakdown of Fossil Fuels and Plant Matter by Carbon, Oxygen, and Hydrogen Content**



SOURCES: The Babcock & Wilcox Company, Barberton, Ohio, 1992; *Fuel Oil Manual* (New York: Industrial Press Inc., 1985); *Shreve's Chemical Process Industries*, (New York: McGraw-Hill, 1986).

consumption of wood had risen to about 45 million tons, while coal consumption had soared to 212 million tons.<sup>12</sup>

Iron and steel smelters used millions of tons of coke as fuel. Coke is made by the destructive distillation of coal, a process similar to that of making charcoal from wood. Like the charcoal process, the production of coke results in a number of byproducts. One ton of coal yields almost 1,500 pounds of coke, about 10,000 cubic feet of gas, 12 gallons of tar and light oils, and almost 20 pounds of liquid ammonia.

In 1880, 3 million tons of coke were produced from coal by the coking process; in 1990, 20 million tons were produced.<sup>13</sup> The huge supply of waste byproducts sparked the interests of chemical experimenters, who learned how to make them into an ever-wider array of useful products. In the 1790s William Murdock, chief engineer for Boulton & Watt, discovered that creosote made from coal tar could preserve wooden ships. In 1798 Murdock used coal gas to light Boulton's Soho Works; in 1812 Samuel Clegg founded the London Gas Light & Coke Company. Charles Macintosh converted naphtha, made from a coal tar distillate, into a rubber solution to waterproof materials. His name, spelled with a K, is associated with the raincoat.

The first major industrial products from fossil fuels were dyes made from coal tars. In the late

1840s, an 18-year-old English youth, William Perkin, dropped a piece of blank cloth into aniline, a coal tar derivative. The next morning he returned to the laboratory to find the cloth dyed a handsome deep purple. This dye proved more durable than existing natural purple dyes. "Perkin Mauve" became an immediate commercial success.

In 1859, a purple-red dye named magenta was synthesized. Aniline Black and Aldehyde Green made their debuts in 1862.

Synthetic dyes quickly displaced traditional natural dyes. In 1869, 400,000 acres in southern Europe were planted in madder, a source of orange-red dye dating back to ancient Egypt. These plantations yielded 70,000 tons of madder root for the dye industry. That year Perkin produced a ton of synthetic alizarin, the chemical pigment of the madder plant. In 1870, 40 tons of synthetic alizarin were produced; by 1878 its production was the equivalent of 950,000 tons of natural madder root. The synthetic product cost only one-third as much as the natural product.

In the 1880s, chemical companies learned to synthesize the much-prized blue dye, indigo. For 10 years thereafter, the industry tried hundreds of techniques to reduce synthetic indigo's high production cost. The key obstacle was a very low process yield of 15 percent. In 1891, a laboratory worker accidentally broke a thermometer into a vat,

spilling mercury into the fluid. Yields soared. The mercury acted as a catalyst, a material that accelerates a chemical reaction without itself being used up. This discovery of catalysts had two results. First, by 1913, production of synthetic indigo had reached 6,500 tons, while production of natural indigo had shrunk by 90 percent from its 1890 peak. Second, chemists set about the task of finding other catalysts to speed up and increase the yield of other industrial processes, lowering the cost of production and making synthetic products competitive with natural products.

By the end of the nineteenth century, coal tar derivatives were used to make a wide variety of products, from insecticides to antiseptics, explosives, anesthetics, and even food items like vanilla flavoring and saccharine. Just before World War I, German engineers learned to liquefy coal and were hoping to use it as a transportation fuel to compete with gasoline and grain-derived alcohol.

In 1925, despite the inroads made by coal derivatives, plant matter still represented about 30 percent of all materials consumed in the U.S. and 35 percent of all industrial materials. But another hydrocarbon was about to dominate the materials economy. The age of oil was about to begin.

## Age of Oil

In 1861 Edwin Drake discovered a cheap way to extract oil when he drilled the first commercial oil

well in Titusville, Pennsylvania.<sup>14</sup> For many years kerosene was the only marketable product derived from crude oil. Gasoline was a wasted byproduct. The automobile changed that. By 1907 gasoline sales topped kerosene sales. In 1915 Henry Ford's assembly line began mass producing vehicles. By 1919 almost 5 billion gallons of gasoline were sold, equivalent to 17 million tons.<sup>15</sup>

Petroleum had two great advantages over coal and plant matter. As a liquid, it could be transported cheaply over long distances, and it was easier to convert into chemicals than were the solids of coal and plant matter.

Engineers learned how to boost the yield of the valuable gasoline component of the crude oil by "cracking" the larger crude molecules. In 1913 Friedrich Bergius invented a process that yielded as much as 50 percent gasoline, up from the 10 percent or lower yields previously achieved. Cracking processes not only produced more gasoline. This procedure also resulted in a variety of chemicals, that, like coal tars before them, became the basis for new products.

Vinyl chloride was introduced in 1913, nylon in 1930, and Lucite, a clear, tough plastic resin, in 1938. Teflon, neoprene, synthetic rubber, Orlon, Dacron, polyester, and Mylar soon followed. Between 1921 and 1939 production of petrochemicals rose from 10,500 tons to 1.5 million tons. In 1939 the average price of petrochemicals was 13 cents per pound; the price of coal tar derived chemicals was 82 cents per pound.<sup>16</sup>

**Table 1. Production Trend of Natural and Synthetic Fibers (in millions of tons)**

	Cotton	Wool	Rayon/ Acetate	Fossil Fuel- Based	Total Fibers	Fossil Fuel Portion
1946	2.45	0.368	0.333	0.016	3.167	0.51%
1955	2.50	0.206	0.428	0.179	3.313	5.40%
1970	2.20	0.120	0.350	0.90	3.570	25.21%
1980	1.56	0.083	0.374	3.58	5.597	63.96%
1988	1.98	0.106	0.306	4.33	6.722	64.42%

SOURCES: U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, Washington, D.C., 1976; U.S. Bureau of the Census, *Statistical Abstract of the United States: 1991* Washington, D.C., 1991.

**Table 2. Industrial and Energy Uses of Fossil Fuels (in millions of tons)**

	Petroleum		Natural Gas		Coal	
	Industrial	Fuel	Industrial	Fuel	Industrial	Fuel
1925	6.6	107.3	—	30.0	0.8	562.1
1990	167.1	746.1	14.1	482.9	1.2	641.3
1989	161.0	758.3	10.9	462.9	0.7	811.8

SOURCES: U.S. Department of Commerce, *Petroleum Refining: 15th Census of the United States*; U.S. Department of Commerce, *Census of Dyes and other Synthetic Organic Chemicals: 1925*; U.S. Department of Energy, *Annual Energy Review: 1980, 1989*. Kevin Swift, personal communication, Chemical Manufacturers Association, Washington, D.C., April 1992.

Petroleum began to edge out plant matter and coal derivatives as an industrial feedstock. Paint manufacturers created synthetic petroleum-based resins to more accurately control the drying times of their products. Ford switched from cellulosic lacquers to petroleum-based alkyd resins in 1932. Cellulose acetate plastics were displaced by cheaper polyvinyl butyral resins.

Within a generation, most of our industrial materials and our energy came from oil. In 1870 wood had provided 70 percent of our fuel. In 1920 coal supplied 70 percent. In 1970 oil accounted for 70 percent of our energy.

We were not only burning oil; we were wearing oil. The share of the fibers market captured by oil rose from 0.5 percent in 1946 to 25 percent in 1970 and almost 64 percent in 1980. See Table 1.

The production of plastics exploded, but plant matter-derived plastics virtually disappeared. Cellophane production fell to 192,000 tons in 1961, and to 50,000 tons by 1985.<sup>17</sup> Meanwhile, petrochemical-based plastics continued to challenge an ever-wider array of materials. Plastics production increased from 6 million tons in 1965 to 30 million tons in 1990. In the same period, industrial materials fell from 131 to 100 million tons.<sup>18</sup>

Plastics displaced metal in cars, wood in cabinets and tables, paper in egg cartons and trash bags, and glass in containers. In 1963, for example, 65 percent of milk containers were made of paper and 35 percent of glass. By 1989, 75 percent were plastic

and 25 percent were paper.<sup>19</sup> By the 1990s, Australia had introduced plastic money, and in the United States, plastic horseshoes and nails were available.

In the 1950s, natural gas became a significant source of industrial materials. Nevertheless, petroleum continued to account for 93 percent of industrial hydrocarbon use up through 1990, while natural gas only about 6 percent of all the fossil fuels used for industrial purposes. See Table 2.

With the building of interstate gas pipelines in the 1950s, the consumption of natural gas as a fuel increased substantially, opening the door for its use as an industrial raw material.

The oil embargo of the late 1970s pushed the U.S. petrochemical industry into developing more flexibility in its choice of raw materials, and stimulated technological innovation. Instead of switching to natural gas for a greater percentage of raw materials, as was predicted, the petrochemical industry now refined crude oil into many more products than before and actually increased its dependence on petroleum. Accordingly, the industry's consumption of natural gas declined from over 14 million tons in 1980 to less than 11 million tons in 1989.

The share of natural gas, and even of crude petroleum oil, as a feedstock of the petrochemical industry is projected to go down, however slightly, in the 1990s, due to an expected increase in the utilization of plant matter for industrial and consumer end-products.

# PART TWO

## Present Status and Near Term Prospects

### The U.S. Materials Economy: A Statistical Snapshot

In 1989 Americans consumed 5.4 billion tons of raw materials, 650 million tons more than in 1980 and 4 billion more than in 1925. See Tables 3-6, page 12, and Figures 3 & 4, page 13.

On a per capita basis, materials consumption rose by 70 percent between 1925 and 1980, then rose by less than 4 percent between 1980 and 1989. This reduced growth rate was probably a result both of the economic slowdown and of the substitution of lighter materials, such as plastic and aluminum, for heavier materials, such as steel.

Per capita consumption of food and feed remained relatively constant between 1925 and 1989. In the period 1980-1989, there was a significant increase in per capita consumption of construction materials, a modest decrease in per capita consumption of industrial materials, and a small decrease in per capita consumption of fuels. The latter was due to the increased efficiency of conversion processes, the rise in energy prices after 1970, and federal regulations mandating energy efficiency.

Since 1925 the amount of plant matter used for nonfood purposes increased in all categories, rising by 10 million tons as a fuel, by 56 million tons as a construction material, and by 52 million tons as an industrial feedstock. However, these increases were swamped by the astonishing rise in the consumption of fossil fuels and inorganic minerals. The fuel use of organic minerals rose by 1.3 billion tons from 1925 to 1989. The industrial use of organic minerals rose by 165 million tons over the same period. The use of inorganic minerals like stone and clay rose even faster, by 2.2 billion tons, although 80 percent of this increase was accounted for by the use of this material in the construction industry.<sup>1</sup>

The 52 million ton increase in the use of plant matter by industry between 1925 and 1989 was almost entirely due to the increased use of paper. Meanwhile, the amount of petroleum used for industrial purposes increased by 150 million tons, and the amount of inorganic minerals used in industry rose by 230 million tons. Ceramics and semiconduc-

tors accounted for most of the rise in inorganic mineral use.

As a result of these trends, plant matter, which had accounted for over 30 percent of industrial materials in 1925, dropped to less than 16 percent in 1989. Research and development in industrial uses for plant matter virtually disappeared between 1950 and 1980. Carbohydrate chemistry had been replaced by petrochemical chemistry in most engineering departments.

Currently, 87.5 million tons of plant matter are used for industrial purposes. Of this amount, almost 81 million tons are used to make paper. Excluding paper, the industrial product market for plant matter is about 6.5 million tons. See Table 7, page 14.

### The New Economics of Plant Matter

Plant matter will not regain its position as a significant feedstock overnight. However, two trends are creating favorable conditions for dramatically expanding the role of plant matter in industry. One of these trends is technological; the other is political.

### Technological Advances

We are witnessing a revolution in materials processing technologies. Scientists are learning to disassemble and reassemble bits of matter to achieve virtually any desired property. Advances relevant to plant matter include developments in pyrolysis techniques, steam explosion technologies, and ultracentrifuges and membranes. The use of microbes and enzymes as infinitesimal biological factories is also a very promising development.

These technological advances enable us to extract chemicals and make final products from plant matter at a significantly lower cost than was possible only a few years ago. We can also improve the properties of plant matter-derived chemicals and products so that they are equivalent or even superior to those derived from petroleum or natural gas.

**Table 3. Trend in Material Use, by Material Type (In millions of tons)**

Material	1925	Percentage	1980	Percentage	1989	Percentage
Plant Matter	362.1	25.3	604	12.5	726	13.3
Organic Mineral	709.0	49.5	2074	43.1	2229	40.8
Inorganic Mineral	360.3	25.2	2136	44.4	2508	46.0
Total	1431.4	100.0	4813	100.0	5463	100.0

**Table 4. Trend in Uses of Plant Matter (In millions of tons)**

End Use	1925	Percentage of Plant Use	Portion Plant Matter Derived (%)	1989	Percentage of Plant Use	Portion Plant Matter Derived (%)
Food	191.4	52.9	100.0	436	60.0	100.0
Fuel	39.6	10.9	5.4	50	6.9	2.4
Construction	95.9	26.5	24.4	152	21.0	6.4
Industrial	35.2	9.7	32.6	88	12.1	15.8
Total	362.1	100.0	25.3	726	100.0	13.3

**Table 5. Trend in Per Capita Materials Use, by End Use**

End Use	1925 (million tons)	Per capita (tons)	1980 (million tons)	Per capita (tons)	1989 (million tons)	Per capita (tons)
Food	191.4	1.66	367	1.61	436	1.75
Fuel	739	6.41	1917	8.41	2083	8.36
Construction	393	3.41	1974	8.65	2388	9.58
Industrial	108	0.94	555	2.43	555	2.23
Total	1431.4	12.42	4813	21.10	5463	21.92

**Table 6. Trend in Industrial Materials Use, by Material Type (In millions of tons)**

Material	1925	Percentage	1980	Percentage	1989	Percentage
Plant Matter	35.2	32.6	75	13.5	87.5	15.8
Organic Mineral	7.4	6.9	181	32.6	172	30.9
Inorganic Mineral	65.4	60.5	299	53.9	296	53.3
Total	108	100.0	555	100.0	555	100

SOURCES (Tables 3-6): U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, Washington, D.C., 1976. U.S. Bureau of the Census, *Statistical Abstract of the United States: 1991*, Washington, D.C., 1991.

## Environmental Changes

The growth of environmental consciousness since the late 1960s has created a phenomenon sometimes called "green consumerism." A significant number of consumers are willing to pay a premium for items that promise a safer environment (e.g., organic foods, phosphate-free laundry detergents, degradable plastics). Thus plant-based products may cost more, yet still occupy a niche in the marketplace.

The support for environmental protection has also given rise to numerous environmental regulations that affect the comparative economics of plant matter and fossil fuels. Regulations (such as the rule requiring oxygen in gasoline to lower carbon monoxide emissions) may raise the cost of organic mineral-based products (gasoline), making plant-derived products (ethanol) more competitive. Regulations that ban certain materials, such as phosphates in detergents, synthetic dyes in food, or non-degradable plastic resins, also open up new markets for plant matter.

Not only do environmental regulations raise the cost of petroleum-derived materials; they also may lower the cost of raw materials for plant matter-derived products. Regulations have increased the costs of waste disposal, creating incentives for manufacturers and processors to reduce and recycle their wastes. This holds true for all sectors of the economy, including farms, which generate huge amounts of plant matter waste, and cities, which generate significant quantities of yard wastes.<sup>2</sup>

Unlike chemical manufacturing processes for organic minerals, biological processes for plant-based products are inherently environmentally benign. Breaking down organic minerals requires high pressures (several times the normal atmospheric pressure) and high temperatures. Breaking the carbon-carbon bonds of coal, for example, requires temperatures of about 200° C (twice the temperature of boiling water); breaking carbon-hydrogen bonds requires temperatures over 600° C.

Figure 3. Trend in Total Material Usage in the U.S. (In millions of tons)

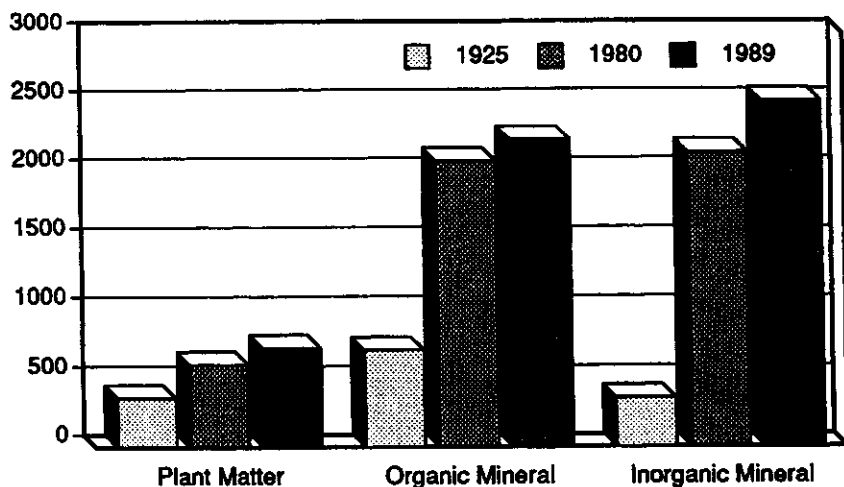
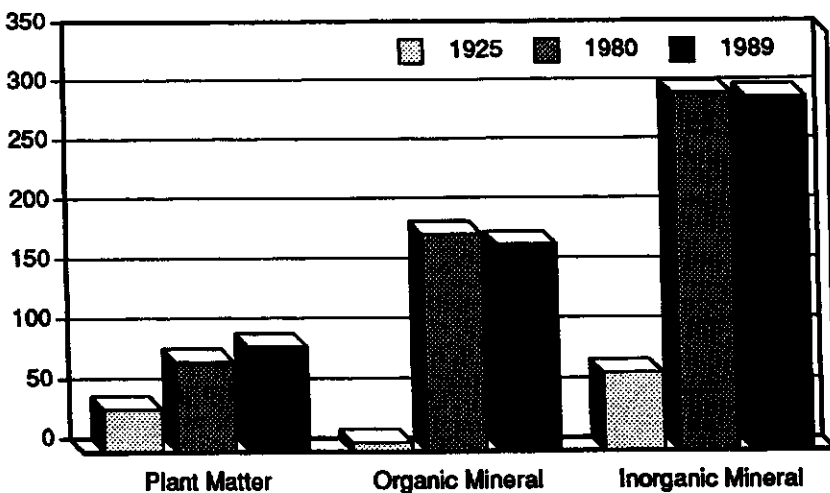


Figure 4. Industrial Material Use, by Material Type (In millions of tons)



SOURCES (Figures 3 & 4): U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, 1976. U.S. Bureau of the Census, *Statistical Abstract of the United States: 1991*, Washington, D.C., 1991.

**Table 7. U.S. Use of Plant Matter in Industrial Products: 1989  
(in millions of tons)**

Plant Matter Raw Materials (Examples of Uses)	Amount
Wood (Paper and Paperboard, Lignocellulosic Composites)	80.9
Cellulose (Polymers, Textile Fibers, Fermentation Products)	0.5
Lignin (Nonfuel Uses: Vanillin, Adhesives, Tanning, Dispersants)	0.2
Wood Extractives (Wood Chemicals, Oils, and Gums)	0.9
Vegetable Oils (Surfactants, Ink and Paint Solvents, Resins, Adhesives)	1.0
Industrial Starch (Polymer Components, Adhesives, Resins)	3.0
Natural Rubber (Automobile Tires, Durable and Household Goods, Copolymer Resins)	1.0
<b>Total</b>	<b>87.5</b>

SOURCES: U.S. Bureau of the Census, *Statistical Abstract of the United States: 1991* (111th edition) Washington, DC, 1991; *Chemical and Engineering News*, May 13, 1991; G. Robbelen, R.K. Downey, and A. Ashri, eds., *Oil Crops of the World* (New York: McGraw-Hill, 1990).

Most chemical processes also employ large quantities of strong inorganic acids and bases such as sulfuric acid and sodium hydroxide. These cause either very low or very high acidity levels during processing and result in effluent streams that are harmful to the environment.

The hydrogen-oxygen and oxygen-carbon bonds of cellulose are weaker and easier to manipulate than the chemical bonds of organic minerals. Almost all bioprocesses occur at 30-40° C, at near-normal atmospheric pressures, and at near-neutral pH levels. (pH is the degree of acidity. A pH of 1 is most acidic, a pH of 14 is most basic, and a pH of 7 is neutral.)

This is readily understandable when we consider that most plants and animals live and reproduce at 30-40° C, in a neutral pH environment, and at normal atmospheric pressures, whereas fossil fuels have been formed at increased temperatures and pressures over long periods of time.

### Strategies for Displacing Minerals With Vegetable Matter

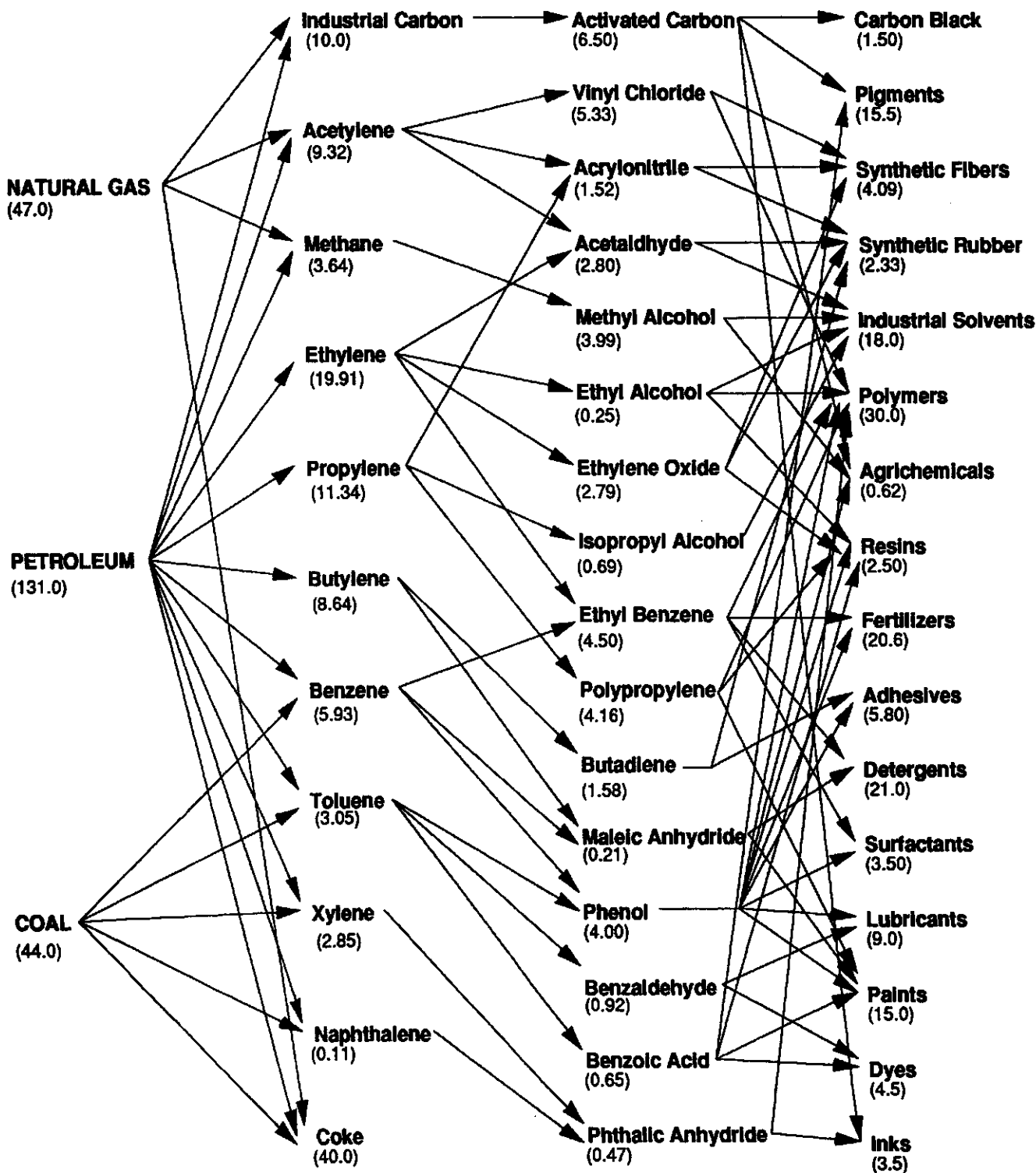
Plant matter can displace organic or inorganic minerals in three ways.

One is to synthesize from plant matter a chemical identical to the organic mineral-based chemical. For example, acetylene and phenols made from wood have characteristics identical to phenols made from natural gas, coal, or crude oil. The final products made from these intermediate chemicals can also have identical properties. See Figure 5 for the network of fossil-based interrelationships.<sup>3</sup>

Plant matter cannot, however, yield chemicals and products identical to those made from inorganic minerals such as sand, clays, and metals.

The second way to displace minerals is to synthesize from plant matter a product that, while not identical, serves as an adequate or superior substitute for its organic or inorganic mineral-derived

**Figure 5. Interrelationship of Major Precursor Chemicals Derived from Fossil Fuels for the Manufacture of Consumer End-Products in the U.S. (in millions of tons)**



NOTE: In addition to precursor chemicals indicated here, several inorganic and other minerals are used in making the end products presented in the last column. Production figures include all related product types in each class. SOURCES: *Chemical and Engineering News*; *Chemical Week*; U.S. Department of Energy, Washington, D.C., 1991-1992.



counterpart. Starch-or sugar-based plastics, for example, have a different chemical composition and structure from their petrochemical counterparts, but their particular properties make them competitive. Enzymes can replace phosphates in detergents. Vegetable oils can replace mineral oils in paints and inks.

**Table 8. Total 1990 Organic Chemicals Production in the U.S.**  
(In millions of tons)

Organic Chemicals	Amount
Ethylene	18.74
Propylene	11.06
Ethylene dichloride	6.65
Benzene	5.93
Xylene (incl. ortho & para)	5.92
Vinyl chloride	5.33
Ethylbenzene	4.50
Styrene (monomer only)	4.01
Methanol	4.00
Terephthalic acid	3.85
Formaldehyde	3.21
Toluene	3.05
Ethylene oxide	2.79
Ethylene glycol	2.52
Cumene	2.16
Acetic acid	1.88
Phenol (synthetic only)	1.76
Butadiene	1.58
Acrylonitrile	1.51
Carbon black	1.44
Vinyl acetate	1.28
Butanol	0.63
Isobutylene	0.57
Ethanol (synthetic only)	0.27
Other	13.77
<b>Total Organic Chemicals</b>	<b>108.41</b>

SOURCE: *Chemical and Engineering News*, vol. 69, no. 25, June 24, 1991.

The third way to displace minerals is to change manufacturing processes to reduce the need for intermediate chemicals. Enzymes can reduce the need for chlorine in the wood bleaching process. Bioprocessing techniques do not require the large amounts of acids and bases used in chemical processing. A significant proportion of inorganic chemicals like sulfur and nitrogen are used in the processing of organic materials.

Restoring plant matter to 32.6 percent of the industrial materials market—its 1925 share—would require expanding its markets by 160 million tons. This would represent a tripling of the overall quantity of plant matter used for industrial purposes.

**Table 9. Total 1990 Inorganic Chemicals Production in the U.S.**  
(In millions of tons)

Inorganic Chemicals	Amount
Sulfuric acid	44.28
Nitrogen	28.66
Oxygen	19.50
Ammonia	16.96
Phosphoric acid	12.18
Sodium hydroxide	11.69
Chlorine	10.94
Sodium carbonate	9.93
Urea	7.91
Nitric acid	7.75
Ammonium nitrate	7.11
Ammonium sulfate	2.50
Hydrochloric acid	2.34
Aluminum sulfate	1.21
Titanium dioxide	1.08
Sodium silicate	0.88
Sodium sulfate	0.73
Other	18.89
<b>Total Inorganic Chemicals</b>	<b>204.54</b>

SOURCE: *Chemical and Engineering News*, vol. 69, no. 25, June 24, 1991.

**Table 10. Annual Availability of Waste Bioresources for Fuels, Chemicals, and Biomaterials in the U.S.**

	Amount Available (million tons per year)
Waste Corn Cobs from Mills <sup>1</sup>	13.5
Corn Stalks, Leaves, and Sheaths from Corn Mills <sup>1</sup>	55.6
Wheat Straw <sup>2</sup>	31.2
Husk from Other Grain Mills <sup>3</sup>	20.0
Sawdust from Wood Mills <sup>4</sup>	7.0
Other Wood Mill Residues <sup>4</sup>	47.2
Waste Vegetable Oils from Food Processing Facilities <sup>5</sup>	2.7
Municipal Solid Waste (Cellulose Portion) <sup>6</sup>	46.5
Kraft Lignin from Paper Mills <sup>7</sup>	19.0
Sulfite Waste Liquor from Sulfite Paper Mills <sup>7</sup>	60.8
Molasses from Sugar Mills <sup>8</sup>	5.1
Cheese Whey from Dairy <sup>8</sup>	28.4
Peanut and Other Hulls from Nut Processing Mills <sup>9</sup>	3.2
Other Miscellaneous <sup>10</sup>	7.3
<b>TOTAL</b>	<b>347.5</b>

1 Based on total domestic utilization of corn in 1990-1991 crop season in the U.S. of 6,020 million bushels for both food and industrial use at 8 percent cob content and 33 percent stalk, leaf, and sheath content by weight. About 30 percent of 55.6 million tons of leaves, sheaths, and stalks are returned to the field, about 25-30 percent is mixed with hay and used for silage, 5 percent is used on chicken farms as bedding, and the remainder is discarded to decompose.

2 10-15 percent is used as absorbent/feed on farms and in compost. Most wheat straw is burned.

3 Based on total U.S. utilization of feed grains in 1990-1991 crop season of 200 million tons at 10 percent husk recoverability.

4 Represents total sawdust currently generated in U.S. sawmills. Other wood waste includes bark, wood chips, and wood shavings from sawmills at total recoverability.

5 Based on a 30 percent recoverability of all vegetable oils used in the U.S. food industry (both fast food and food processing) at 1990 level of 9 million tons per year.

6 Based on 45 percent recoverability of 103.4 million tons of paper and yard waste portions of the municipal solid waste generated in the U.S. in 1988.

7 Represents total lignin currently recovered annually in kraft mills and waste liquor generated in sulfite paper mills in the U.S.

8 Represents total amounts generated in sugar and cheese processing in 1990.

9 Total amount of hulls generated in the processing of dry nuts in the U.S.

10 Includes 25 percent recoverable post-consumer food waste of 13.2 million tons generated in 1988 in the U.S. and other miscellaneous biowastes such as potato wastes.

SOURCES: U.S. Department of Agriculture; U.S. Environmental Protection Agency, Washington, D.C., 1991; Whey Institute, Chicago, Ill, 1991.

**Table 11. Projection of Plant Matter Potential and Its Current Utilization in the Production of Industrial Materials and Important Intermediate Chemicals in the U.S.**

Product	Current Production (million tons)	Plant Matter-Derived (current percentage)	Plant Matter-Derived (1996 potential)	Conventional Product Cost (\$ per pound)	Plant Matter Product Cost (\$ per pound)	Percent Reduction in Plant Matter Product Cost (since 1985)	Percent Reduction in Plant Matter Product Cost (by 1996)
Wall Paints	7.8	3.5%	9.0%	0.50	1.20	14.0%	10.0%
Special Paints	2.4	2.0%	4.5%	0.80	1.75	3.0%	5.0%
Pigments	15.5	6.0%	9.0%	2.00	5.80	20.0%	15.0%
Dyes	4.5	6.0%	15.0%	12.00	21.00	25.0%	20.0%
Inks	3.5	7.0%	16.0%	2.00	2.50	30.0%	10.0%
Detergents	12.6	11.0%	18.0%	1.10	1.75	—	10.0%
Surfactants	3.5	35.0%	50.0%	0.45	0.45	20.0%	5.0%
Adhesives	5.0	40.0%	48.0%	1.65	1.40	15.0%	2.0%
Plastics	30.0	1.8%	4.3%	0.50	2.00	—	50.0%
Plasticizers	0.8	15.0%	32.0%	1.50	2.50	20.0%	20.0%
Acetic Acid	2.3	17.5%	28.0%	0.33	0.35	5.0%	2.0%
Furfural	0.3	17.0%	21.0%	0.75	0.78	10.0%	2.0%
Fatty Acids	2.5	40.0%	55.0%	0.46	0.33	5.0%	5.0%
Carbon Black	1.5	12.0%	19.0%	0.50	0.45	10.0%	25.0%

NOTE: All 1996 potential market projections for plant matter-based products are based on their performance over the past 5 years, and the expected contributions of recent technical breakthroughs. Market share of plant matter represents both wholly and partially plant matter-derived products. The cost premium of plant matter-based products is calculated based on the average median costs of commercially available products in a given category.

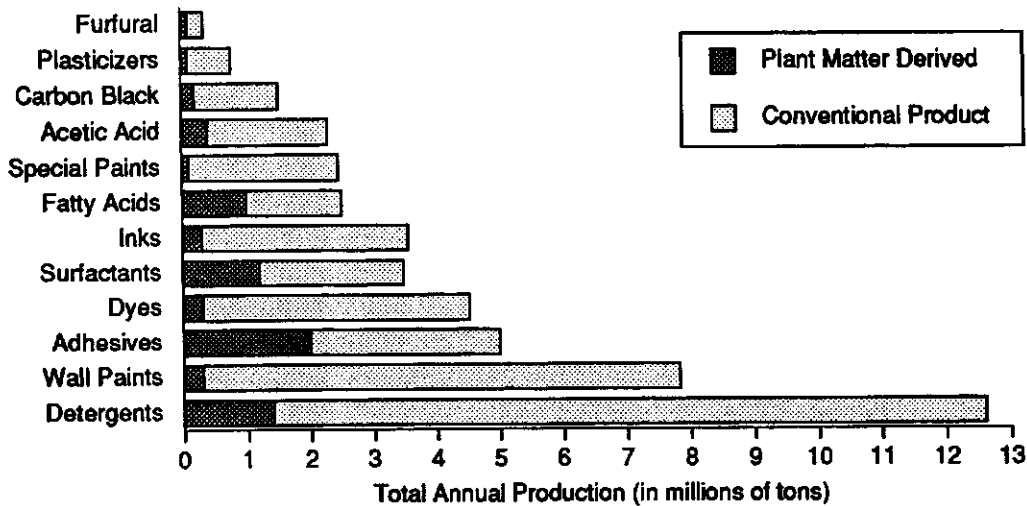
SOURCES: *Chemical Marketing Reporter; Chemical & Engineering News*; U.S. Department of Commerce, "U.S. Industrial Outlook," Washington, D.C.; *Chemical Week*.

However, if we exclude paper, the degree of expansion required to reach this mark is much greater. In 1990 the U.S. used about 6.5 million tons of plant matter for industrial purposes other than in the manufacture of paper. It used 108 million tons of organic chemicals and 205 million tons of inorganic chemicals. Therefore, for plant matter to capture one-third of the organic chemical market, production would need to expand almost five-fold; capturing

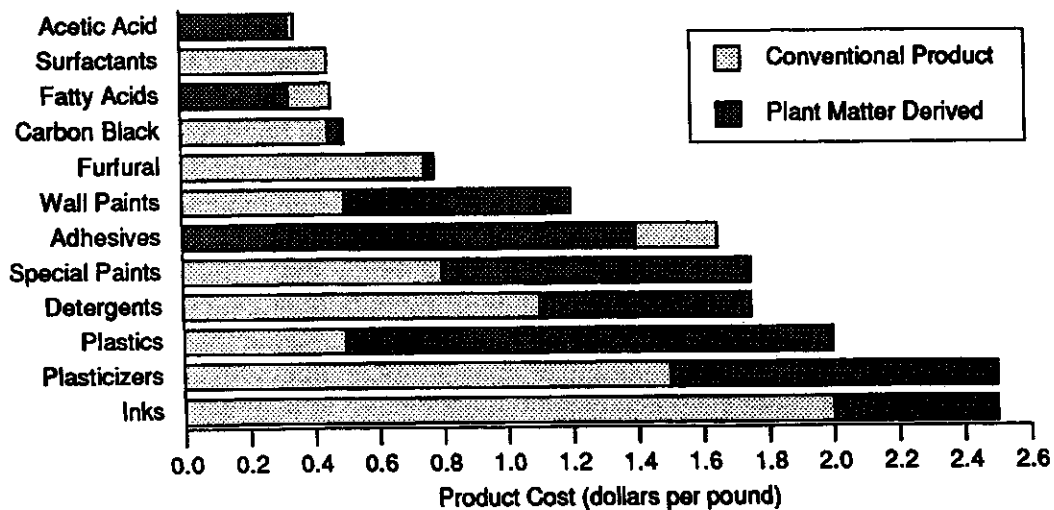
one-third of the overall chemical market would require a 15-fold increase. See Tables 8 and 9, page 16, for current chemical production figures.

The long-term goal of making plant matter an equal partner with organic and inorganic minerals should become a public policy objective. Although this would mean an unprecedented increase in new market creation, the raw materials are clearly avail-

**Figure 6. Market Share of Plant Matter-Derived Chemicals and Industrial Materials in the U.S.**



**Figure 7. Cost Premium of Plant Matter-Derived Chemicals and Industrial Materials in the U.S.**



NOTE: Market share of plant matter represents both wholly and partially plant matter-derived products. The cost premium of plant matter-based products is calculated based on average median costs of commercially available products in a given category. Fatty acids, carbon black, and adhesives derived from plant matter are cheaper than their conventional synthetic counterparts; however, they do not replace all types of synthetics.

able. Indeed, the nation's needs for chemicals could theoretically be met simply from existing agricultural wastes.

Table 10 page 17 shows that 347.5 million tons of agricultural waste are potentially available for conversion into fuels and industrial materials. This amount does not include wastes left in the fields or forests, but only those that have been transported to a relatively centralized location and therefore are readily available for further processing.

One ton of agricultural waste cannot produce one ton of organic chemicals. Nor can plant matter in every case produce chemicals identical in properties to those currently synthesized from oil, coal and natural gas. Nevertheless, it is instructive to note that the total tonnage of agricultural waste available is about three times greater than the tonnage of all organic chemicals produced in the U.S., and is roughly equivalent to the total production of all organic and inorganic chemicals.

### The Current Comparative Economics of Plant Matter-Derived Industrial Products

Just a few years ago, virtually no plant matter-derived consumer products were available, although there has always been a market for certain plant matter-derived intermediate chemicals. Because of technological advances and regulatory changes, carbohydrate-derived products are making a remarkable comeback. ILSR has analyzed plant matter-derived products in the 15 product categories that represent over 90 million tons of the 108-million-ton market for organic chemicals. Table 11, page 18 and Figures 6 and 7, page 19, present our conclusions.

As we can see, plant matter has made inroads into petrochemical markets in virtually every category. Plant-derived paints have captured about three percent of the paint market, while vegetable oil-based inks have six percent of the printing ink market, and more than ten percent of the detergents on the market are primarily plant matter-based.

In all cases, the prices of plant matter-derived products have dropped over the past seven years. For example, the cost of pigments from plant matter has dropped by 20 percent since 1985, while the cost of inks has dropped by over 30 percent. Most plant matter-derived consumer products are not yet cost-competitive with their petrochemical counterparts.

The price premium varies from about 20 percent for inks and 50 percent for detergents to 100 percent for paints and 200 percent for plastics. (See Figure 5).

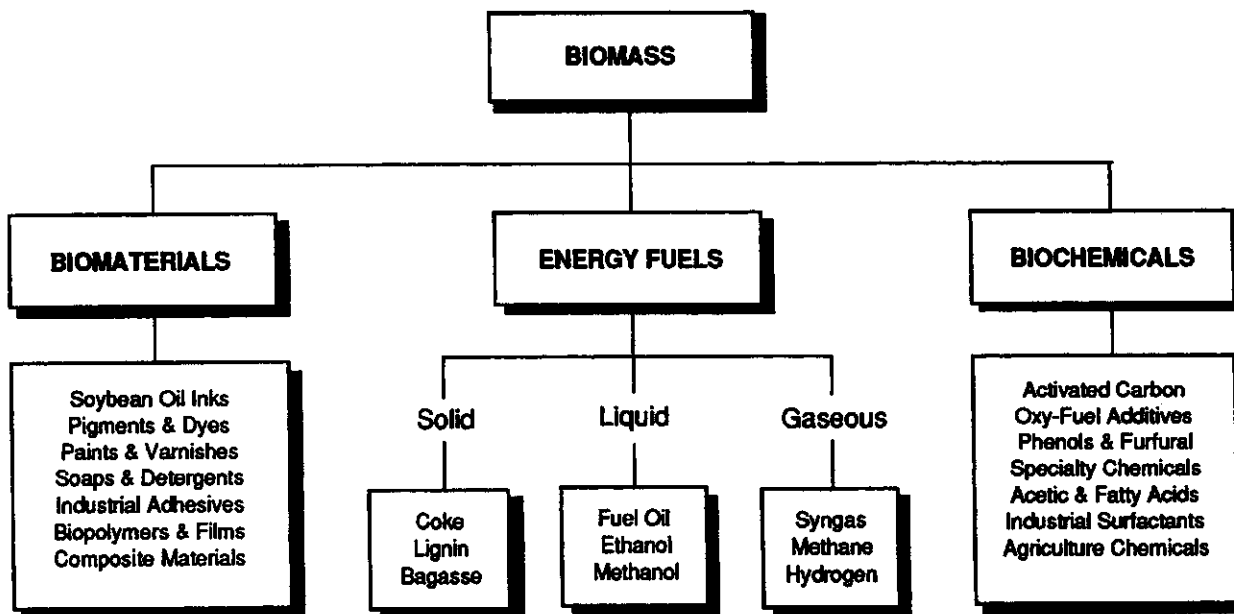
Despite their higher cost, plant matter-based products have gained in market share because of a combination of green consumerism and direct regulation. Plant matter-based detergents, for example, have benefited equally from the 75 percent drop in enzyme costs over the past few years and from the

**Table 12. Projected Increase in the Industrial Products Derived from Plant Matter by 1996**

Product Category	Projected Increase by 1996 (In tons)
Detergents	882,000
Plastics	750,000
Surfactants	525,000
Pigments	465,000
Wall Paints	429,000
Dyes	405,000
Adhesives	400,000
Fatty Acids	375,000
Inks	315,000
Acetic Acid	241,000
Plasticizers	136,000
Carbon Black	105,000
Special Paints	60,000
Furfural	12,000

growing bans on phosphates. Printers have two incentives to purchase printing inks based on vegetable oils: first, regulations may soon be promulgated limiting the evaporative emissions of hydrocarbons from inks; and second, vegetable oil-based inks reduce the need for clean-up chemicals, which may themselves create environmental problems. This is another cost to include with petroleum-based ink usage. Paint manufacturers already face regulations on hydrocarbon compound emissions, which are an

Figure 8. Representative Product Spectrum of Biomass Processing



important ingredient in the formation of ground-level ozone.

The cost of producing plant matter-derived industrial materials should continue to drop and their market share should continue to expand. We have projected that the cost of plant matter-based products will continue to decline, although at a somewhat slower pace than occurred in the 1980s. The major exception is plastics where dramatic cost reductions are likely in the next few years. In some cases, we project five year growth rates exceeding 100 percent. In most cases the projected growth is a more modest 10 to 20 percent.

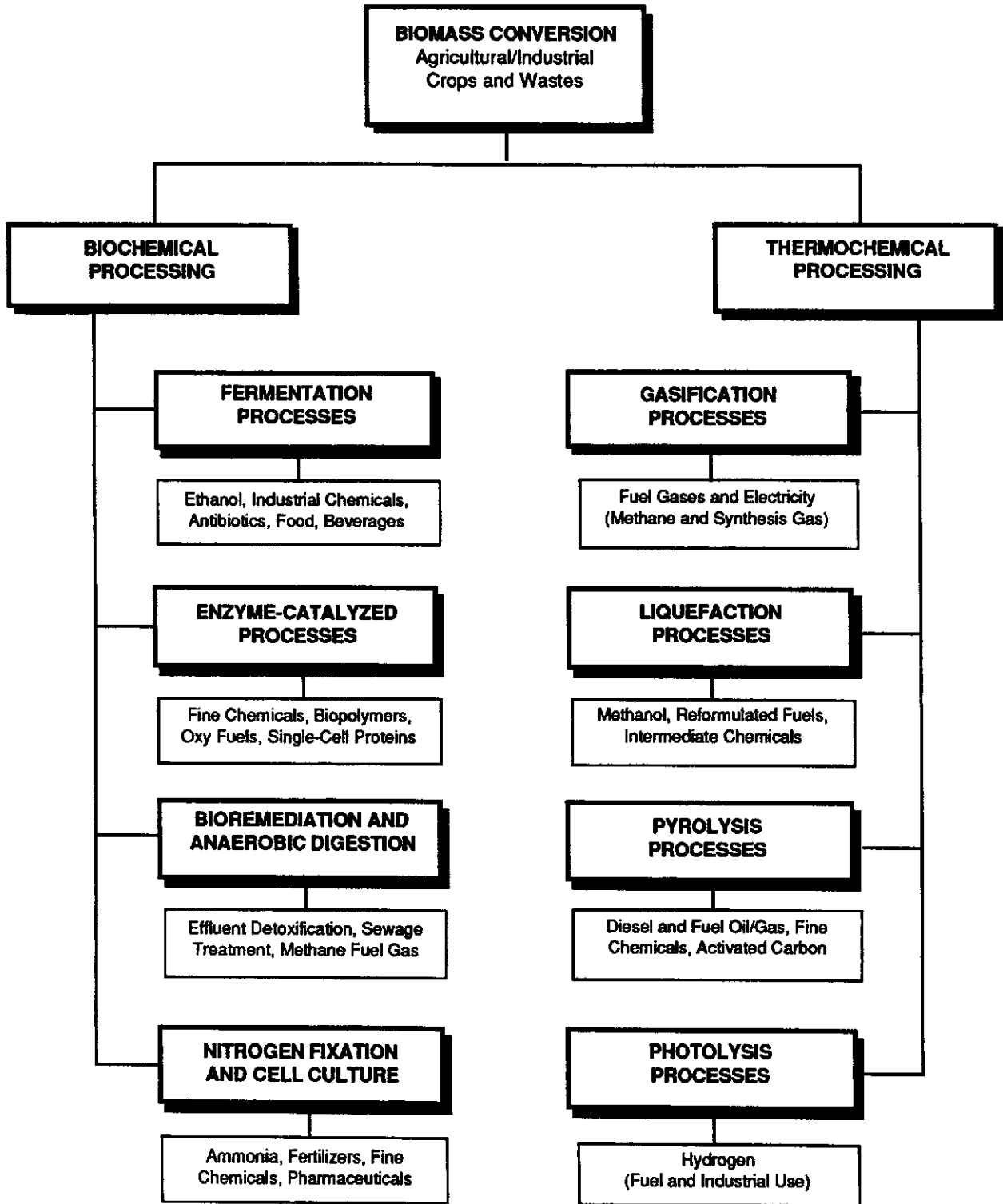
In the next three years, the amount of plant matter used in making industrial materials, excluding paper and natural rubber, could increase by over five million tons. This would almost double the amount of plant matter used for these purposes from their 1990 level. The biggest increases would come

in detergents and plastics, which together would account for one-third of the total projected market expansion. See Table 9, page 16.

Relatively little attention has been paid to the growing industrial market for plant matter in comparison to its use for fuel markets. Yet in the next five years, the former might well outpace the latter. The most optimistic projections for increases in fuel ethanol production during the 1990s, for example, are in the 3-million-ton range.

Figure 8, page 21, and Figure 9, page 22, show the product spectrum and processes that are currently employed in the conversion of plant matter in the United States. In this report, we have placed emphasis on the biomaterials and biochemicals that are derived primarily through fermentation, pyrolysis, and enzyme catalyzed processes. Energy fuels will be the subject of another study.

Figure 9. Conceptual Diagram of Biomass Conversion Processes and Products



# PART THREE

## A Detailed Examination of the Current Use of Plant Matter

### End Products

#### Surface Coatings Industry (15 million tons)

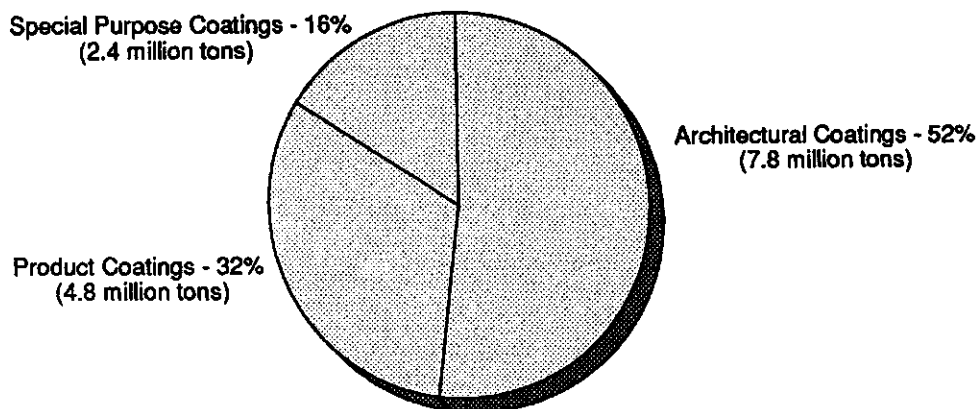
About 5 percent of the chemical market consists of sales of coating materials that protect a variety of surfaces against weather, dampness, pollution, chemical corrosion, and saltwater and freshwater damage.<sup>1</sup> Fifteen million tons of chemicals and other raw materials were used for paints, lacquers, varnishes, and specialty coatings in 1990. Of these chemicals and materials, 75 percent, or 12 million tons, were used in making paints.<sup>2</sup> The largest segment of the paints market is in the architectural coatings with a share of over 52 percent, followed by product coatings and special purpose coatings. Architectural paints are liquid paints, whereas special purpose and product coatings are made in both powder and liquid forms. See Figure 10.

Liquid paints consist of a liquid vehicle or carrier, which transports the pigment to the surface;

resin, which makes the pigment adhere to the surface; and the pigment, which provides the color. In addition, several other components, such as tinting agents, thickeners, plasticizers, and pigment extenders, are added in smaller quantities both to achieve the desired properties and to control the production costs of paints. Pigment extenders, also known as fillers, are materials that cost less than pigments but serve a similar purpose – providing opacity and adding to the durability of the finish. See Figure 11.

The liquid vehicle or carrier usually consists of petroleum-derived organic chemicals called solvents that have high volatility and evaporate completely from the paint formulation during its application to a surface.<sup>3</sup> Resins, pigments, and pigment extenders each comprise about 18 percent of a typical surface coating product, while the vehicle or carrier typically comprises over 40 percent. Measured in Pigment Volume Concentrations (PVCs), the combined contents of pigments and pigment extenders can be as high as 50 percent for the flat paints and about 30 percent for exterior house paints. Titanium dioxide

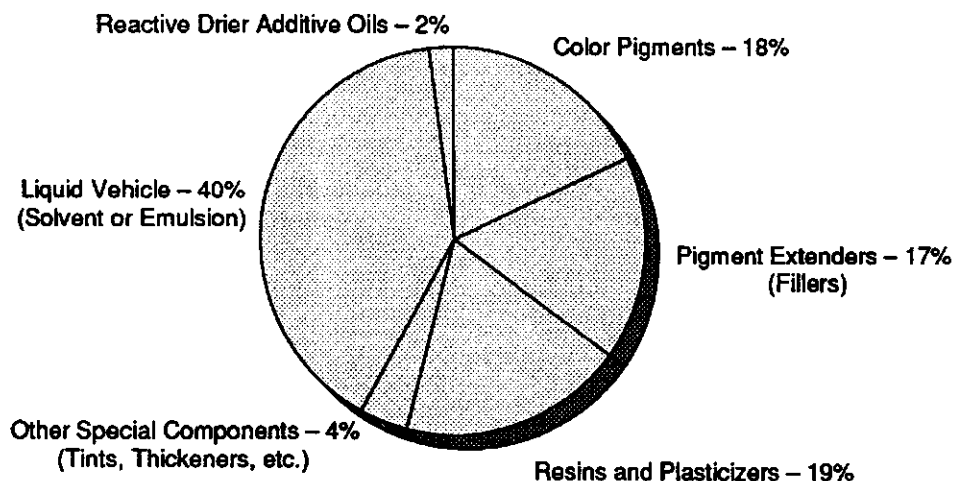
**Figure 10. Production of Surface Coating Products in the U.S. by Application Type in 1990 (Total Production: 15.0 million tons)**



SOURCE: *Chemical and Engineering News*, vol. 69, no. 41, October 14, 1991, 29-58.



Figure 11. Typical Liquid Paint Composition (percent by weight)



SOURCE: *Shreve's Chemical Process Industries*, ed. G.T. Austin (New York: McGraw-Hill, 1986).

(TiO<sub>2</sub>) is by far the most widely used pigment and pigment extending material in paints today.

As with all plant matter-based products, market developments with respect to plant matter-based surface coatings depend on a combination of technological advances and environmental regulations.

The principal environmental consideration is the emission of volatile organic compounds (VOCs), light hydrocarbon gases released by the drying of solvents in surface coatings, as well as in inks and other hydrocarbon-based liquids. In the presence of sunlight, these gases react with other gases present in the atmosphere—primarily oxides of nitrogen—to produce harmful concentrations of ground level ozone, a potent pollutant that contributes to smog. Currently a typical gallon of architectural paint emits about 5-8 pounds of VOCs. High-temperature paints, used for painting cars, refrigerators, and other consumer appliances, typically emit 8 pounds per gallon of paint.

By the end of 1990, more than 30 states across the nation had restricted the use of paints with high VOC emissions. For example, California's southern coast regulations limit VOC emissions from high-temperature coatings (application temperature 1000°F) to 6.0 pounds per gallon now, and 3.5 pounds per gallon by the year 1994.<sup>4</sup> The limit for heat-resistant coatings (application temperature 400°F) is currently 3.5 pounds per gallon, and will drop to 2.8

pounds by 1994.<sup>5</sup> In some categories, VOC emissions must drop as low as 2.5 pounds per gallon.

Beginning in 1994, the EPA will limit VOC emissions from paints and other surface coatings to a maximum of 2.8 pounds per gallon under the Clean Air Act; permissible levels are expected to drop even more by the year 2000.<sup>6</sup> Already, the surface coatings industry in the United States regards this 2.8 pound limit as the unofficial national standard.<sup>7</sup> Several paint manufacturers, both in the United States and abroad, have begun formulating paints that are lower in VOCs and comply with the 2.8 pound per gallon limit.<sup>8</sup>

In response to the new regulations, manufacturers are reformulating coatings to reduce the proportion of liquids and, consequently, the amount of evaporative emission. However, this strategy increases the proportion of solids, extends the drying time, and makes the coating harder to apply. Since a certain ratio of solids to solvents is necessary to form a topcoat, it takes more of a high-VOC coating, in the current formulations than one having a greater amount of solids to produce a satisfactory finish. Several leading paint manufacturers, including Du Pont, Sherwin-Williams and PPG, are engaged in extensive research and development aimed at lowering the VOC content of their products without losing finish properties or durability.<sup>9</sup>

Paints for bridges and other industrial applications are often based on vinyl and chlorinated rubber resins, which are resistant to acids and other corrosive chemicals and are very difficult to reformulate to meet VOC restrictions without a loss in their properties.<sup>10</sup> However, several alternative paint product technologies have been introduced to the marketplace in recent years, offering a solution to this problem. Two of the most important developments are radiation-curable coatings and powder-coatings systems, both targeted to the product coatings market.

Radiation-curable coatings reduce emissions dramatically. Radiation-curable paints dry almost instantly upon exposure to either electron beam or ultraviolet radiation. They are ideal for assembly lines and can easily be applied to three-dimensional surfaces. The radiation equipment also takes up considerably less space than conventional curing ovens used for drying conventional paints.

Radiation-curable coatings have been under development for at least two decades but are only now establishing themselves, with a 1992 market projected at \$250 million.<sup>11</sup> These coatings cost \$15 to \$100 per gallon, compared to an average price of \$10 to \$15 a gallon for solvent-based paints. A direct comparison is misleading, however, because smaller quantities of radiation-curable coatings are needed for the same application. Moreover, considerable quantities of paint are saved because less waste is generated during the coating process.

While radiation-curable coatings reduce volatile organic emissions dramatically, powder paints are said to virtually eliminate the problem. Powder coatings are 100 percent solids, a mixture of resin and pigment with no liquid carrier or solvent. However, the resins in powder paints may still produce low levels of VOC emissions upon application. Powder paints containing vegetable oil-based resins are solving this problem by modifying the paint drying mechanism.

The market for powder coatings has been growing by about 25 percent a year. Since 1984 the number of powder coating manufacturers and suppliers has grown from 14 to more than 35 in North America. Sales reached 60,000 tons in 1990, and are expected to exceed 100,000 tons by the end of 1992, giving powder coatings 2 percent of the product coatings market in the U.S.

VOC reductions in architectural liquid paints may be achieved by substituting vegetable and other plant oils for mineral oils functioning as carriers. In

addition to substituting for mineral oils as carriers, vegetable and plant oils can also serve as resins – required in paint formulations both for binding pigments to the application surface and to provide a desired finish to the painted surface. Unlike petrochemical solvents, which dry by evaporation, vegetable and plant oils dry by oxidation, thus emitting less VOCs. Furthermore, oxidation causes the monomeric vegetable oils to polymerize into a film-forming resin, which, like synthetic resins in paints, serves to bind pigments to the application surface and to provide the desired finish to the painted surface. The use of vegetable oils as the vehicle in a paint formulation has the synergistic effect of reducing the need for synthetic resins. For example, linseed oil used as a pigment carrier will oxidize to form an elastic film called linoxyn. About 90 percent of the linseed oil forms a linoxyn film, while other oils have lesser film forming properties. In addition to linseed, several other natural oils, including soybean, castor, safflower and tung oils, are being incorporated in many liquid paint formulations today for this unique and environmentally friendly property.

Although replacing conventional petrochemical solvents with plant oils reduces the need for certain resins in liquid paint formulations, it does not eliminate the need for resins completely. This is especially true in those formulations where resins serve a unique purpose like providing corrosion protection or glossy surface. For such purposes, plant matter can also be used to produce these special purpose resins. These resins can then be included in formulations with plant oil vehicles, producing paints that exhibit the same properties as synthetic systems based on petrochemical solvents and resins.

### **Resins from Plant Matter**

Plant oils do not completely eliminate the need for resins in liquid paint formulations, especially where resins serve a unique purpose, such as providing corrosion protection or achieving a glossy finish. However, plant matter can be used to produce resins with the same properties as petrochemical-based resins.

In the early days of the surface coatings industry, all resins used in the manufacture of paints came from natural sources. These included copals derived from fossil gums, balsams derived from softwoods, rosin-based resins from wood, and amber. However, when petroleum-derived resins (alkyds, acrylics, epoxies, urethanes, and others) with improved

**Table 13. Normalized Price Comparison of Bio-Based with Petrochemical-Based Wall Paints**

	Paint Area Coverage (sq. ft. per gallon)	Unit Paint Cost (dollars per gallon)	Normalized Paint Cost (dollars per 100 sq. ft.)
Casein Wall Paint <sup>1</sup> (Plant-Based)	267	16.00 - 20.30	6.00 - 7.60
Latex Vinyl Paint <sup>2</sup> (Petrochemical-Based)	400	11.10 - 20.20	2.80 - 5.05
Dubron Natural Resin Based Wall Paint <sup>1</sup> (Plant-Based)	350	33.80 - 40.70	9.65 - 11.60
Latex Acrylic Resin Wall Paint <sup>2</sup> (Petrochemical-Based)	350	15.25 - 22.75	4.35 - 6.50
Canto Enamel Interior <sup>1</sup> Paint (Plant-Based)	530	96.65 - 102.10	18.25 - 19.25
Interior Enamel Paint <sup>2</sup> (Petrochemical-Based)	400	19.00 - 20.00	4.95 - 5.00
Vindo Enamel Exterior <sup>1</sup> Paint (Plant-Based)	450	97.85 - 108.70	21.75 - 24.16
Exterior Enamel Paint <sup>2</sup> (Petrochemical-Based)	400	15.70 - 21.95	3.95 - 5.50

<sup>1</sup> Casein, Dubron, Canto, and Vindo paints are marketed under the general trade names "Livos" and "BIO SHIELD." Unit paint price range includes natural coloring pigments marketed separately.

<sup>2</sup> Petrochemical-based paints in each category are chosen to correspond to the plant-based paint in terms of application properties. Unit price range is based on tinting level similar to that achieved by plant-based paints.

SOURCES: "The Natural Choice," Eco Design Co., Santa Fe, New Mexico, April 1992; Capital Paint Center, Washington, D.C., May 1992.

water and chemical resistance qualities were introduced, natural resins lost almost their entire share of the paint market. Very recently, a few plant matter-based resins have made a comeback, and some newer varieties and sources have been discovered.

Copolymer resins based on palmitic and stearic acids derived from natural oils such as linseed, soybean, and coconut are already in use in certain specialty paint formulations. Large-scale commercial farming for the production of shellac has been underway for almost a decade in India. Produced by a parasitic insect, *Coccus lacca*, that feeds on softwood and other plant matter, shellac resins have excellent binding properties, are compatible with a variety of carrier liquids, and can substitute for several classes of petroleum-derived resins in paint manufacture.

Phenolic resins are conventionally made from the phenolic fractions of petrochemical feedstocks.

Similar phenolic compounds can now be made from the lignin fraction of wood via fast pyrolysis; these compounds, in turn, can be used to produce phenolic resins for paints. Lignin is available in great quantities as a waste product of the pulp and paper industry. Kraft paper mills alone produce an estimated 19 million tons of lignin annually in the U.S. Interchem Industries of Leawood, Kansas, is looking into producing phenolic compounds from waste lignin. The company has recently gone into commercial production of fast pyrolysis oils from wood waste – the first step in the production of phenolics from plant matter.

About 60,000 tons of petroleum-derived urethane resins are used annually in the U.S. coating industry today. A new process currently under development promises to substitute resins in urethane formulations with epoxy resin based on Vermonia oil, a vegetable oil.<sup>12</sup> In addition, several

resins and resin-intermediate systems based on plant matter, such as a cellulose acetate and Butyrate, are being developed as substitutes for petrochemical resins in other classes of paints.

Livos Plant Chemistry, a company founded in West Germany in the late 1970s, began production of natural-based paints for the small-but-growing market. Eco Design, a mail order retailer based in Santa Fe, New Mexico, makes these products available in the U.S. In addition, Eco Design offers its own casein-based "Bio Shield" paint. Casein is a milk-derived protein that acts like a resin, binding the coloring pigments to the paint application surface.

Casein paints have been used for more than 5,000 years. However, with the advent of the petrochemical industry and the availability of mineral solvent-based paints, casein lost its entire share of the liquid paints market. Eco Design markets casein paints as a system: a dry powder and coloring pigments to which water is added. These paints are comparable to the paints produced from petroleum-based solvents, both in terms of application and of properties.

Casein paints have a long shelf life in powder form, but a short shelf life once they are mixed with water. They are described as "lightly washable" after application; that is, the surface is washable unless abrasive soaps are used. These paints can be used for interior walls of wood, drywall, or plaster. The result is a breathable solid white wall coating (color added by including pigments) which can be applied over wallpaper or an existing coat of paint.

In terms of applications and properties, mid-grade, vinyl resin-based latex paints are the closest counterparts to casein-based paints. Casein paints cost almost the same as petrochemical-based mid-grade latex paints on a per-gallon basis. But because casein paints cover about one-third less area than latex paints, they cost 1.5 to 2.0 times more on an application basis. Both paint types require two coats for proper coverage. Eco Design claims that, besides generating no VOCs, its casein paints have low allergenic properties – a feature that may encourage consumers to pay the higher price.

Table 13, page 26, compares the costs of plant matter-based and petrochemical-based wall paints. While costs vary widely within each paint category, overall, the plant matter-based paints are more expensive, with prices per application ranging from about 25 percent to 400 percent higher. The greatest disparity occurs with exterior enamel paints.

## Pigments and Dyes Industry (20 million tons)

Pigments, the coloring component of paints, are used in a wide range of other products as well, and consequently represent an independent product category. Most pigments and dyes are derived from inorganic minerals like titanium dioxide (TiO<sub>2</sub>) and zinc oxides. However, a regulatory trend to restrict the use of heavy metals in pigments began in the mid 1970s, when lead carbonate-based pigments were banned. Since then, several bills have been introduced at the state and federal levels that would restrict the use of lead chromate and other heavy metal-based pigments. Senate Bill 3169, for example, would limit pigments in packaging materials to those containing less than 100 ppm of heavy metals (lead, cadmium, mercury, and hexavalent chromium).

In the past, natural dyes were produced by growing whole plants and then extracting the coloring from them. These processes were slow, and the natural dyes could not compete with cheaper products made from coal tars, petrochemicals, and inorganic minerals that were introduced in the nineteenth and twentieth centuries. Recently, though, some developments have taken place that promise a revived role for plant-derived pigments. The Eco Design Company has introduced Bio Shield Earth Pigments, which are primarily derived from refined rocks such as silica and lime rock, and contain no heavy metals or other toxics. These pigments are available in 24 basic colors; mixing them can produce almost all the colors available today in latex paints. Cabot, the world's largest producer of carbon black-based pigments, now markets several grades of black and color-blendable carbon black pigments derived from plant matter. Warner-Jenkinson, the leader in food, pharmaceutical, and cosmetic dyes, is currently marketing a wide range of natural colorings, including a food-grade red dye, betanin, derived from table beets.

Ciba Geigy, a major pharmaceutical company and one of the major pigment and additive suppliers to the surface coatings industry, has been developing plant matter-based color pigments for food and pharmaceutical applications for the past 10 years. The company is currently producing several coloring pigments for specialty use, at a cost of \$20 to \$50 per pound. Another company, Mitsui Industries of Japan, has recently introduced a plant cell culture-based red dye called *shikonin*. *Shikonin* is produced by growing plant cells in laboratory bioreactors in

**Table 14. Cost Comparison of Inorganic, Synthetic Organic, and Natural Plant-Based Coloring Pigments and Dyes**

		Average Product Price (dollars per pound)	Material Resource Base
PIGMENTS/DYE RAW MATERIALS	Titanium Dioxide	1.00	Inorganic mineral
	Iron Black	0.88	Inorganic mineral or petroleum
	Carbon Black	0.32	Natural gas or plant matter
	Precipitated Calcium Carbonate	0.27	Inorganic mineral, atmospheric or industrial waste carbon dioxide
INDUSTRIAL GRADE COLOR PIGMENTS	Bio-Shield Natural Coloring Pigments	27.00	Metal-free inorganic minerals
	Carbon Black Pigment	5.80	Plant matter
	Carbon Black Pigment	1.30	Natural gas or petroleum
	Ultramarine Violet	2.25	Petroleum, inorganic mineral, metals
	Pigment Green	2.00	Inorganic minerals and metals
FOOD GRADE COLOR DYES	Betanin Red Dye <sup>1</sup>	3.00	Plant matter (table beets)
	Red FD&C No. 40	13.60	Petroleum and metals
	Red FD&C No. 3	30.20	Petroleum and synthetic organic
	Shikonin Red Dye <sup>2</sup>	90.00	Plant cell culture biotechnology

1 Betanin red food grade dye is produced by Aunt Nellie's Country Kitchen and is marketed in a very dilute form by the Warner-Jenkinson Company at a cost of \$3.00 per pound. Roughly 15 times the quantity of Red FD&C No. 40 must be used to achieve the same results.

2 This is an experimental product, not yet available commercially, that shows great potential. Projected costs are within the range of petroleum-based dyes. Current target applications are pharmaceuticals and cosmetics.

SOURCES: *Chemical Marketing Reporter*, March 9, 1992; Eco Design Company, Santa Fe, New Mexico, April 1992; Aunt Nellie's Country Kitchens; Warner-Jenkins Company, St. Louis, Missouri, April 1992; Mitsui Petrochemical Industries, Tokyo, Japan, May 1992.

large quantities and at an accelerated pace by applying recent biotechnological advances. Although *shikonin* currently costs \$90 per pound – 3 to 4 times more than other synthetic dyes in its class – it is environmentally friendly and exhibits superior properties in terms of health, safety, and application compatibility in food, pharmaceutical, and cosmetic products. Projections point to a reduction in the cost of these plant cell-based pigments. Soon their price will be competitive with petroleum-derived synthetic organic pigments currently used. See Table 14 for summarized price information.

Plant-based pigments offer a safe alternative to pigments containing heavy metals. The organic coloring pigments occurring in plants are synthesized from carbon, hydrogen, nitrogen, oxygen, and traces of sulfur. Metal ions may be present in complex

molecules, but plants assimilate lighter metals whenever possible in preference to heavy metals. Furthermore, the metal ions taken up by plants or by plant cell cultures during the synthesis of pigments are locked into organic complexes and never released into the atmosphere in their free state. The concentration of metals in natural dyes is usually much lower than the concentration of heavy metals in synthetic pigments imparting the same coloration.

Prospects for replacing pigments based on inorganic or organic minerals with pigments derived from plants vary according to color. White pigments, which are mainly based on titanium and zinc oxides, will be difficult to replace due to the low cost of titanium dioxide, as well as limited sources of white pigments. Red, yellow, and orange pigments are based on lead, zinc, cadmium, molybdenum,

and iron; in applications where stability is not critical, these could be replaced by Betanin red, Turmeric yellow, and Beta Carotene or Carmine orange dyes, derived from plant matter or insect cell-based sources. See Table 15. Green, brown, and many of the blue pigments are almost always based on metals such as chromium, aluminum, antimony, and bronze alloys; for the most part, biopigments to replace these are not currently available. Certain shades of green can be made from plant matter, but they are not as bright as metal-based greens.

Carbon black pigment can be synthesized from plant matter. Black pigments offer a significant opportunity, since they account for roughly 35 to 40 percent of all pigments, and are used in the manufacture of different shades as well as for black coloring.

In addition to their coloring properties, inorganic pigments are used as fillers and builders, increasing the strength of the product while reduc-

ing the need for higher-value components. Titanium dioxide is one of the leading pigment fillers, with production of titanium dioxide-based pigments at 3.2 million tons per year, and revenues of \$6.0 billion.<sup>13</sup> Concerns about the toxicity of heavy metal pigments, in general, and a ban on lead carbonate, in particular, has boosted the market share of titanium dioxide to 70 percent of white organic pigments.<sup>14</sup> Although titanium is a heavy metal and its production by sulfate hydrolysis and precipitation reportedly generates significant pollution, use of titanium dioxide in the pigment industry continues to grow due to its low cost and abundance.<sup>15</sup>

Edward Lipinsky of Battelle Memorial Laboratories suggests that precipitated calcium carbonate (PCC), made from atmospheric carbon dioxide or from carbon dioxide generated as an industrial waste, could replace titanium dioxide as a white filler/pigment, at a cost of 27-35 cents per pound.<sup>16</sup> As a

**Table 15. Price Comparison of Natural, Extracted Colorings with Food, Drug and Cosmetic Grade Synthetic Dyes**

	Price Per Pound (dollars)	Raw Material Sources
Annatto Powder Colors (natural)	39.95	Seed extract of Bixa orellana shrub
FD&C Yellow No. 5&6 Blends (synthetic)	10.95	Intermediate petrochemicals
Beta Carotene (natural)	13.61	Extract of alga Dunaliella salina
FD&C Yellow No. 6 (synthetic)	7.95	Organic intermediate chemicals
Carmine Liquid Colors (natural)	14.89	Extract of cochineal insect
FD&C Red No. 3 (synthetic)	30.20	Petrochemicals and inorganic minerals
Paprika Oil Soluble (natural)	40.75	Extract of red pepper
FD&C Yellow No. 6 Lake (synthetic)	10.70	Petrochemicals and inorganic minerals
Betanin Red Dye (natural)	3.00	Extract of red table beets
FD&C Red No. 40 (synthetic)	13.60	Organic intermediate chemicals
Red Cabbage Dye (natural)	55.00	Extract of red cabbage
FD&C Red No. 40 (synthetic)	13.60	Organic intermediate chemicals
Turmeric Yellow (natural)	9.90	Extract of turmeric roots and blends
FD&C Yellow No. 5 (synthetic)	8.95	Intermediate petrochemicals

SOURCES: Warner-Jenkinson Company, St. Louis, Missouri, May 1992; Aunt Nellie's Country Kitchen, Watertown, Wisconsin, May 1992; *Chemical Marketing Reporter*, March 9, 1992.

pigment in alkyd resin enamel paints, calcium carbonate gives good coverage and intense brightness. As a plastics filler/pigment, calcium carbonate would not only replace higher-cost components, but also help increase impact resistance, critical crack resistance, and surface smoothness in hard polyvinyl chloride plastics.<sup>17</sup> Calcium carbonate is neither toxic nor dangerous to human health. Purified calcium carbonate is used as a food additive, as a mineral supplement in animal feed, and as an ingredient in toothpaste.

Table 14, page 28, compares the price of raw materials for pigments, industrial-grade color pigments, and food-grade dyes made from metals, organic minerals, metal-free inorganic minerals, and plant matter. Note that the price of titanium dioxide, \$1.00 per pound, is more than triple that of precipitated calcium carbonate, \$0.27 per pound. Raw material-grade carbon black costs almost the same whether it is derived from natural gas or plant matter; however, processing the coarser plant matter-derived carbon black into coloring pigments costs almost four times as much as producing the same pigment from natural gas. The advantage of plant matter-based carbon black is its smaller particle size, which translates into a deeper black (pitch black), making it more valuable and narrowing the price differential between the two sources of this pigment.

In 1967 the Food and Drug Administration established a new category of pigments and dyes: Food, Drug, & Cosmetic (FD&C) grade. When health concerns later led the FDA to ban several synthetic food colorings, companies began to search for naturally derived colorings. Currently, natural pigments and dyes use as their feedstock plant matter (e.g., shrubs, roots, beets), insects (e.g., cochineal insects), microbial cells (e.g., proprietary recombinant cell lines of bacteria, higher microbes, and algae), and inorganic earth minerals free of heavy metals (e.g., lime rocks containing calcium carbonate, silica sand, and china clay). Virtually all the natural pigments and dyes listed in Table 15 were approved by the FDA only in the last 10-15 years.

Most of the FD&C pigments and dyes derived from natural sources cost two to three times as much as their petrochemical counterparts. However, as we can see from the table, this is not always the case. Turmeric yellow, for example, is nearly competitive with petrochemical-derived yellow colorings. In general, pigments and coloring dyes are commercially divided into three categories: inorganic, low-end synthetic organic, and high-performance synthetic organic. Inorganic pigments and dyes are

primarily based on titanium dioxide and other heavy metals, and cost \$1.00-\$2.00 per pound. This will be the most difficult category for natural pigments and dyes to compete with; only if health and environmental concerns lead to regulations of these pigments will their natural counterparts become cost-competitive.<sup>18</sup> Most of the FD&C-grade dyes have been derived from either organic or synthetic organic petrochemicals in the past, however, since the late 1980s, several plant matter-based dyes have been introduced to the market.

Extraction-based natural pigments can drop in price not only through breakthroughs in the manufacturing process, but also through breakthroughs in plant yield. Aunt Nellie's Country Kitchen has developed a superbeet that yields 600 percent more coloring per acre than ordinary beets. The company expects the breakthrough to reduce the price of the betanin red dye to a level competitive with petroleum-based food-grade dye. Beet dye is about 15 times more dilute than synthetic red - using beet dye to achieve the same effect as one pound of FD&C Red No. 40 (\$13.60 per pound) currently costs \$45.00. The new beet will potentially reduce the price to \$10.00 per pound of synthetic equivalence.

## Printing Inks Industry

(3.5 million tons)

Printing inks are similar to paints in composition and properties. In general, inks consist of a fine dispersion of pigments or dyes in a drying oil or solvent, with or without a resin, a drier, and a thinning component. Conventionally, drying oils, solvents, and resins have been derived mainly from petroleum oils and chemicals. Pigments are made both from inorganic heavy metals and from petrochemical feedstocks. Unlike paints, the composition of printing inks varies widely depending on color and application type. For example, black inks have only small amounts of pigments (20-30 percent) and over 70 percent solvents, while colored inks are predominantly pigments and only 25-30 percent solvents. See Table 16, page 31.

Since conventional inks depend heavily on petroleum-based raw materials for most of their components, the ink industry began searching for alternatives after the 1973 oil price hike, and again in 1979 after the second oil shock.

### Vegetable Oil-Based Inks

Technically, any vegetable oil can be used as the vehicle/resin component in ink formulation. Soybean oil has become the oil of choice. Soybeans are about 18 percent oil by weight; a bushel of this commodity contains about 11 pounds of oil. In 1990, 6.0 million tons of soy oil were produced in the U.S.; over 97 percent of this oil was used in the food industry.

As a result of the research efforts of the American Newspaper Publishers Association (ANPA), soy inks first entered the U.S. market in 1987. In that year, six newspapers used soy inks. Today, 50 percent of the 9,100 newspapers in the U.S. and 75 percent of the 1,700 daily newspapers print with soy ink.<sup>19</sup> Today, ANPA continues its research in developing cheaper, better, and environmentally friendlier grades of inks based on soy oil and other plant oils.

If all U.S. newspapers switched to soy ink, the manufacture of soy inks would consume 3 percent of current soy oil production. If all ink for all purposes were made from soy oil, its manufacture would consume 10 percent of current soy oil production. See Figure 12, page 32.

Like paints, inks produce volatile organic compound emissions as they dry. Inks based on mineral solvents dry by evaporation, thereby releasing these volatile organic compounds (VOCs). Soy oil-based inks dry through oxidation; the oil forms a resin that

never leaves the ink application site. Little or no evaporation of organic compounds occurs. Soy oil inks emit only 1 percent of their weight in VOCs, while mineral oil inks emit 8-22 percent.

Currently, soy oil-based inks are competitively priced with traditional inks containing petrochemical solvents. In early 1992, a pound of petroleum-based mineral oil cost 18-20 cents per pound; refined soybean oil cost 25 cents per pound.

Colored inks have a lower oil content—about 25-30 percent by weight—than black inks, which are 70-80 percent oil by weight. Pigments are the major cost component for colored inks, while oil is the major cost component for black inks. For this reason, colored soy inks penetrated the market first. When they were first introduced in the mid-1980s, the premium for soy oil-based colored inks was about 5 percent, as opposed to a 20 percent premium for black soy oil-based inks. Currently, a pound of colored soy ink costs from \$1.50 to \$2.50, depending on color and application; black soy inks cost slightly more. These prices compare to costs ranging from \$1.50 to \$2.00 per pound for both black and colored conventional inks.<sup>20</sup>

About 75-80 percent of the soy ink made today is used for the production of colored inks. These are produced in three primary colors, red, yellow and blue, that can be used in combination to produce over 100 different colors.

**Table 16. Typical Range of Composition of Soy Oil-Based Inks (Color and Black) and Water-Based Inks**

Ink Component	Colored Soy Inks (Red, Blue, Yellow)	Black Soy Inks (Different Grades)	Water-Based Inks
Pigment	70 - 75%	20 - 30%	10 - 45%
Binder (Resin)	5 - 8%	3 - 5%	10 - 25%
Solvent <sup>1</sup>	25 - 30%	70 - 80%	0 - 20%
Water	—	—	40 - 75%
Additives <sup>2</sup>	1 - 5%	1 - 3%	1 - 7%

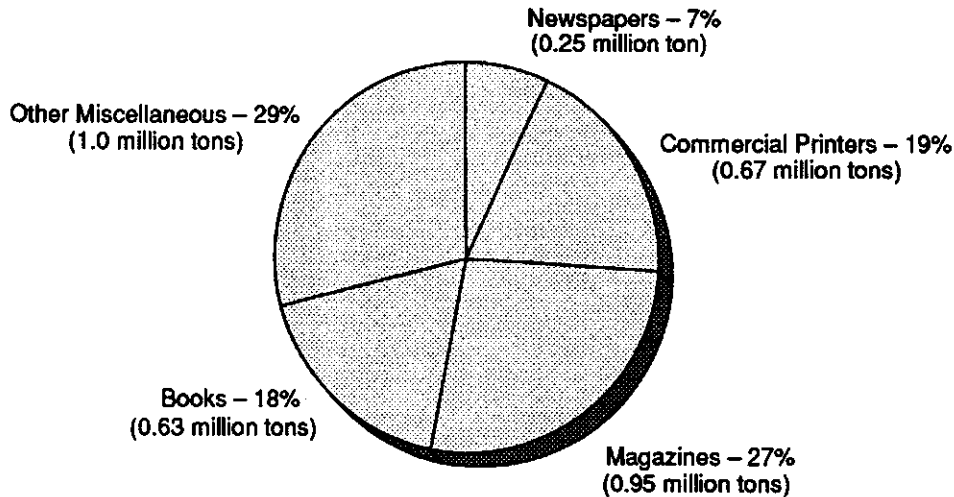
<sup>1</sup> The solvent in soy inks (color and black) is soybean oil. The solvent in water-based inks is alcohol derived from petroleum.

<sup>2</sup> Additives are used for the adjustment of final ink properties. Typical additives are surfactants and waxes.

SOURCES: American Soybean Association, St. Louis, Missouri, March 2, 1992; R. C. O'Boyle, "Water-Based Inks for Packaging Films," *TAPPI Journal*, vol. 74, no. 8, August 1991.



Figure 12. Ink Market Breakdown by Application Type in the U. S.  
(Total 1990 Printing Ink Consumption: 3.5 million tons)



SOURCES: *American Ink Maker*, November 1991; American Soybean Association, St. Louis, Missouri, March 1992.

Some printers are willing to pay slightly more for soy oil-based inks because soybeans are a domestically grown product, and the inks are environmentally friendly. Says John Irvin, vice president of operations at the *St. Petersburg Times*, "We would prefer using ink that's safer and grown in the United States rather than ink that uses foreign petroleum. We get good reproduction and it's a good American-made product."<sup>21</sup>

Vegetable oil-based inks may offer some economic advantages over traditional inks. They have better ink transferability and produce a more uniform dot or solid area; these properties have been shown to reduce ink consumption for a given job.<sup>22</sup> Some printers report that they can print more copies with soy oil inks. Soy inks flow more smoothly, reducing paper waste. Since newsprint accounts for 40 percent of the operating costs of newspapers, the cost savings can be significant.<sup>23</sup> Machines using soy inks clean well after use.

Forty different ink producers have been licensed to produce soy inks by ANPA.<sup>24</sup> Key companies include General Printing Ink of Carlstadt, New Jersey; J.M. Huber of Edison, New Jersey; Sinclair and Valentine L.P. Ink Company of St. Paul, Minnesota; and Daicolor-Pope, Inc. of Clifton, New Jersey. AKZO, of Matteson, Illinois, and Sun Chemicals,

based in Cincinnati, Ohio supply refined oils as a solvent vehicle for soy inks. AKZO also supplies resins and has recently introduced vehicle oils other than soybean (e.g., corn oil and linseed oil) for inks.

Magruder, a French pigment company, has introduced two commercial-grade pigments especially for soy oil-based inks. Marketed as Bio-Glo and Bio-Set, both are derived primarily from plant matter and refined inorganic earth minerals. These pigments have the lowest metal oxide content of any pigment currently available in the market, and exhibit excellent coloring and blending properties in soybean oil-based formulations. The heavy metals or metal oxides present in conventional pigments pollute the environment if paper printed with inks containing such pigments is burned. Inks formulated with Bio-Glo or Bio-Set cost 30-50 percent more than conventional petroleum-based inks and 20-30 percent more than soy inks. Advantages claimed for these pigments are better compatibility with soy and other natural oils and improved printing quality for sheet-fed offset printing.

Soy inks used for newspapers contain over 50 percent soy oil; sheet-fed printing inks contain 20-40 percent soy oil; and magazine inks contain 10-15 percent soy oil.<sup>25</sup>

Drying time and quality are important considerations for printing inks. The major disadvantage of soy inks has been their slowness to dry which, until recently, has restricted their use to newspapers. Since soy inks dry by oxidation, and the rate of oxidation decreases as the drying proceeds, it is very difficult to dry the last 5 percent of the soy oil without an additive. New ink formulations containing resins and special solvents to speed drying have been introduced, but these additives raise the price. Resins are the most expensive component of inks, costing as much as \$2.00 to \$3.00 per pound. Even a small percentage of resins may drive the cost of soy ink above the competitive range.

Improved soy inks for sheet fed presses are now entering the market. Sinclair and Valentine of Saint Paul, Minnesota, have introduced a soy-based sheet-fed ink marketed under the name of Soy XL that dries more quickly than its predecessors but still requires almost twice the drying time of conventional inks. Earlier soy ink formulations were essentially restricted to the use of high ink absorption paper. Printing on glossy surfaces, which have low absorption capacity, led to smudging. The new inks are more acceptable for glossy surfaces. Work continues on reducing drying times.

Heat-set soy inks, which have been marketed since 1989, are still on the fringes of the magazine printing industry. In a heat-set printing process, the printed paper is dried in an oven where any solvent present as a pigment carrier is flashed out very rapidly. Soy oils take much longer to set and may not dry completely due to their higher "heat of vaporization." Current heat-set soy ink formulations take over 2 hours to dry in the same oven that dries conventional inks in 15-30 minutes.

The price of soy oil-based inks may come down in the near future because of a new process patented by researchers at the Agricultural Research Service laboratory in Peoria, Illinois. Marvin Bagby, with the ARS in Peoria, reports that his laboratory is producing an ink that contains only soy oil and pigment, with no hydrocarbon-based varnishes, resins, solvents or other chemicals. But, eliminating resins and other bridge solvents (used in small quantities to optimize the function of soy oil and pigment compatibility) increases the proportion of soy oil in the ink to 80-90 percent. Although the drying process of soy oil is primarily based on oxidation, some evaporation does take place - increasing the proportion of oil increases evaporative drying, and as a consequence, VOC emissions.

Also, work is currently being done on developing pigments for soy inks that are environmentally friendlier than conventional metal-based pigments.

The Occupational Safety and Health Administration (OSHA) has established workplace exposure standards for conventional newspaper inks. Under the Clean Air Act, VOC emissions from printing inks must be monitored in large printing facilities. Under a proposal pending, the EPA is planning to limit VOC emissions from each printing facility to 10 tons per year in ozone nonattainment areas, and 25 tons per year in the rest of the country. In California, the South Coast Air Quality Management District currently requires that the VOC content of inks not exceed 2.5 pounds per gallon. VOC concentrations in conventional inks range between 4.0 and 6.5 pounds per gallon.<sup>26</sup> No separate guidelines exist for soy-based inks.<sup>27</sup>

It will be hard for soy inks to capture the flexographic and rotogravure printing markets because both currently use specially formulated solvent-based inks that have time-controlled shut-off (drying) properties. But, research to develop soy inks with such properties is being conducted, with concerns about VOC emissions providing the impetus.

Besides curbing VOC emissions, soy oil inks may offer another environmental advantage: they may facilitate recycling. During the paper recycling process, paper pulp must be deinked. Researchers at Western Michigan University have found that papers printed with soy inks deink faster and clearer than those containing petroleum-based inks, resulting in improved fiber length and quality in the final recycled paper product.<sup>28</sup> Moreover, the degradability of soy ink is a decided advantage when disposing of the sludge left from deinking.

### Water-Based Inks

Environmentally friendly versions of water-based inks, which have been used for porous substrate like paper and paperboard for many years, can replace solvent-based systems, and thus reduce VOC emissions from printing inks. Developing water-based inks for use on non-porous glossy paper and other surfaces such as film or foils poses a major challenge, however. Printing inks for nonporous paper, which comprise most of the printing inks market, are generally based on high-VOC solvents.

The adhesion of water-based ink to nonporous surfaces is poor. Printability is also poor. Manufac-

turers of water-based inks have attempted to minimize these problems by adding solvent to their formulations. But adding a solvent increases VOC emissions and decreases the environmental benefits of water-based inks. The use of surfactants and water-soluble or water-dispersible resins, either of which could be derived from plant matter, is being investigated.

Conventional water-based inks can contain as much as 20 percent alcohol by volume, resulting in VOC emissions equal to those of inks derived from petrochemicals. Newer formulations are replacing alcohols with vegetable oils, and are also developing water-emulsion based systems that emit low levels of VOCs.

Ordinary water-based inks cost \$1.50 to \$2.00 per pound; special-purpose inks cost upwards of \$2.50 per pound. Conventional inks for foils and films currently cost \$2.00-\$2.50 per pound. Water-based inks have an estimated 2 to 3 percent share of the ink market.

## **Soaps and Detergents Industry (21 million tons)**

Twenty-one million tons of soaps and detergents were marketed in 1990.<sup>29</sup> Laundry detergents accounted for 60 percent of the total, or 12.6 million tons. About 200 companies in the U.S. currently supply materials and finished products in the soaps and detergents category.

Conventional soaps and detergents have been derived primarily from a combination of fossil fuels and inorganic minerals. With the exception of inert materials, mainly inorganic minerals that are added for bulk and to control costs, the active ingredients have been shown to have negative environmental effects of one kind or another. In order to produce environmentally friendlier soaps and detergents, it may not be necessary to use 100 percent plant matter-based raw materials. Reformulations replacing fossil- and phosphate-derived active ingredients with plant matter-based components would suffice.

The soap industry traces its roots back over 2000 years into the past. A soap factory has been found in the Pompeii excavations. However, soap itself was never actually "discovered," but instead gradually evolved. Up to the early 1800s, soap was believed to be a mixture of animal fat and alkali, which was derived from the crude leaching of wood ashes or

from the evaporation of naturally occurring alkaline waters such as those of the Nile River. The raw material shortages of World War I led Germany to develop "synthetic soaps," now known as detergents. The detergents were composed of short-chain fatty acids derived from naturally occurring plant and vegetable oils, animal fats, and fossil fuels – petroleum and coal.

Fatty acids, characterized by a chain length based on the number of carbon atoms in the acid molecules, are the active ingredients of commercially produced soaps and detergents. They form surface active agents (surfactants), changing the physical properties of the wash water and increasing the wetting action of the detergent. From the original short-chain fatty acids – alkyl naphthalene sulfonates – used in the manufacture of detergents at the turn of the century, the industry has progressed to long-chain alcohol sulfates in the 1920s and 1930s, alkyl-aryl long-chain sulfonates in the 1940s, branched-chain compounds in the 1950s and 1960s, and presently the continuing development of "tailored" fatty acids that are easily biodegradable.

Two-thirds of the bulk of a typical soap consists of builders and fillers, mostly inert materials like soda ash (sodium carbonate) and phosphates. Soaps can also contain other additives such as coloring agents and perfumes.

Soaps, however, are incompatible with hard water and therefore unsuited to automatic washers. Hard water contains calcium and magnesium ions. The fatty acids in soaps react with these ions and precipitate out from the liquid phase, forming insoluble deposits. When soaps are used with hard water in automatic washers, drain pipes tend to become clogged by precipitates.

The first machine detergents, developed in the 1960s to replace soaps in automatic washing machines, were petrochemical in origin. Detergents differ from soaps primarily in their action in hard water; unlike soaps, they form soluble compounds with the unwanted dirt particles or hard-water minerals. Detergent molecules can aggregate in the water, locking in several dust particle clusters without reacting with them individually. The detergent formulations also contained phosphates, which prevent the formation of calcium and magnesium deposits in washing machines and increase the cleaning action, particularly of cotton fabrics.

In the latest detergents, various other ingredients are added to speed up the cleaning action, prevent felting, and make clothes whiter and brighter.

Most detergents manufactured today also contain small amounts of carboxymethyl cellulose, which prevents the gradual yellowing of cotton fabrics.<sup>30</sup> Today's detergent chemistry has evolved to become an art form in which proportions of individual ingredients (whether active or inert) are considered as important as their specific characteristics. The overall detergent performance is no longer determined by its cleaning action alone but also by factors like its long-term effect on the cloth properties, its corrosiveness to the washing machines and drainage pipes, and its environmental effects.

### Phosphates

Phosphates act as sequestering agents; that is, they react with undesirable molecules (in this case, magnesium and calcium ions) and keep them from being redeposited on the washed surface. They raise the alkalinity of the cleaning water, thus improving the action of surfactants and other active ingredients present in the detergent. Phosphates are also used as builders because of their low cost. A typical detergent contains 8-14 percent phosphates, in the form of sodium tripolyphosphate (STPP) and tetrasodium pyrophosphate (TSPP). See Table 17.

Phosphates, however, have deleterious environmental effects. In combination with nutrients like carbon, nitrogen, and potassium that occur naturally in lakes, streams, and seas, phosphorous encourages excessive growth of algae and underwater plants, which consume most of the dissolved oxygen available for both plant and animal life. The high biochemical oxygen demand (BOD) of this excessive growth reduces the amount of oxygen available to fish.

There are two ways to mitigate the effect of phosphates on water quality: reduce the use of phosphates, or upgrade water treatment systems. Upgrading water treatment is costly. Almost all municipal treatment facilities in the U.S. are primary or secondary, or a combination of both; yet only tertiary systems can remove phosphates. Primary treatment, in which the effluent is usually chlorinated to destroy bacteria and viruses, removes 30 to 60 percent of suspended solids and reduces BOD to about half of

its original value. Secondary treatment uses air to oxidize dissolved organic materials, reducing BOD to 10-15 percent of its original value, and removing much of the suspended solids.

Tertiary systems remove phosphates by precipitation with limestone (calcium carbonate) at a cost of 2-4 cents per ton of sewage treated; but this treatment does not work on polyphosphates and other complex phosphate molecules containing nitrogen and other ions. In order to remove these, metallic hydroxides, such as aluminum oxides, are needed.

**Table 17. Typical Composition of the Latest Powdered and Liquid Detergent Formulations Replacing STPP and TSPP with Enzymes and Zeolites (percent by weight)**

	Compact Heavy-Duty Powdered Detergent	Heavy-Duty Liquid Detergent
Surfactants	6 - 50	8 - 55
Enzymes	2.3 - 6.3	0.8 - 2.2
Zeolites	0 - 40	0 - 30
Builders	2 - 50	0 - 30
Fillers	5 - 23	0 - 5
Additives	15.4 - 31.6	1.1 - 10.5
Blinder/Water	1 - 3	30 - 50

SOURCE: Novo Nordisk Bioindustrials Inc., Detergent Enzyme Division, Danbury, Conn., March 1992.

A tertiary facility using both these types of treatment can remove 90-95 percent of phosphates at a cost of 6-10 cents per ton of sewage treated. Half of this cost, or 3-5 cents per ton of sewage treated, is attributable to removal of phosphates from soaps and detergents.<sup>31</sup> The capital costs of a tertiary treatment facility can add another 5-8 cents per ton of sewage treated.

Therefore, a tertiary treatment facility constructed today to treat phosphate from laundry detergents alone would cost 4-8 cents per load of laundry washed with a 15 percent phosphate detergent (P<sub>4</sub> basis).<sup>32</sup>

The Federal Water Pollution Control Act Amendments of 1972 required that by 1985 indus-

tries treat their waste streams to reduce BOD to acceptable levels before discharging them to local sewage treatment facilities. Although industrial discharges have come largely under control, consumer use of phosphate-based laundry detergents continues to burden sewage treatment facilities. Currently, an estimated one-third of all the phosphate present in the wastewater in the U.S. comes from laundry detergents alone.

The other way to mitigate the environmental impact of phosphates — reducing their use — is more effective and less costly than upgrading water treatment systems. Phosphates in detergents already have been banned in a quarter of the states in the U.S., mainly those on the East Coast.<sup>33</sup> Phosphate consumption has declined by about 50 percent na-

Since phosphates work as both sequestering agents and builders, replacements for phosphates must perform both these functions. Soda ash, zeolites, and enzymes have been used as substitutes, with varying degrees of success.

### Soda Ash

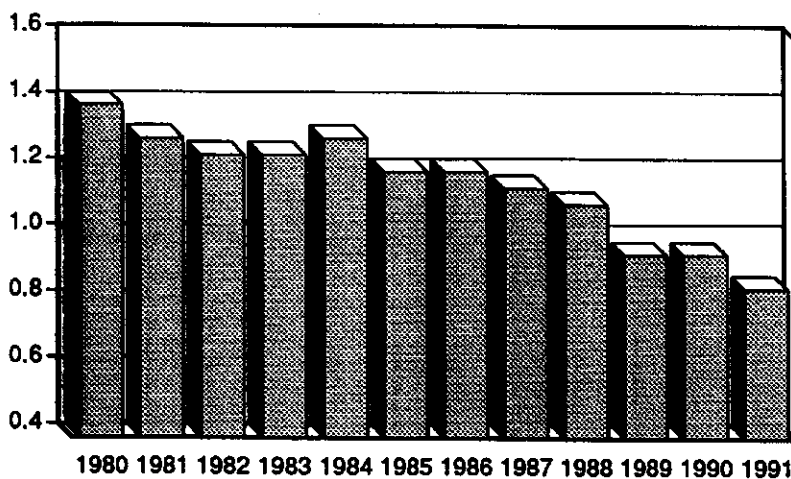
Soda ash, the most commonly used non-phosphate filler in detergents, removes calcium ions from the water by precipitating them as calcium carbonate. However, it is difficult to keep calcium carbonate in suspension while using soda ash alone. Often it is redeposited on the laundry, giving a harsh feel and gray tint to white clothes and a dull appearance to colored fabric.<sup>34</sup>

Soda ash is derived from a variety of processes and raw material sources. The most important source has been limestone. In addition, dry lake beds in California and Wyoming have inorganic mineral ore deposits called trona which are an excellent source for soda ash. In addition, soda ash is also produced from lakes that have high concentrations of borax-containing brine waters. All these are natural sources and have proven to be environmentally inert.

### Zeolites

Zeolites and inorganic silicates are a special class of synthetic inorganic compounds designed to target and remove particular chemicals and/or metal ions.<sup>35</sup> They have been used in chemical processing for many years, and are now being used as sequestering agents in detergents. But zeolites cannot match the properties of phosphates. Since they have low water solubility, their use is limited to super compact powder detergents. Furthermore, zeolites can remove calcium ions but not magnesium ions; another sequestering agent is needed to remove magnesium. In today's phosphate-free formulations, zeolites are used as a partial replacement for STPP. They cost less than STPP and are widely available. U.S. production capacity of detergent-grade zeolite is 165,000 tons a year.

**Figure 13. Annual Demand for Phosphates in the U.S. (Combined STPP and TSP, in millions of tons)**



SOURCE: *Chemical Week*, vol. 150, no. 4, January 29, 1992.

tionwide since 1980. See Figure 13. About one-third of all detergents sold in the U.S. in 1990 were phosphate-free. Other countries have also taken steps to reduce or eliminate the use of phosphates. In Canada, detergents containing phosphates dropped from 90 percent of the market to 40 percent in a 6-month period during 1990. Japan fully eliminated the use of STPP in laundry detergents in the mid-1980s. Many European countries expect to achieve zero phosphate use in the next 2-3 years.

Regulations banning or reducing the use of phosphates have spurred the search for alternatives.

Current market prices for zeolites range from 26.5 to 33.0 cents per pound, depending on the grade.<sup>36</sup> Polyphosphates cost 30.0-32.5 cents per pound.

### Enzymes

A major development in the detergent industry was the introduction of enzymes as active cleaning agents in the 1980s. Enzymes are large protein molecules which consist of chains of amino acids folded in a complex way. They act as nature's catalysts, speeding the splitting apart and stitching together of molecules. Enzymes for industrial use are produced by microbial cells - fungi, yeasts, and bacteria. Being a protein, enzymes break down readily in the disposal process, with no need for water treatment.

In 1990 over \$100 million worth of enzymes, representing over 16 percent of the nation's enzyme market, were utilized in detergent formulations. Tide, Wisk, and Breeze are a few of the many detergents containing enzymes. Even so, only 50 percent of detergents in the U.S. contain enzymes, compared to 90 percent in Europe and 95 percent in Japan.

Until very recently, the high cost of enzymes restricted their use to very high-value products, such as pharmaceuticals. Naturally occurring microbial cells of fungi, yeast, and bacteria produce small quantities of enzymes at very slow rates. Bioseparation techniques used in the past to isolate and purify these enzymes were expensive and produced only low-grade (less active) enzymes.

The recent availability of ultra-centrifuges and chromatography techniques for the isolation and purification of enzymes, combined with improvements in other protein separation techniques such as gel electrophoresis, has helped reduce the cost of industrial enzyme production. The single most important development, however, is the use of recombinant DNA technology. Over 40 percent of industrial enzymes for low-value products and processes, including cellulose-based ethanol fermentation and laundry detergents, are synthesized by genetically altered microbial cells capable of producing large quantities of the desired enzymes in a short period of time.

The first genetically engineered product to reach the general public was the fat-splitting enzyme lipolase, now a common ingredient in many wash-

**Table 18. Average Composition of Conventional Dry Phosphate-Based Powdered and Liquid Detergents Produced in the U.S. (percent by weight)**

	Light-Duty Powdered Detergent	Heavy-Duty Powdered Detergent	Heavy-Duty Liquid Detergent
Surfactants <sup>1</sup>	25 - 40	20 - 35	10 - 57
Builders <sup>2</sup>	2 - 30	30 - 50	6 - 12
Fillers <sup>3</sup>	30 - 70	10 - 25	—
Additives <sup>4</sup>	0.10 - 4.65	4.60 - 9.52	7.1 - 17.85
Moisture/Water	1 - 5	3 - 10	10 - 45

1 Detergents may contain both anionic (alkylbenzene sulfonates, fatty alcohol sulfates, etc.) and nonionic (alkyl and nonylphenyl polyethers, etc.) surfactants in different proportions depending upon type and manufacturer's brand.

2 Builders are mainly dry phosphates (sodium tripolyphosphate [STPP] and tetrasodium pyrophosphate [TSP]) and certain inorganic salts (e.g. sodium sulfate, sodium citrate, sodium silicate) added in small quantities.

3 Fillers are used to extend the formulation quantities. Soda ash is the main filler used by this industry.

4 Additives include a variety of compounds incorporated for different purposes, such as perfumes and color pigments for presentation, fluorescent dyes for brightness, quaternary ammonium salts as fabric softeners, and other formulation aids like ethanol, propylene glycol, and straight-chain fatty alcohols as binding agents.

SOURCES: G.T. Austin, *Shreve's Chemical Process Industries*, 5th ed. (New York: McGraw-Hill, 1985); Henkel Chemical Company, *Gulph Mills*, PA, 1992.

**Table 19. Comparative Cost Differential Analysis of Powdered and Liquid Laundry Detergents Derived from Petrochemicals and Bio-Based Components**

Detergent Type	Detergent Unit Cost (dollars per unit)	Number of Loads (loads per unit)	Detergent Use Per Wash Load (oz. per load)	Detergent Cost Per Wash Load (cents per load)
<b>Regular Tide Powder (Old<sup>1</sup> Formulation with 7-14% Phosphates)</b>	1.10 (pound)	5	3.2	22
<b>Ultra Tide Powder<sup>2</sup> (Phosphate-Free and Enzyme-Based)</b>	1.75 (pound)	7	2.3	25
<b>Ultra Fab Liquid<sup>2</sup> (Phosphate-Free and Enzyme-Based)</b>	10.25 (gallon)	32	4.0	32
<b>Bio-Shield Liquid<sup>3</sup> (Phosphate-Free, 100% Bio-Based, with Enzymes)</b>	19.90 (gallon)	43	3.0	46

1 Conventional formulation derived primarily from petrochemical components and containing as much as 14 percent phosphates in the form of STPP and TSPP.

2 Concentrated formulations in which phosphates and petrochemical-derived surfactants have been replaced by environmentally benign inorganic zeolites and plant-based enzymes and surfactants. These formulations may still contain petrochemical-derived components, yet show a better biodegradation profile than older, 100 percent petrochemical-based formulations.

3 Completely bio-based highly concentrated liquid laundry detergent (marketed in concentrations three times as high as shown in the table above) containing vegetable oil-based ionic surfactants, bio-based enzymes, and citrus oils. It is completely phosphate-free and completely biodegradable.

SOURCES: Procter and Gamble Company, Cincinnati, Ohio, 1992; Colgate-Palmolive Company, New York, New York, 1992; Eco Design Company, Santa Fe, New Mexico, 1992.

ing powders. Alone among phosphate replacements, lipolase is an excellent oils and cosmetics remover. It can dissolve fat at relatively low temperatures and thus reduce energy consumption. Other detergent enzymes include protease, which dissolves protein stains, and amylase, which dissolves starch stains. Protease is the best-selling detergent enzyme, accounting for over 90 percent of the detergent enzyme market worldwide.

Lipolase costs over \$7.50 a pound. Other detergent enzymes, such as protease and amylase, have an average price of about \$3.50 a pound.<sup>37</sup> The cost of detergent enzymes is expected to drop to \$2.50-\$3.00 per pound by 1994.

"Supercompacts," or ultra powder detergents, have recently captured over one-quarter of the laundry detergent market, facilitating the use of enzymes, which have generally been less effective in liquids. Enzymes present in liquid detergents become deactivated during the storage period prior to

use. However, there have been encouraging developments in liquid detergents as well. The New York-based Colgate-Palmolive Company was the first to introduce an enzyme-based liquid ultra detergent, marketed under its brand name, Fab. Procter and Gamble of Cincinnati, Ohio, is planning to introduce a Tide line of liquid detergents with enzymes. Eco Design of Santa Fe, New Mexico, markets an enzyme-containing liquid ultra detergent that is also free of any fossil fuel-based components—probably the only detergent of its kind.

Research is proceeding on another track. Enzymes currently used in detergents are inactivated in the presence of bleach. A new enzyme stable under harsh conditions (such as in bleach solutions) is under development and is expected to be commercialized by 1993.

Zeolites and enzymes work well together. Sodium silicates increase the alkalinity (reduce the acidity) of wash water, a necessary condition for

optimum enzyme activity. Detergent enzymes work best in a pH range of 9-10. (See Table 17, page 35 for formulation contents.)

Table 19, page 38, shows the costs of various types of detergents: regular phosphate-based powders; phosphate-free, enzyme-based ultra powders; phosphate-free, enzyme-based ultra liquids; and 100 percent bio-based liquids. Regular phosphate-based detergents cost \$1.00-\$2.00 per pound. Supercompacts cost \$1.50-\$2.00 per pound, but a pound of supercompacts washes more loads of laundry than a pound of regular detergent. Assuming an

liquids is substantial. The only 100 percent bio-based liquid detergent on the market is twice as expensive as conventional detergent, on a per wash load basis.

Strides have also been made in the use of plant-based ingredients for household cleaners. Table 20, shows the comparative costs of petrochemical- and bio-based all-purpose cleaners. The biological cleaners are often based on acids derived from fruits, such as citric acid from lime and other citrus fruits. In many cases, they are already competitive with petrochemical-based cleaners.

**Table 20. Cost Comparison of Petrochemical and Bio-Based All-Purpose Cleaners**

All-Purpose Cleaner		Retail Price (dollars per 16 oz)	Recommended Dilution to Application Strength	Diluted Application Cost (cents per 16 oz)
BIO-BASED	Bio-Shield	9.95	20-28	35-50
	Citri-Solv	2.10	4-16	13-52
	Earth Wise	1.40	0-16	9-140
FOSSIL-BASED	Simple Green	3.20	16-32	10-20
	Mr. Clean	1.90	0-16	12-190
	Lysol Pine Action	1.60	0-16	10-160
	Ammonia	0.60	0-16	4-60

SOURCES: Eco Design Company, Santa Fe, N. M., 1992; Chempoint Products Company, Danbury, Conn., 1992; Celestial Seasonings, Inc., Boulder, Co., 1992; Sunshine Makers, Huntington Harbor, Cal.

average cost of \$1.10 per pound for regular and \$1.75 per pound for supercompact detergents, we find that ultra-grade detergents cost 25.0 cents per load as opposed to 22.0 cents per load for regular grade detergent.<sup>38</sup> When the costs of phosphate removal through tertiary treatment facilities are taken into account, the 3.0 cent net cost of supercompacts without phosphates becomes a 5.0 cent or greater net cost advantage.

We can see from Table 19 that while the price difference between old phosphate-based powders and new phosphate-free, enzyme-based detergents is very small, the difference between the old powders and the new phosphate-free, enzyme-based

### Adhesives and Glues Industry (5 million tons)

Over 600 adhesive manufacturers operate in the U.S., producing hundreds of natural and synthetic adhesives and sealants, with an annual value of more than \$2.0 billion.<sup>39</sup> About 5.0 million tons of adhesives were used in the U.S. in 1990. Natural adhesives accounted for more than 40 percent of this – about 2.0 million tons. See Table 21, page 40.

Environmental regulations, such as those limiting VOC emissions, are forcing changes in the formulations of adhesives. As in the cases of surface coatings and printing inks, the VOC emission prob-



lem of adhesives is being addressed by increasing the solids content of the formulation and substituting plant matter-derived components for petrochemical solvents and resins. Although "adhesives and glues" is the industrial product category in which plant matter-based or "natural" products have the largest market share, there is still considerable room for replacing fossil-based or "synthetic" category with natural products.

In 1991 the federal government imposed a 13 percent tax on chlorinated solvents, including trichloroethane (TCE), an important component of some synthetic adhesives. Manufacturers are responding by increasing the solids content of their products. Last year, Swift Adhesives of Downers Grove, Illinois increased the solids content of its adhesives from 15-20 percent to 40-50 percent, with a corresponding reduction in solvents. According to

the company's president, Andrew Katai, "additional reductions [in solvent content] will require further formulations development. One barrier is that the adhesive becomes increasingly difficult to apply as spreadability decreases with solvent content."<sup>40</sup>

Adhesive manufacturers may have to decrease the amounts of, or find substitutes for, other ingredients as well as solvents. The preservative compounds used in adhesives are usually derived from organic chemicals (fossil fuel-based) and heavy metals; many of them are either known or suspected to be toxic to humans or the environment. Unlike other products, adhesives must contain certain antimicrobial chemicals or preservative chemicals to protect the product during storage.

The German company Henkel is the leading adhesives manufacturer in the world. Planners in

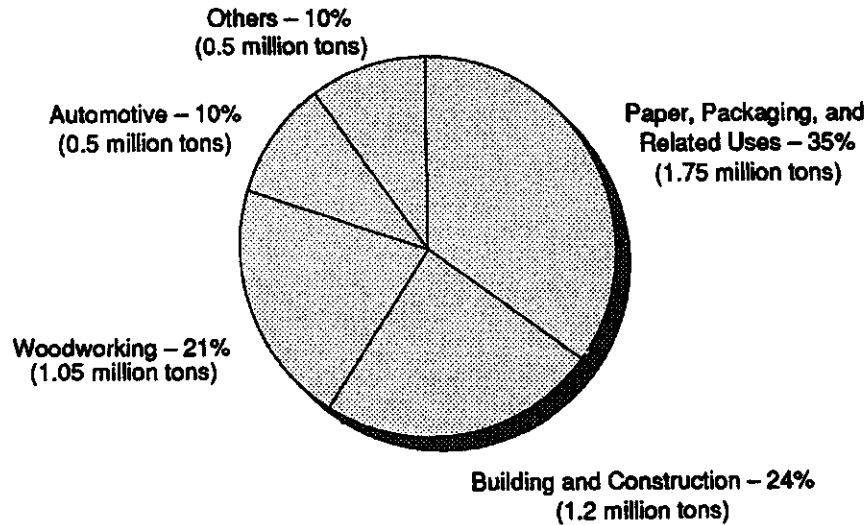
**Table 21. Total Production of Natural and Synthetic Adhesives in the United States (In millions of pounds)**

		1980 Production	1990 Production	1995 Projection
SYNTHETIC ADHESIVES	Phenolics	1,139	1,480	1,675
	Vinyl	742	1,023	1,180
	Synthetic Rubber	694	925	1,070
	Hot Melts	527	878	1,035
	Amino	834	869	960
	Acrylics	214	325	400
	Polyurethanes	51	103	130
	Epoxy	33	49	60
	Polyester	17	37	50
	Other synthetics	80	156	200
	<b>Total Synthetics</b>	<b>4,331</b>	<b>5,845</b>	<b>6,760</b>
<b>Total Natural</b>	<b>3,585</b>	<b>4,005</b>	<b>4,290</b>	
<b>Total Adhesives</b>	<b>7,916</b>	<b>9,850</b>	<b>11,050</b>	

<sup>1</sup> Natural adhesives are primarily derived from starch, soybean proteins, zein (corn proteins), egg albumin, casein (milk-derived protein), peanut protein hydrates, and several other plant matter sources. Starch-based adhesives represent the largest segment of natural adhesives produced commercially in the U.S.

SOURCES: The Freedonia Group, Inc., Cleveland, Ohio, 1992; *Adhesives Age*, October 1991, 35-36.

**Figure 14. Adhesives and Sealants Market, by Use  
(Total 1990 U.S. Market: 5.0 million tons)**



SOURCE: "Adhesives and Sealants: Innovating Under Pressure," *Chemical Week*, March 11, 1992.

this company view waste management, especially at the manufacturing end, as the main environmental issue facing the industry. The company is working on expanding its recycling operations and substituting plant matter-derived materials for some heavy metal and petrochemical ingredients. In addition to solvents and preservative compounds, adhesives also contain resins, plasticizers, and small quantities of specialty chemicals that impart specific properties to the adhesive and glue, such as rapid drying, strength, and ability to bind to a specific surface.

In general, natural and synthetic adhesives have different applications. Synthetic adhesives are tougher and more water-resistant; they are used in many applications ranging from construction to automotive assembly to woodworking. See Figures 14, and 15, page 42. Natural adhesives are cheaper, but their applications are limited by lack of water resistance and durability. These low-cost adhesives are used mostly in the paper industry, for stationery, book binding, and paperboard fabrication. The entire price range for adhesives, both natural and synthetic, runs from 15 cents per pound to \$50 per pound or more (for specialty products).<sup>41</sup> The prices of individual formulations for specific applications vary significantly within this range, but synthetic adhesives generally cost more than natural (plant- and animal-based) products. Epoxy-based adhesives cost \$1.30-\$1.40 per pound; phenolic adhe-

sives, \$0.56-\$0.89 per pound; bone-extracted animal glues, \$0.56-\$0.89 per pound; casein-based glues, \$14.00-\$17.00 per pound; soy-based glues, \$1.50-\$2.00 per pound; and synthetic biodegradable adhesives, \$3.00-\$3.50 per pound.<sup>42</sup>

The oldest adhesives are animal glues, extracted from bones, hides, and scraps through a process similar to gelatin extraction. These date back at least 3300 years. Casein- and starch-based adhesives and glues entered the U.S. market in the late nineteenth century; soybean protein-based adhesives, in the twentieth century. Synthetic adhesives were introduced only after World War II, and they have steadily grown to dominate the market.

Natural adhesives, however, made a comeback in the late 1970s, primarily due to improvements in their performance. Synthetic adhesives have very specific formulations with very specific applications; the product binds only the two surfaces specified and none other. This precision has been difficult to achieve with natural adhesives. Drying time has also been a factor; synthetics performed better than natural products. However, in recent years several natural formulations have shown considerable improvements in their application properties, and some have even matched the performance of synthetics. Yet, several categories of adhesives currently derived from synthetics are very difficult to replace with natural products.

Casein, a milk-based protein, can be used in both water-resistant and non-water-resistant formulations for such applications as food container coatings and woodworking. Eco Design, a natural products company based in Santa Fe, New Mexico, has developed a class of casein wood glues under the trade name Bio Shield. These glues have limited water resistance but good resistance to common organic solvents.

Soybean protein glues are used for several food packaging applications. They are susceptible to biodeterioration and have limited water resistance as well as poor resistance to heat. But this biodegradability, as well as low price, make soy protein glues popular.

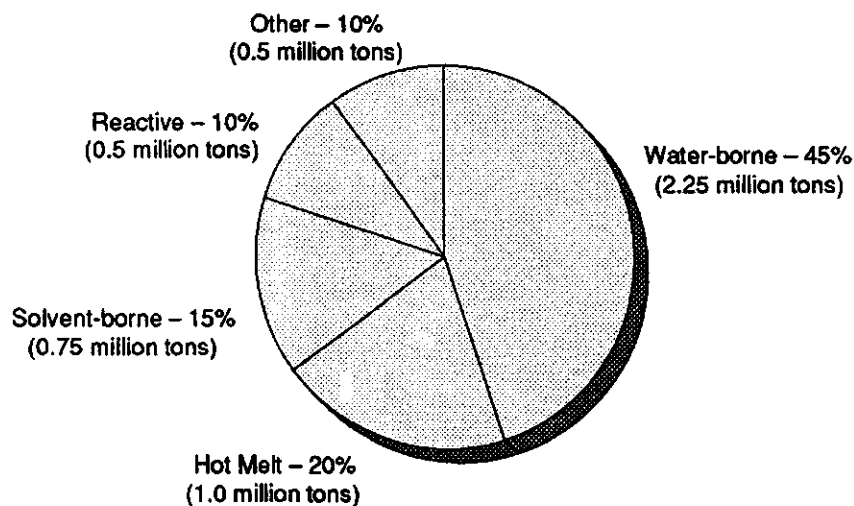
Starch-based adhesives are the most widely used of all natural adhesives. Sources of starch include corn, tapioca flour, wheat flour, and potatoes; uses include paper carton and bottle labeling, stationery, postage stamps, and some interior plywood fabrication. Nearly 1.7 million tons of cornstarch are used annually to make adhesives for the paper/paperboard industry and in other applications.<sup>43</sup> Starch adhesives have properties similar to those of soy and casein adhesives, do not emit the unpleasant odors characteristic of animal glues, and are less expensive than synthetic adhesives. Dextrin, for example, is available for as little as 32 cents a pound.

Other adhesives can be based on these bio-products: albumin, a protein derived from eggs; zein, a corn protein; peanut protein; and fish. In addition, adhesives can be made from agricultural and industrial wastes. Bone-extracted glue is one example. Lignin from kraft pulp mills possesses adhesive properties; it has been used commercially for binding and molding, as a road dust controller, and as a rubber additive. Currently, 10,000-20,000 tons of lignin a year are used for adhesive purposes in the U.S.<sup>44</sup>

Many industrial adhesives are hybrids of synthetic polymers and bio-based proteins. Synthetic resins such as epoxy are grafted onto an adhesive backbone made of bio-based protein (such as gelatin) to form a remarkably strong bonding adhesive. Like thermoset plastics, these adhesives cannot be altered once set with heat and pressure. Other specialty formulations, when used as biomedical adhesives in situations where heat and pressure cannot be applied (as in bonding bone fragments), can be cured with enzymes.

Research currently under way in the field of bio-based adhesives is focused on the development of specialized, high-value adhesives and on the testing of carbohydrate-based sugars for adhesive properties.<sup>45</sup>

**Figure 15. Adhesives and Sealants Market, by Type of Adhesive (Total 1990 U.S. Market: 5.0 million tons)**



SOURCE: "Adhesives and Sealants: Innovating Under Pressure," *Chemical Week*, March 11, 1992.

## Plastics and Resins (30 million tons)

The production and use of plastics in the United States have more than quadrupled during the past two decades. Between 1984 and 1990, U.S. plastics and polymeric resins production increased by over 30 percent - from about 23 million tons to 30 million tons. Industry sources estimate that in the coming years, plastics will continue their traditional average growth of about 4 to 5 percent annually in major categories.<sup>46</sup>

Plastics and polymer resins differ in their applications. Plastics, marketed as both monomers and polymers to industrial molders and consumers, are used primarily as raw materials for solid end products such as household appliances, durable goods, car bumpers, machine parts, packaging film materials, bottles, photographic films, lenses, electrical and electronic components and insulation, toys, medical equipment, pipe and tubings, and magnetic tapes for audio, video, and computer applications.

Resins, on the other hand, are used as components in a wide variety of consumer goods to provide durability. For example, paints incorporate polymeric resins for corrosion resistance and a smooth finish; adhesives include resins for strength and to enhance their capacity to bind to a specific surface; papers and textile products are coated with resins for smoother surfaces and durability. Kitchen appliances like frying pans are coated with polymer resins to create a nonstick surface. Floor tiles and many other appliances are coated with resins for texture and toughness. The list of applications is endless.

Plastics and resins are divided into two basic categories: thermosets and thermoplastics. Each type has its individual properties and characteristics that make it useful for certain applications. Thermosets, for example, are the toughest class of plastic polymers available today; they are used in the manufacture of heat-resistant appliances and parts. Once set in a molded form, thermosets cannot be melted and remolded into other shapes. Thermoplastics, on the other hand, can be melted and remolded; they can be flexible and are not heat resistant. Recently, within these two categories, several new classes have emerged and are now beginning to command their own markets - engineering plastics, graft polymers, and biopolymers.

Engineering plastics are high strength, high performance synthetic polymeric materials that can be substituted for metals in many applications. These

materials are thermosets or thermoplastics that have been carefully manufactured to impart special properties. Graft copolymers (petroleum-derived polymers with a bio-based component) and biopolymers are thermoplastics that are derived either partially or totally from plant matter through mechanical or biotechnological means. The plant material most commonly used in these plastics is starch. Biopolymers show excellent potential for replacing several categories of thermoplastics in both consumer goods and packaging.

Thermoplastics account for over three-fourths of all the plastics produced in 1990, with polyvinyl chloride (PVC) production at 4.5 million tons, followed by high density poly-ethylene (HDPE) at 4.35 million tons. Table 22, page 44, lists the annual production of leading plastics categories in the U.S. The total number of polymer grades of plastics and resins that are produced in the United States have increased by threefold since 1980, to over 13,000. Packaging is currently the largest single application for plastics produced in the United States. In 1990, 7.5 million tons of thermoplastics - accounting for about 25 percent of the total plastics market - were used for packaging.

It is interesting to note that the first plastics were produced predominantly from biomass and coal. Plastics and resins have been produced and used in the United States since early the 1860s, when John Wesley Hyatt developed cellulose nitrate (celluloid) from wood pulp and used it to produce billiard balls and eyeglass frames. The development of commercial phenolic resins by Leo Baekeland in 1909 marked the beginning of the synthetic plastic industry as we know it today. Although the phenols used in plastic manufacturing in the early 1900s were derived exclusively from wood extractives, fossil fuels became the industry's primary feedstock after World War I.

The three most important petrochemical feedstocks utilized by the polymer industry in the United States are ethylene, propylene, and benzene. We estimate that in 1990 ethylene was by far the most common feedstock, accounting for over 45 percent of the total U.S. plastics and resins production. Propylene and benzene followed with a 15 percent share each. These three intermediate chemicals account for 75 percent of all feedstocks going into the plastics industry today.

The period 1930-1940 saw the development of today's major thermoplastic materials, such as polystyrene, low-density polyethylene (LDPE), HDPE, and PVC - all derived from petroleum and natural

gas feedstocks. By the end of World War II, petroleum and natural gas completely replaced agricultural materials and coal as raw materials for the production of plastics.

An estimated 425 million barrels of crude oil equivalent were consumed in the production of 30 million tons of petrochemical-derived plastics and resins in the United States in 1990.<sup>47</sup> See Figure 16. This figure represents almost 7 percent of total U.S. petroleum consumption for that year.<sup>48</sup> Today, the U.S. plastics industry depends on petroleum for about 75 percent of its raw materials, with natural gas supplying the remainder.<sup>49</sup> The share of coal has been reduced to less than 0.1 percent of all chemical feedstocks used in the plastics industry.

During the past 40 years, petroleum-based plastics and resins have replaced many traditional materials such as wood, glass, steel, aluminum, stone, wool, and cotton in a wide variety of consumer applications. While conventional plastics are less costly than the materials they replace and have properties that make them attractive for many applications, they also have many disadvantages.

In addition to the most obvious disadvantage of the use of conventional plastics—heavy dependence

on petroleum and natural gas—environmental concerns, both of pollution from production processes and of solid waste disposal of end use products, have forced the industry to look for raw material substitutes and to improvements in the recyclability and biodegradability of plastics.

Recent developments, both technical and economic, have made commercial production of resins and plastics from bioresources possible. Such production can entail either direct processing of biomaterials or the use of intermediate precursor chemicals derived from biomass. First-generation biopolymers can potentially replace some conventional thermoplastics: the largest segment of the plastics industry.

Substitution of conventional petrochemical plastics with biomass-based plastics can be achieved either directly or indirectly. Direct substitution refers to the substitution of biomass-derived intermediate chemical feedstocks for petrochemical-derived intermediate chemical feedstocks. In the production of phenolic resins, phenol derived from lignin (wood) may be substituted for phenol derived from petroleum. In this type of substitution, the physical properties of the biomass-derived resins are identical to those of their petrochemical-derived counterparts.

Indirect substitution refers to the substitution of plastics currently made from petrochemicals with plastics manufactured from biomass materials. In this type of substitution, the bio-based plastic may or may not exhibit identical properties as compared with the plastics they are replacing, yet they still serve the same function. In many cases, these different characteristics are desirable. For example, Warner-Lambert Company has developed a starch-based polymeric resin called NOVON which competes directly with petroleum-based thermoplastics in its class. NOVON has identical molding properties to the plastics it is replacing but differs from them considerably in biodegradability and density.

**Table 22. Production of Major Product Categories of Plastics in the U.S. (In millions of tons)**

Major Category	1980 Production	1985 Production	1990 Production
PVC	2.60	3.25	4.50
HDPE	2.10	3.25	4.35
Polypropylene	1.80	2.50	4.10
LDPE	3.30	3.00	3.60
Polystyrene	1.75	2.00	2.55
LLDPE	0.40	1.40	2.35
Phenolic Resins	1.10	1.25	1.45
Unsaturated Polyester	0.45	0.60	0.60
Other	5.50	6.75	6.50
<b>Total</b>	<b>19.00</b>	<b>24.00</b>	<b>30.00</b>

SOURCE: B. F. Greek, "Plastics Producers Look for Turnaround by Year's End," *Chemical and Engineering News*, vol. 69, no. 23, June 10, 1991.

The primary advantage offered by plant-based plastics is their biodegradability, which is especially important for products that are difficult to recycle, such as fast food packaging, and leaf bags that hold compostable materials. Questions, however, have been raised regarding the disposal of these plastics. In order to decompose properly, they should be composted. It is thought that if they are mixed with "regular" plastics taken to recycling facilities, an inferior material will result from processing. The makers of the bioplastic NOVON dismiss these concerns, asserting that NOVON will dissolve out of the mix in the recycling process before petrochemical-based plastics reach their melting point.

### General Survey of Uses of Plant Matter in Plastics

Conventionally, all petrochemical-derived plastics have been classified as thermoplastics or thermosets. However, in recent years, two more classifications have emerged: copolymers (plastics with two or more individual resin components that can be either petrochemical-based or bio-based), and biopolymers (plastic resins that are derived primarily from plant matter). This development is primarily due to the increased use of plant matter in the manufacture of plastics, a result of environmental concerns.

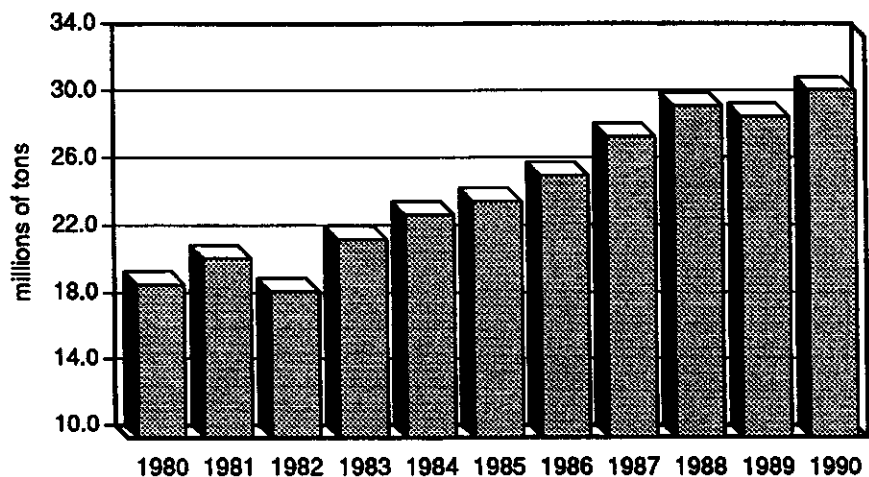
Copolymers are formed by mixing two or more different kinds of plastics together in order to achieve certain application properties such as flexibility, mechanical strength, or temperature resistance. In recent years, copolymers have become the first plastics to incorporate plant matter-based raw materials. Copolymers with a biocomponent have properties inherent to petrochemical-derived plastics, yet are highly biodegradable. Biopolymers are resins derived primarily from plant matter; biopolymer plastics, for the most part, behave as thermoplastics.

Plasticizers, which were considered only an additive of plastics a few years ago, have come to be considered a separate product class, and are increas-

ingly being derived from plant matter sources. Plasticizers are compounds that are added to plastic resins to improve workability during fabrication or molding of plastic end products. They also impart flexibility and other desired properties to the finished product.

In addition to plasticizers, most plastics consist of a base resin and additives such as glass, asbestos, graphite, or cellulose. A plastic's end properties are determined both by its base resin and by its additives. Most virgin resins, whether they are derived from petrochemicals, plant matter, or a mixture of

Figure 16. Total Annual Production of Plastics and Resins in the U.S.



SOURCE: *Chemical and Engineering News*, vol. 69, no. 25, June 24, 1991.

both, can be formulated into plastics with any desired properties, provided the right mix of additives and plasticizers is used. Cost, not technical feasibility, is the limiting factor. There are a few plastics, however, that cannot be synthesized from plant matter; most of these are thermosets. These plastics have extremely high temperature resistance; once molded into a particular shape or form, they cannot be remelted. Research has indicated that lignin-based phenolic resins could be formulated as thermosets, but these materials have not yet been developed.

Table 23, pages 46-49, shows the price, heat resistance, mechanical strength, specific gravity, base properties, applications, and biodegradability of plastics in four broad categories: thermoplastics, thermosets, copolymers with biocomponents, and biopolymers (plant-based plastics).

**Table 23. Comparison of Typical Property Ranges for Plastics Derived from Petrochemical and Plant Matter Sources by Polymer Type and Applications**

Plastic Type (price: \$/lb)	Maximum-Use Temperature by Grade (°C)	Mechanical or Tensile Strength (MPa)	Specific Gravity (times heavier or lighter than water)	Base Properties	Applications	Biodegradability
<b>THERMOPLASTICS</b>						
<b>Acrylonitrile- Butadiene-Styrene</b> (1.00-1.35)	55-110	33-51	1.01-1.20	Good resistance to mild acids and alkalis. Chemical and solvent resistance.	Durable household goods, auto accessories, synthetic rubber blends.	Very Low
<b>Acetals</b> (0.70-0.90)	90-100	61-69	1.41-1.42	Excellent resistance to most organic solvents. Properties not satisfactory for use with strong acids and alkalis. One of the strongest thermoplastics.	Automobile and other machine parts. Construction and other composites. High-temperature applications up to 220°C possible with proper additives.	Very Low
<b>Acrylics</b> (0.70-1.00)	55-110	39-76	1.11-1.19	Clear and noncrystalline. Superior dielectric strength. Excellent optical properties, lightweight, flexible & moldable. Trade name Plexiglas.	Camera, scientific instrument, and spectacle lenses. High-voltage line spacer. Resins used in textile finishes and in paints and coatings.	Low
<b>Polyethylenes (Low-Density)</b> (0.30-0.39)	80-100	6-17	0.91-0.93	Lowest-cost plastic commercially available. Mechanical properties are generally poor above 50°C.	Packaging films and sheets, linings, coatings. Lighter than water.	Very Low
<b>Polyethylenes (High-Density)</b> (0.29-0.34)	80-120	20-37	0.95-0.96	Excellent chemical and moisture resistance, poor mechanical/tensile strength. Carbon-filled grades are resistant to sunlight and weathering.	Containers, wire cable insulation, pipe coatings, molds, toys, housewares. Lighter than water.	Very Low
<b>Polyethylene Terephthalate</b> (0.62-0.65)	80-140	55-72	1.31-1.37	Low heat, chemical, and flame resistance; good mechanical strength.	Containers, bottles, packaging materials, appliance components, and film materials.	Low
<b>Polypropylenes</b> (0.31-0.39)	105-150	33-38	0.90-0.91	Colorless and odorless, low-density. Good heat resistance. Unbreakable. Chemical resistance and electrical properties. Good surface hardness.	Housewares, medical equipment that can be sterilized. Appliances, toys, electronic components, tubing and pipe, fibers and coatings.	Very Low

Table 23 (continued)

Plastic Type (price: \$/lb)	Maximum-Use Temperature by Grade (°C)	Mechanical or Tensile Strength (MPa)	Specific Gravity (times heavier or lighter than water)	Basic Properties	Applications	Biodegradability
Polystyrene (0.42-0.55)	65-80	41-50	1.04-1.07	Low-cost, easy to process. Good resistance to acids, alkalis, salts.	Commonly foamed with water for insulation, pipes, thin-walled containers. Appliances, rubber, automotive instruments and panels.	Low
Polyvinyl Chloride (0.23-0.62)	100-110	33-55	1.05-1.20	Excellent physical properties, chemical resistance, ease of processing, relatively low cost.	Pipe and tubing, pipe fittings, adhesives, raincoats, shoes, building panels.	Very Low
<b>THERMOSETS</b>						
Alkyds (0.65-0.74)	150-230	21-66	1.30-2.15	Excellent thermal and electrical properties. Range of flexibility. Chemical resistance.	Electrical insulation and electronic components. Glass-reinforced products. Paints and coatings.	Very Low
Epoxies (1.28-1.41)	120-290	28-90	1.06-1.40	Excellent chemical properties. Good adhesion, strong and tough, low cure shrinkage, Heat resistance.	Laminates, adhesives, flooring, linings, propellers, surface coatings, filament-wound structures.	Very Low
Phenolics (0.56-0.89)	120-290	21-62	1.34-1.45	Good strength, heat stability, impact resistance, chemical and water resistance, machinability.	Impregnating resins, brake linings, rubber resins, electrical components, structural boards, glues, molds.	Very Low
Polyesters (0.68-0.90)	150-180	28-138	1.70-2.30	Extreme versatility in processing. Good heat, chemical, and flame resistance; mechanical strength.	Construction, laminates, skis, boats, bottles, aircraft components, coatings.	Low
Silicones (5.81-6.40)	300-320	28-45	1.70-2.80	Good thermal/oxidative stability, flexible, excellent electrical properties, and general inertness.	Mold release agents, rubbers, laminates, anti-foaming agents, water-resistant uses, encapsulating resin for various chemicals and fertilizers.	Very Low
Polyurethanes (1.68-2.43)	90-95	31-58	1.10-1.50	Excellent copolymer properties. Mostly used in blends with other thermoplastics and rubbers.	Rubber blends both natural and synthetic. Urethane resins for paints and surface coatings.	Very Low



Table 23 (continued)

Plastic Type (price: \$/lb)	Maximum-Use Temperature by Grade (°C)	Mechanical or Tensile Strength (MPa)	Specific Gravity (films heavier or lighter than water)	Basic Properties	Applications	Biodegradability
<b>COPOLYMERS WITH BIOCOMPONENTS</b>						
<b>Cellulosics</b> (acetate, butyrate, nitrate, propionate) (1.62-2.07)	45-105	21-55	1.10-1.40	Tough, flexible, high impact strength, high dielectric strength, low thermal conductivity. High surface luster.	Lacquers, hot melt coatings, textile and paper finishes, thickening agents, magnetic tapes, packaging, and pipes.	Low
<b>Melamine</b> (cellulose-filled) (0.49-0.62)	110-120	34-62	1.45-1.52	Excellent heat, solvent, and chemical resistance. Good surface hardness. Resistance to discoloration.	Laminating resins, paper coating, textile treatments, plywood.	Low
<b>Starch-PVC Films</b> (50% starch)	80-110	20-25	1.20-1.40	Strong when wet. Moderate lifespan when exposed to light. Photodegra- dation. Good biodegradability.	Degradable agricultural mulch. Packaging films. Low-strength articles.	Moderate
<b>LDPE-Starch-EAA</b> (40-60% starch)	110-145	10-25	1.00-1.35	Sufficient strength, flexibility, water resistance, and heat sealability. Low cost.	Mulch and packaging films.	Moderate
<b>ADM Polyclean-C</b> <b>Resin System</b> (55-65% starch) (2.00-2.50)	60-100	15-25	1.00-1.20	Strength similar to unfilled polymer. Embrittlement in compost. Good biodegradation profile. Photodegradable.	Films for packaging. LDPE mix bags. Packaging materials.	Moderate
<b>Uni-Star</b> <b>Starch Graft</b> (0.85-1.00)	80-100	15-25	1.00-1.20	Starch graft copolymerization results in more consistent material. Variable starch content determines rate of biodegradation.	Loosefill packaging. Disposable cutlery. Foams, injection-molded products, films.	Variable
<b>BIOPOLYMERS</b>						
<b>NOVON Reels</b> (starch-based) (1.50-3.00)	170-200	—	1.40-1.45	Water-soluble, suitable for injection molding.	Pharmaceutical plastics (capsules). Packaging materials like "peanuts." Golf tees. Candle stands. Cutlery for fast-food restaurants.	Very High
<b>ICI's PHBV Reels</b> (sugar-based) (8.00-10.00)	110-180	—	1.25	Good shelf stability, suitable for injection and blow molding. Good soil microbial degradation.	Shampoo bottles, disposable razors injection molded articles.	High

Table 23 (continued)

Plastic Type (price: \$/lb)	Maximum-Use Temperature by Grade (°C)	Mechanical or Tensile Strength (MPa)	Specific Gravity (limes heavier or lighter than water)	Basic Properties	Applications	Biodegradability
Battelle's Lactic Acid Polymers (Polylactic acid) (1.00-2.00)	120-170	—	1.20-1.40	Excellent molding properties. Copolymerization with glycolic acid and other plant-based polymers.	Commodity plastics for molding applications. Controlled release of agrichemicals and drugs.	Very High
FLEXEL's Cellulose (cellulose film forming resin) (2.40-3.60)	60-100	—	1.10-1.30	Excellent film-forming properties. Superior degradability. Low cost. Good mechanical strength. Flexibility.	Sandwich bags. Packaging films. Uncoated clear films.	High
Mater-Bi Novamont/ Ferruzzi (1.60-2.50)	150-200	—	1.32-1.45	The polymer contains at least 60% starch and other biodegradable materials. Excellent molding prop- erties and film extrusion to 0.36 mm.	Disposable diapers, high heat aging resistant films. Moldable article applications.	High
Ecochem's Polylactide Reelins (2.00-2.50)	130-150	—	1.20-1.40	Recyclable polylactide. Completely compostable. Good extrusion prop- erties and film formation.	Packaging film and sheets.	High
Cargill's Polylactic Acid Reelins (1.00-3.00)	—	—	—	Excellent coating properties. Not soluble in water. Compostable.	Resins in paints and other surface coating products. Liquid-contact applications such as bottles, food cans.	High

SOURCES: *Chemical Engineer's Handbook* (New York: McGraw-Hill, 1984); *Shreve's Chemical Process Industries* (New York: McGraw-Hill, 1984); *Emerging Technologies for Materials and Chemicals from Biomass* (Washington, D.C.: American Chemical Society, 1992); *Chemical Marketing Reporter*, March 9, 1992; *Modern Plastics*, February 1992; Warner-Lambert Company, Morris Plains, N.J., 1992; ICI Americas, Wilmington, Del., 1992; Flexel, Inc., Atlanta, Ga., 1992.

Conventional petrochemical thermoplastics have the highest mechanical strength; biopolymers, the lowest. Technically, however, it is now possible, by incorporating the right kind and quantity of additives, to formulate products from biopolymers which have strength equal to that of thermoplastics. Uni-Star, a Minnesota-based company, has developed several grades of hybrid polymers by mixing petrochemical resins with biocomponents. These hybrids exhibit properties ranging between those of thermoplastics and biopolymers.

The specific gravity of a plastic is the ratio of the weight of a given volume of plastic to the weight of the same volume of water. If a plastic's specific gravity is higher than 1.0, it is heavier than water; if the specific gravity is lower than 1.0, it is lighter than water. In general, low-specific-gravity resins, such as LDPE and polypropylene (PP), are more suitable for film formation and thus have better value for packaging. High-specific-gravity resins, characteristic of most biopolymers, are more suitable for molding processes producing consumer articles and mechanical parts.

High-specific-gravity biopolymers can incorporate a higher percentage of additives than can low-specific-gravity, petroleum-based thermoplastics, thus reducing overall costs, since additives are generally cheaper than base polymers. In addition, a given plastic application requires smaller quantities of material in its formulation if it is made with a high-specific-gravity biopolymer rather than a low-specific-gravity petroleum-derived polymer. This ability to use less material partially offsets the cost differential between biopolymers and regular plastics. Table 23 shows that this differential amounts to a two-to-five times higher price for biopolymers.

### Uses of Plant Matter in Plastics

The use of plant matter in plastics manufacture is well established. Plant matter is the primary raw material for the production of some plastics and polymeric resins; plant matter-derived additives and biodegradable components are also in use. Plant matter use in the polymer industry has come a long way since the early 1980s when it was demonstrated that incorporating starch into low-density polyethylene film enhances its

biodegradability. Today, several grades of plastics that incorporate some form of plant matter — such as starch, cellulose, lignin, plant or vegetable oils — are commercially available. In addition, several grades of plastics that are derived primarily from plant matter have been introduced to the U.S. market.

### Plasticizers

Plant-derived materials may be used as plasticizers — compounds added to plastic resins to improve their workability during fabrication or molding, to improve their properties, or to develop new properties not present in the base resin. Plasticizers reduce viscosity and make shaping and forming easier. Polyvinyl chloride (PVC) is very brittle in its ground resin state; only when a plasticizer is added does it become flexible enough to be molded.

Plasticizers comprise about 3 percent of all raw materials used in making plastics. Of the 770,000 tons of plasticizers produced in the U.S. in 1990,

**Table 24. Plasticizer Production from Plant Oils and Petrochemical Feedstocks in the U.S.**

Category		1990 Production (tons)
PLANT MATTER-BASED	Epoxidized Linseed Oil	3,000
	Epoxidized Soybean Oil	50,000
	Other Epoxidized Esters	7,000
	Isopropylmyristate	2,000
	Oleic Acid Esters	6,000
	Palmitic Acid Esters	3,000
	Sebacic Acid Esters	3,000
	Stearic Acid Esters	4,000
	Other Acrylic Esters	37,000
	<b>Total Plant-Based Plasticizers</b>	<b>115,000</b>
<b>Petrochemical-Based Plasticizers</b>		<b>662,000</b>
<b>Total Plasticizers</b>		<b>777,000</b>

SOURCES: J.H. Pryde and J.A. Rothfus, "Industrial and Nonfood Uses of Vegetable Oils" in *Oil Crops of the World*, ed. G. Robbelen, et al. (New York: McGraw-Hill, 1990); Missouri Soybean Association, Jefferson City, Missouri, October, 1991; U.S. Department of Commerce, Washington D.C.

115,000 tons, or 15 percent, were derived from plant matter. Most of the plant matter sources were vegetable oils. See Table 24, page 50. Soybean oil accounted for 50,000 tons, while acrylic esters, which are derived from a variety of plant sources (including wood extractives and coconut oil), accounted for 37,000 tons.

The current value of the U.S. plasticizer market is \$550 million.<sup>50</sup> Plasticizers cost anywhere from \$0.50 per pound to \$3.00 per pound, depending on their properties. Plant matter-based plasticizers are similar in properties to higher-end petrochemical-derived plasticizers and thus tend to compete better at the upper end of the price market.

Prices of plant-based plasticizers may come down, and, as a consequence, their market share may increase in the near future. Research into the use of soy oil to make substitutes for diesel fuel has brought down the cost of the esterification process considerably. That process, if commercialized, has the potential to produce plant-based plasticizers cheaply.<sup>51</sup>

### Copolymers with Bio-components

Plastics that are a mixture of petrochemical-derived and plant matter-derived polymers were first introduced in the 1980s. The first copolymers were thermoplastics containing about 6-10 percent starch; they were used in packaging films that exhibited enhanced biodegradability.

Not only the quantity but also the quality of the starch used in the copolymer determines the end resin's properties, application potential, and cost. Refined starch is expensive – over 82 cents a pound – compared to regular-grade starch, which costs only 7 cents a pound. However, since biodegradability depends on the starch content of the resin, plastics manufacturers are planning to produce resins that will incorporate as much as 40 to 90 percent starch – depending upon grade – while keeping the costs down.

Currently, biodegradable plastics command about 5 percent of the entire polymer plastics and resins market in the United States. This percentage is expected to double by early 1995. Several graft copolymers have been developed since the mid-1980s; however, none of these have achieved commercial status. The list includes starch-g-polystyrene, starch-g-PAN (polyacrylonitrile), and several others. Uni-Star's starch-g-PMA (polymethylacrylate) class of grafted resins seems to have broken

the cost barrier that almost all classes of grafted copolymers face. The challenge has been to incorporate higher percentages of cheaper-grade starch with environmentally benign petroleum-based monomers without compromising on the properties required for injection molding and film production – at a cost competitive with those of thermoplastic resins.

Starch-based filler products now on the market include Archer Daniels Midland's (ADM's) Polyclean, which is used for trash bags; it is priced 10-15 percent higher than conventional LDPE film. Polyethylene, when filled with this granular starch-and-catalyst additive, will oxidize (degrade) more rapidly than standard polyethylene film. Uni-Star, a Blue Earth, Minnesota-based company is currently producing a graft polymer resin from a combination of petroleum- and starch-based components. A thermoplastic resin in terms of properties, it has been for a variety of product categories: foams, injection moldable products, and packaging films. The resin itself is produced in several different grades depending upon the properties desired and the application needed. The foam grade resin, which does not require high tensile or mechanical strength, contains higher quantities of starch and a lower percentage of petrochemical monomers such as vinyl acetates and methyl acrylates. High-strength grades, especially injection moldable grades, incorporate a higher percentage of petrochemical monomers. Currently, these copolymers are used to make several products including packaging peanuts, cosmetic and personal hygiene bottles, medical packaging films, disposable and degradable cutlery, and shotgun cartridge wads.

Researchers at Michigan Biotechnology Institute in East Lansing and at Italy's Montedison Company have developed 50 percent starch-filled plastics. Starch- and cellulose-based polymers in these plastics act as "compatibilizers," blending starch acetate and cellulose acetate with petrochemical-based polymers. The resulting material has properties similar to those of polyethylene. Although it is not yet produced commercially, the price of lab-scale production is reported as "only slightly higher than [that of] polyethylene."<sup>52</sup>

In general, starch-based grafted copolymers cost about 50-55 percent more than conventional petrochemical-based plastic resins – approximately 85 cents per pound for grafted resins versus 55 cents per pound for conventional resins. Uni-Star is currently selling its starch-g-PMA resin for 70 cents per pound and expects that it will become competitive with

conventional resins when it can be produced on a scale of 100 million pounds a year. According to Don Fisk, president of Uni-Star, the economies-of-scale and the cost of refined starch play important roles in the production of this resin. The company's highly refined grade of copolymer, which contains as much as 90 percent starch, currently costs about \$2.00 per pound.

There is some dispute as to whether copolymers with a biocomponent decompose completely, and under what conditions decomposition takes place. There is also disagreement as to whether recycling these products would result in inferior materials. The biopolymer industry claims that the plant-based components of these plastics would disintegrate quickly during the recycling process, leaving petrochemical-based resin available for recycling.

## Bioplastics

Market estimates for biodegradable polymers derived from plant matter are on the order of 1.5 million tons annually.<sup>53</sup> Currently, there are at least ten large companies in the United States and elsewhere that are producing plant matter-based plastics and resins. The present capacity of U.S. biopolymer production plants is 175,000 tons, shared by eight companies. Leading biopolymer producers include Air Products & Chemicals, Allentown, Pennsylvania; Novon Products Division of the Warner Lambert Company, Morris Plains, New Jersey; ICI, Wilmington, Delaware; Union Carbide, Danbury, Connecticut; Novamont/Ferruzzi Group, New York; and Cargill, Minneapolis, Minnesota.

## NOVON

NOVON is the trademark of a new family of specialty polymer resins derived primarily from corn and potato starch. Warner-Lambert scientists in Switzerland discovered these resins in the early 1980s when they were researching injection-moldable materials that could be substituted for gelatin in pharmaceutical capsules. In the U.S., the Warner-Lambert Company formed a group called the Novon Group in Morris Plains, New Jersey, which has developed several marketable grades of this resin during the past 10 years.

NOVON is a commercially produced biopolymer that uses starch as the base resin. Starch-based polymers had been made before, but scientists had been discouraged in efforts to transform them into

plastics because the heat required for the process burned away the water in the starch, turning it into dust-like particles. The Warner-Lambert process uses a pressurized heating system (like a pressure cooker) to "destructure" the starch without eliminating water from the molecule, thus forming the starch into a malleable substance that can be molded and extruded like other plastics.

Starch used for the manufacture of NOVON is refined so that it is free of proteins and contains starch molecules of a particular weight or size, resulting in a resin that exhibits exactly defined properties. The starch polymer is then blended with 5-25 percent additives to impart the desired flexibility, strength, and color. These additives include biodegradable, nonstarch resins, as well as biomaterials such as gums and proteins. Like traditional thermoplastics, minerals such as calcium carbonate or titanium dioxide can also be included. In addition, pigments can be added to modify NOVON's natural off-white color.

NOVON offers moldability and performance comparable to those of common plastics, coupled with the decomposition characteristics of paper.<sup>54</sup> The resin has been tested for use in a wide range of products, including food packaging, cutlery, packaging loosefill, consumer health products such as tampon applicators, and medical devices. NOVON polymers decompose readily in both aerobic and anaerobic processes. Under aerobic conditions, bacteria break the resin down into water and carbon dioxide. Under anaerobic conditions, methane and water are the by-products.

NOVON resin currently sells for \$1.50 to \$3.00 per pound, depending on the grade and application — three to four times more than its competitors, polyethylene and polystyrene. No cost reduction is expected in the near future.<sup>55</sup>

The first full-scale commercial plant to produce NOVON, with a capacity of 100 million pounds of resin per year, came on line in Rockford, Illinois in January, 1992. It produces NOVON 2020, a foam extrusion grade resin, and NOVON 3001, an injection molding grade resin. Warner-Lambert claims to have developed 20 other experimental grades of NOVON that will be introduced to the market by late 1993.<sup>56</sup>

The Cincinnati, Ohio-based company Storopack, Inc. uses NOVON 2020 to manufacture a water-dispersible loosefill, marketed under the trade name Renature®, that can replace polystyrene "peanuts." Water is used to foam the hollow tube-shaped

NOVON peanuts. Market acceptance of Renature® has been good, even though it costs about twice as much as the polystyrene product. Storopack plans to produce Renature® in all 18 of its manufacturing plants.

NOVON 3001 injection molding grade resins are used to produce higher-strength plastic products, such as golf tees and tampon applicators. The Terraform Company in Dalton, Massachusetts is now producing NOVON golf tees under the name TERRAFORM®; these tees cost twice as much as common wood tees. Biku-Form in Tenningham, Germany manufactures a votive candle cup from NOVON 3001. And Capsugel, a sister division of NOVON is producing capsules under the trade name CAPILL™; these are currently being evaluated by 15 major pharmaceutical companies.

## PHBV

PHBV, or polyhydroxybutyrate-hydroxyvalerate, is a new family of biodegradable thermoplastics made by bacterial fermentation of sugars. Imperial Chemical Industries (ICI), a British company with an American subsidiary, ICI Americas, Inc., developed PHBV in 1990. It is marketed worldwide under the trade name BIOPOL™.

Bacterial plastics were first discovered in 1925. When starved of nitrogen essential to their growth, some bacteria produce minute amounts of plastic, just as bears add a layer of fat before winter. In 1989 researchers at James Madison University in Harrisonburg, Virginia discovered that *Alcaligenes eutrophus* bacteria could produce plastics. The bacterium has been genetically altered to boost its yield. University of Massachusetts researchers recently engineered a superstrain of bacteria that contain up to 75 percent plastic by weight.<sup>57</sup>

The fermentation of sugars to produce polyhydroxybutyrate (PHB) has been known for decades, but PHB was very brittle. When hydroxyvalerate (HV) is added to PHB, the resulting material, PHBV, is flexible and moldable.

PHBV is made entirely from sugars and organic acids derived from cornstarch or potatoes. The production technology is similar to that used for the bacterial fermentation of corn to ethanol. Bacterial strains convert the feed materials into PHBV resin, accumulating the resin as an energy source during the fermentation process. When bacterial cells have accumulated over 75 percent of their body weight as

PHBV, the cells are burst open by steaming and the resin is collected.

Different grades of PHBV have properties similar to those of polypropylene (PP) or polyethylene (PE). It has an extended shelf life compared to starch-based plastic bottles, and is moisture-resistant – a highly regarded quality in a biodegradable polymer, and one that makes it possible to use PHBV in liquid packaging.

PHBV is available in different grades, based on hydroxyvalerate (HV) content. PHB without HV is a relatively stiff, brittle material; ductility improves with increasing HV content to an upper limit of 25 percent HV, which yields a tough, flexible polymer. Other properties can be modified with the use of plasticizers, fillers, or pigments (for reinforcement, impact modification, color).<sup>58</sup>

ICI's Billingham, England pilot plant has produced PHBV in small quantities since 1988, supplying it either as a moldable-grade powder or in granular form. Wella, an international hair care company, was the first to make a product from this material. It began selling "Sanara" brand shampoo in the BIOPOL bottles in Germany in May 1990. Three Japanese companies are also making PHBV molded bottles for similar cosmetic products. ICI expects the first BIOPOL bottles to appear in the U.S. market by the end of 1992.

The ICI plant output is currently about 300 metric tons per year (330 tons). Client companies that have product agreements with ICI pay \$8.00-\$10.00 per pound of the resin.<sup>59</sup> ICI officials expect the price to drop to \$4.00 per pound by the mid 1990s.<sup>60</sup> Even at these lower prices, PHBV would be considerably more expensive than polypropylene, which sells for \$0.50-\$0.60 per pound.

The PHBV process uses refined glucose sugar as its raw material. Since sugar prices are consistently lower in the U.S. than in the U.K. – 15-20 cents per pound as compared to more than 30 cents per pound – PHBV should cost less if produced in the U.S.

## Lactic Acid-Based Plastics

Scientists at Battelle Memorial Institute and Argonne National Laboratories are developing lactic acid-based plastics from agricultural and dairy processing byproducts such as potato and cheese whey wastes. First, the carbohydrates in these materials are processed to form glucose; the glucose is then processed into lactic acid through bacterial

fermentation; finally, the lactic acid is polymerized into plastic sheets.

Polymerization of lactic acid into poly(lactic) acid was first studied 50 years ago. The very high cost of the process restricted the first commercial application to the medical field. Poly(lactic) acid polymers were used in prosthetic devices and in biocompatible, biodegradable sutures, which could cost as much as \$250 per pound.

Battelle combines poly(lactic) acid with glycolic acid to make a plastic called caprolactone, which has potential as a substitute for commercial thermoplastics. Battelle expects to reduce the cost of lactic acid-based plastics to equal that of bulk polyethylene or bulk polystyrene within two years. Low-density polyethylene (LDPE) costs 35-39 cents per pound; polystyrene costs 42-46 cents per pound.<sup>61</sup> Researchers are working on direct routes for converting starch to lactic acid, employing genetically modified microbial strains; such a process would eliminate the intermediate step of converting starch to glucose, permitting significant cost reductions.<sup>62</sup>

Argonne National Laboratories owns the process rights under the name BioLac Process, and has licensed the key step for commercialization to Kyowa Hakko U.S.A. Inc., the U.S. subsidiary of the Japanese fermentation products company Kyowa Hakko. Kyowa Hakko plans to carry out further scale-up

research and development before building a full-scale plant. The company plans to target products such as compost bags; coatings for paper, seed, pesticides, and fertilizers; and agricultural mulch films for timed release of pesticides and fertilizers.

## Intermediate and Specialty Chemicals (100 million tons)

Commodity chemicals have large markets and are usually low in cost, selling for 20-80 cents per pound. Specialty chemicals tend to have smaller markets and command prices over \$2.00 per pound. The U.S. specialty chemical market was \$56 billion in 1990.<sup>63</sup>

### Biosources

#### Vegetable Oils

More than 20 oilseed crops are grown in the U.S., with soybeans generating a larger quantity of oil than any other single crop. About 1 million tons of vegetable oil are used as feedstocks for industrial products such as plastics, surfactants, adhesives, and lubricants; prices vary from 16 cents a pound for sunflower oil to almost \$5.00 a pound for jojoba oil. See Tables 25 and 26.

Vegetable oils have made significant inroads into some chemical markets. As Table 27, page 56 indicates, 20 percent of synthetic lubricants and 35 percent of all surfactants are now made from vegetable oil. In other applications, however, organic minerals still dominate. Of the medium-chain fatty alcohols used in detergents, 80 percent are made from petroleum or natural gas feedstocks, and less than 20 percent from vegetable oils.

Table 25. Industrial Applications Breakdown of Soybean Oil Consumption in the U.S. (in tons)

Category (Example Industry)	1990 Utilization
Drying Oil (Surface Coating)	80,000
Epoxidized Soy Oil (Polymer Resin)	40,000
Dispersion Agent (Pesticide/Agrichemical)	6,000
Oleochemicals (Rubber/Petrochemical)	5,200
Dust Control Agent (Grain Processing)	2,500
Soy Oil Inks (Printing)	1,000
Other Nonfood Uses <sup>1</sup>	15,300
<b>Total Industrial Use of Soy Oil</b>	<b>150,000</b>

<sup>1</sup> Other nonfood industrial products derived from soybean oil include oil recovery agents, mono/diglycerides for detergents, dimer acids, fuel-grade esters, and fatty amines/amides.

SOURCE: *Oil Crops of the World*, ed. G. Robbelen et. al. (New York: McGraw-Hill, 1990).

**Table 26. Yields and Prices of Potential and Conventional Oil Crop Raw Materials for Fuels and Industrial Products Manufacturing in the U.S.**

	Crop Yield (pounds per acre)	Oil Yield (pounds per acre)	Oil Price (dollars per pound)	Important Product Categories
<b>Bladderpod</b>	2,000	780	—	Plastics, Fatty Acids, Surfactants
<b>Buffalo Gourd</b>	2,760	1,076	—	Epoxy Fatty Acids, Resins, Paints, Adhesives
<b>Castor</b>	892	446	0.39	Dyes, Paints and Varnishes, Polymer Resins, Cosmetics, Biopesticides
<b>Coconut</b>	2,230	1,605	0.23	Polymer Resins, Cosmetics, Soap, Pharmaceuticals, Plasticizers, Lubricants
<b>Corn</b>	6,800	1,360	0.31	Ethanol, Fermentation Products, Resins
<b>Crambe</b>	1,500	600	0.73	Paints, Industrial Nylons, Lubricants, Plastics, Foam Suppressants, Adhesives
<b>Cuphea</b>	2,000	800	—	Surfactants, Lubricants, Glycerine, Biochemicals
<b>Euphorbia</b>	1,784	892	—	Surfactants, Lubricants, Paints, Cosmetics
<b>Honesty (Money Plant)</b>	2,000	800	0.72	Plastics, Foam Suppressants, Lubricants, Cosmetics, Industrial Nylon
<b>Joboba</b>	3,000	1,650	4.80	Cosmetics, Pharmaceuticals, Plastics Additives, Varnishes, Adhesives, and Inks
<b>Lesquerella</b>	1,500	375	—	Paints, Lubricants, Hydraulic Fluids, Cosmetics
<b>Linseed</b>	1,032	412	0.25	Drying Oils, Paints and Varnishes, Inks, Polymer Resins, Plasticizers
<b>Meadowfoam (Limnanthes)</b>	2,230	645	—	Cosmetics, Liquid Wax, Lubricants, Rubber, Higher Fatty Acids (C20-C22)
<b>Palm Oil</b>	—	2,540	0.17	Fermentation Products, Soap, Wax, Tin Plating, Fuel Processing, Polymers
<b>Rapeseed</b>	2,000	800	0.64	Plastics, Foam Suppressants, Lubricants, Cosmetics, Adhesives
<b>Safflower</b>	1,338	562	0.39	Paints, Varnishes, Fatty Acids, Adhesives
<b>Soybean</b>	1,900	380	0.20	Inks, Paint Solvents, Resins, Plasticizers, Adhesives, Lubricants, Pharmaceuticals
<b>Stokes Aster</b>	1,780	783	—	Plastic Resins, Plasticizers, Paints
<b>Sunflower</b>	1,160	835	0.16	Plastic Resins, Plasticizers, Surfactants, Fuel Additives, Cosmetics, Agrichemicals
<b>Vermonia</b>	1,500	375	0.80	Plastics, Alkyd Paints, Epoxy Fatty Acids

SOURCE: Office of Technology Assessment, *Agricultural Commodities as Industrial Raw Materials*, Washington, DC: 1991; *Oil Crops of the World*, ed. G. Robbelen et al. (New York: McGraw-Hill Co., 1990); *Chemical Marketing Reporter*, March 9, 1992.



## Tree Oils

Oils obtained from trees can also serve as feedstocks for industrial products. Tall oil, extracted from the black liquor residue generated from pine woods in kraft paper mill digesters, was initially used in the manufacture of turpentine. Current applications include alkyd resins, coatings, soaps, detergents, cosmetics, resins for printer's ink, and waterproofing. (Twenty-five percent of all plant-derived fatty acids used in the coatings industry come from tall oil.)

Since the disposal of tall oil causes considerable water pollution, environmental regulations passed in the early 1980s mandated extraction of tall oil as an integral part of pulp and paper processing. By 1982 all U.S. kraft mills combined had a tall oil fractionating capacity of about 860,000 tons per year.<sup>64</sup> In 1990, 550,000 tons of tall oil were recovered from U.S. kraft mills.<sup>65</sup> The cost of fractionating sodium tall oil salts into tall oils has declined over the past ten years from 22-25 cents per pound to 18 cents per pound. However, this cost may increase in the near future, since less pine is being used in U.S. paperboard manufacture than formerly, and supplies of tall oil are expected to diminish accordingly.

## Lignin

Lignin, a bridge substance that holds cellulose and hemicellulose together, constitutes 15-20 percent of all plants. About half a ton of lignin is

generated for every ton of wood pulp produced. In 1990 alone, about 63 million tons of pulp were produced in the U.S. paper industry, yielding 35 million tons of lignin as a byproduct. Only 2 percent of the lignin was separated; the rest was burned. Less than 500,000 tons of lignin were sold for such applications as binders, dispersants, and drilling muds.

## CHEMICALS FROM PLANT MATTER

### Surfactants

(3.5 million tons)

Surfactants are compounds that change the surface tension of materials. As ingredients in soaps and detergents, they increase the wetting ability of water so that it can more easily penetrate fabrics and interact with dirt particles; in paints, they improve the adhesion of paint particles to the surface. Surfactants were first introduced by the soaps and detergents industry, which manufactured them for its products; as more uses were discovered for surfactants, an independent industry arose. Of the 3.5 million tons of surfactants produced in the U.S. in 1990 (up from 2 million tons in 1980) at a value of \$12.8 billion,<sup>66</sup> 26 percent was used in soaps and detergents; 20 percent in dishwashing liquids, shampoos, other cleaning agents, and toiletries; and about 42 percent in industrial processes.<sup>67</sup>

Surfactants have been derived either from petrochemical feedstocks or from vegetable oils. Many different plant-derived oils, such as soybean, coconut, palm, and many other tropical oils, can be used to make surfactants. Coconut oil has become a favorite because its price plummeted from 60 cents per pound in 1984 to 17 cents per pound in 1986 after the FDA banned its use in confectionery, citing studies showing adverse health effects due to the oil's high cholesterol content. Currently, prices of both coconut and palm oils range from 14 to 17 cents per pound; ethylene, a major petroleum-based source of surfactants, sells for 20 to 22 cents per pound. See Figure 17.<sup>68</sup>

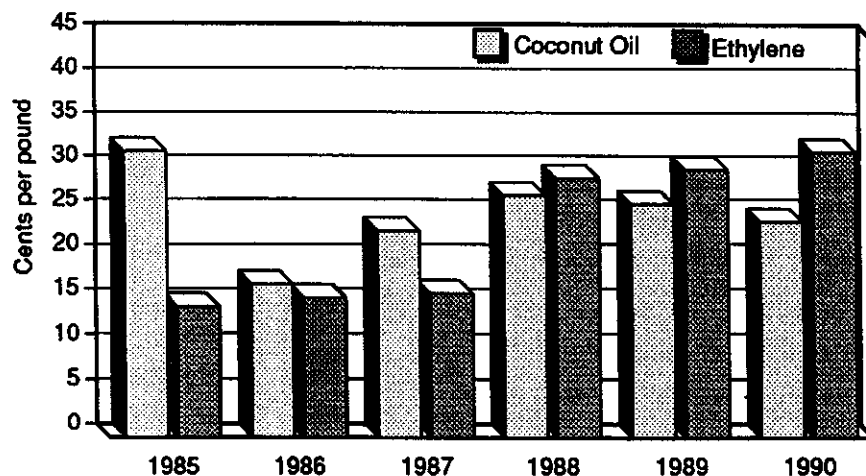
Environmental concerns may increase the market share of plant-based surfactants in the near future. While surfactants have long been considered environmentally neutral prod-

**Table 27. Estimated Vegetable Oil Contributions to Specialty and Intermediate Chemicals Production in the U.S.**

	Percent from Vegetable Oil
Surfactants (Food + Industrial)	35
Synthetic Lubricants	20
Plastic Additives	15
Agrichemicals	10
Engineering Thermoplastics	2
Adhesives	1

SOURCE: E.H. Pryde and J.A. Rothfus, "Industrial and Nonfood Uses of Vegetable Oils," in *Oil Crops of the World*, eds. G. Röbbelen, R.K. Downey, and A. Ashri (New York: McGraw-Hill Book Co., 1990), 87-117.

**Figure 17. Price Comparison Between Coconut Oil and Ethylene: Raw Materials for the Manufacture of Surfactants**



SOURCE: *Chemical Week*, vol. 146, no. 4, January 31, 1990.

ucts, recent studies have found traces of carcinogens – nitrosamines, dioxanes, and ethylene oxides – in some surfactants derived from petrochemical feedstocks.<sup>69</sup>

In March 1992, Henkel Corporation of Gulph, Pennsylvania, a leading surfactant manufacturer, announced plans to produce a new line of plant-based surfactants for the soaps and detergents industry. These products will be made from corn, coconut, and palm kernel oils, and will be marketed under the trade name Plantaren. Henkel's Cincinnati plant will produce 27,500 tons of Plantaren per year.

Environmental concerns have also spurred the replacement of petrochemical-derived branched-chain alcohols in detergents with straight-chain fatty alcohols derived from vegetable oils. Straight-chain alcohols decompose more easily than branched-chain compounds.

### **Fatty Acids (2.5 million tons)**

All fats and oils, including vegetable oil, rosin oils from wood, and animal tallow, are made up of two components: fatty acids and glycerine. Originally used only in the manufacture of soaps and detergents, fatty acids now serve as feedstocks for producing three important classes of intermediate chemicals – esters, ethoxylates, and amides – which

are used in the manufacture of specialized surfactants, cosmetics, alkyd resins, nylon-6, plasticizers, lubricants and greases, paper, and pharmaceuticals. The market for fatty acids more than doubled during the 1980s, from less than 1 million tons in 1978 to 2.5 million tons in 1990. See Table 28, page 58. Currently, 35 percent of all surfactants produced in the U.S. are made from natural fatty acids.

Sixty percent of all fatty acids currently produced in the U.S. are derived from petrochemicals; the remaining 40 percent are derived from vegetable oils and other natural oils – up from 10 percent in 1978. (One million tons of vegetable oils are used annually in fatty acid production.)<sup>70</sup>

Since the early 1980s, it has been cheaper to produce fatty acids from natural oils than from petrochemicals. As Table 29, page 59 shows, the crossover was wholly attributable to increases and fluctuations in the costs of petrochemical feedstocks as well as to reductions in the costs of vegetable oils. Processing costs remained stable for production of fatty acids from vegetable oils and actually came down for production from petrochemicals.

### **Acetic Acid**

About 24 large pulp and paper mills in the U.S. use the sulfite pulping process. These mills convert

only 50 percent of their wood to pulp. The remaining 50 percent, consisting mainly of hemicellulose and lignin, is dissolved in the cooking liquor by the end of the pulping process. This liquor, called 'spent liquor' or 'sulfite liquor,' contains a mixture of organic acids, 5- and 6-carbon sugars, methanol, furfural, lignin compounds, and some inorganic compounds used in the cooking process. Since the 1960s, this liquor has been evaporated to a combustible consistency and burned. The energy from burning is used in the process; the inorganic compounds are recovered and reused in the cooking liquor; the condensates from evaporation, which contain low concentrations of organic acids (primarily acetic acid), are generally discharged untreated, or are treated to reduce biochemical oxygen demand (BOD), and then discharged.

The lack of cost-effective solvent extraction or membrane separation systems has posed an obstacle to the recovery of acetic acid from sulfite liquors. The Technical Association of the Pulp and Paper Industry in Norcross, Georgia has researched the recovery of acetic acid in the form of organic esters, such as methyl acetate or ethyl acetate, with the aid of activated carbon. Esters have a higher market value than organic acids, and require less energy of vaporization for their removal from dilute solutions. Recovery of acetic acid in the form of organic esters also matches well with market needs, since 35-40 percent of acetic acid is used in the form of acetic anhydride or acetic esters.

A preliminary economic analysis shows that every pound of acetic acid burned contributes 4.5 cents in energy value; every pound of acetic acid recovered in the form of an ester contributes about 20 cents in revenues.

**Table 28. Market Trends of Fatty Acids (C8-C14) Production from Synthetic and Plant Oil Hydrolysis Routes in the U.S. (in millions of tons)**

	1978 Production	1984 Production	1990 Production
Fatty Acids from Petrochemical Route	0.90	1.35	1.50
Fatty Acids from Vegetable Oil Route	0.10	0.45	1.00
Total Fatty Acids U.S. Production	1.0	1.8	2.5

SOURCES: *Oil Crops of the World*, ed. G. Röbbelen et al. (New York: McGraw-Hill 1990); *Chemical Marketing Reporter*, 1990-1991; *Chemical and Engineering News*, vol. 69, no. 49, December 9, 1991.

Some states, such as Washington, require treatment of this stream to reduce BOD. As a consequence, several sulfite mills are considering either recovering acetic acid from the condensates or switching to coal as their boiler fuel and utilizing the entire sulfite stream for organic chemicals recovery. Acetic acid derived from petrochemical feedstocks now has a 1.9 million ton market.<sup>71</sup>

The 61 million tons of waste liquor generated each year could yield over 2.2 million tons of acetic acid from condensates alone, if the spent liquor continued to be burned. However, the low concentrations of acetic acid in the condensate render its recovery unprofitable. The economic potential for acetic acid production is more promising if it is recovered directly from spent liquor.

### Activated Carbon and Phenolics

About 6.5 million tons of activated carbon and 4.0 million tons of phenolic acids were produced in 1990. Of this amount, over 85 percent came from petrochemicals and only 15 percent from plant matter. Activated carbon is primarily derived from natural gas and coal. It is used in making carbon black for inks, in toners for copiers and laser printers, in wastewater treatment systems, and in industrial processes as a catalyst.

Technological advances and environmental regulations have combined to advance the substitution of plant-derived carbon black, activated carbon, and phenols for their petrochemical counterparts. Landfills are unwilling to accept sawdust because of blowing problems. In Missouri, sawmills store sawdust in open piles until they can be disposed. These piles leach tannic acid into the groundwater. Thus, the mills have an incentive either to manufacture a saleable product from the sawdust, or to market it to a company that does.

The Interchem Company of Kansas City established a sawdust pyrolysis plant in Mountain View, Missouri in late 1991. The plant will convert 12,600 tons of sawdust into 1.4 million gallons of fuel oil and 1,890 tons of charcoal per year. Charcoal sells for \$80

**Table 29. Comparative Economic Crossover Analysis for the Production of Fatty Acids (C8–C14) from Synthetic Vs. Plant Oil Hydrolysis**

		Synthetic Petrochemical Route (dollars per pound)	Natural Vegetable Oil Route (dollars per pound)
1978	Raw Materials	0.24	0.37
	Processing Cost	0.14	0.03
	<b>Total Production Cost</b>	<b>0.38</b>	<b>0.40</b>
1982	Raw Materials	0.42	0.30
	Processing Cost	0.14	0.03
	<b>Total Production Cost</b>	<b>0.56</b>	<b>0.33</b>
1988	Raw Materials	0.32	0.29
	Processing Cost	0.12	0.03
	<b>Total Production Cost</b>	<b>0.44</b>	<b>0.32</b>
1992	Raw Materials	0.34	0.30
	Processing Cost	0.12	0.03
	<b>Total Production Cost</b>	<b>0.46</b>	<b>0.33</b>

SOURCES: Organic Chemicals from Biomass, ed. D.L. Wise (Menlo Park, CA: The Benjamin/Cummings Publishing Co., 1983), 407-451; Oil Crops of the World, ed. G. Röbbelen et al. (New York: McGraw-Hill, 1990).

per ton; no. 6 fuel oil, for \$5.00 per million BTUs.<sup>72</sup> Interchem also plans to refine the charcoal into activated carbon.

The destructive distillation of wood by pyrolysis yields oils from which specialty chemicals can be produced; these include acetylene, butanediol, acetic acid, phenols, methyl esters, and ethers. Acetylene black has conductive and antistatic applications, and is used for dry coils and tire curing bags. Butanediol is used in plastics, solvents, and chemicals. A variety of other primary products such as liquid smoke (a meat flavoring agent), carbon black, phenolic neutrals, and a gasoline substitute, can also be produced from pyrolysis oils. Until recently, however, the process for producing phenolics from lignin was expensive, requiring temperatures of 400° C and pressures of 1000 psi.

The National Renewable Energy Laboratory (NREL; Golden, Colorado) achieved a technological breakthrough during the 1980s by developing a fast pyrolysis process using rapid heat transfer, thereby allowing measurably lower reaction pressures. Interchem is commercializing this technology. With

a \$500,000 grant from the New York State Energy Research and Development Authority (NYSERDA), the company is now undertaking R&D and feasibility studies for a fast pyrolysis plant in Oswego, New York, to be built in 1993 at a cost of \$25 million. The plant will process 100,000 tons of wood waste a year, producing 400 gallons per day of pyrolysis oil. This oil can be fractionated into a host of chemicals including fuel oils and phenol. According to NREL's preliminary projections, phenols produced by this fast pyrolysis process will cost 10-27 cents per pound (based on a feedstock cost of \$10-\$40 per dry ton), compared to 42 cents per pound for petrochemical-derived phenols; activated carbon and carbon black from this process will cost less than 30-45 cents per pound, compared to 50 cents to \$1.00 per pound for carbon black derived from natural gas.

In fact, the product stream from fast pyrolysis is so wide ranging that NREL has formed a consortium, including Allied-Signal, Aristech, Plastics Engineering, Interchem, and MRI Ventures, to commercialize pyrolysis chemicals research. Residues of the process will be made into activated carbon; the

remaining gases will be burned to produce electricity to run the plant. Interchem plans to construct a greenhouse on the site, in which carbon dioxide, released during the pyrolysis process, can be used for production of algae, fish, and vegetables.

### **Methyl Aryl Ethers (9.4 million tons)**

Methyl aryl ethers (MAE) produced from lignin can potentially replace the two most important petrochemical-derived solvents: toluene and xylene. In 1990, 5.92 million tons of xylene and 3.5 million tons of toluene, equivalent to a total of 1.5 billion gallons, were produced in the U.S. and used in the manufacture of plastics, paints, lubricants, and many other products.

The cost of producing MAE from lignin was prohibitive a few years ago; now, advances in lignin separation and fast pyrolysis may bring costs down enough to make MAE competitive. Toluene and xylene derived from petrochemicals sell for \$0.65 to \$1.51 per gallon (based on crude oil prices of \$15-\$35 a barrel). A recent pilot-scale study projects the production cost of lignin-derived, phenol-based MAE at \$0.76 to \$1.41 per gallon, depending on the source and cost of lignin feedstock and on the phenol process conversion efficiency.<sup>73</sup>

Industrial fermentation of various plant matter-based raw materials is now used to produce several intermediate and specialty chemicals, including the industrial solvents ethanol, isopropanol, and butanol; the organic acids, acetic, citric, gluconic, itaconic, and lactic; polyols, glycerol, and 1,4-butanediol; the ketone group (e.g., acetone); and oxychemicals such as maleic anhydride and fumaric acid.

More than 100,000 tons of sorbitol are produced each year by fermentation. Sorbitol is used extensively for making surfactants and emulsifiers, especially for food applications.<sup>74</sup> Increasing amounts of sorbitol are used in making specialty polyethers for urethane foam production.

The Horizon Chemicals Division of the A.E. Staley Company is producing methyl and alkyl glucosides by fermentation of carbohydrates. These chemicals have applications as surfactants, alkyds, and urethane foams, and show great potential for commercial expansion. Ethylene glycol alone has a 2.5 million ton market.

### **Polyol (1.5 million tons)**

Polyol, traditionally produced from petrochemical feedstocks, is the basic compound used in the production of polyurethane and several other classes of plastics. End products include foam, elastomers, marine coatings, adhesives, polymer concrete, and housing components. Natural Resources Group, a British company, now produces polyols from vegetable oil in eight plants throughout the world. Vegetable oil-based polyols have slightly different properties from petrochemical-derived polyols; they cannot substitute generically for petrochemical-derived polyols in the manufacture of polyurethane and related products, but they do exhibit exceptional blending properties that have given rise to a new generation of polymeric products.

Polyol can be produced from a variety of raw materials, both virgin and waste, including canola oil, castor oil, peanut oil, sunflower seed oil, olive oil, cottonseed oil, palm kernel oil, coconut oil, and fish oil. Polyconcrete, a construction material produced in different strengths for applications ranging from construction blocks to household appliance housing, can be made by polymerizing canola oil-based polyol with fuel ash from coal-fired power plants, or with carbon black from biomass.

Large industrial complexes are needed for the production of petrochemical-based polyols used in the manufacture of polyurethane polymers. In contrast, vegetable oil-derived polyols can be produced on a small scale. The basic 4-ton production unit is capable of producing 3,500-5,000 tons a year. Natural Resources Group has reportedly constructed a standard-size polyol plant, complete with a testing and research laboratory, on a 40-foot truck.

According to the company, it costs 15-20 percent more to produce polyol from vegetable oil than from petrochemicals. A gallon of polyol derived from vegetable oil costs \$15.<sup>75</sup> Competitiveness varies by end product. Vegetable oil-based polyol is 10-15 percent cheaper than its petrochemical counterpart when used in the manufacture of electrical cords, but 15-20 percent more expensive when used in the manufacture of fire-retardant foam. In the latter case, however, the vegetable oil-based product offers decided environmental benefits. Petroleum-based flame-retardant foams not only use carcinogenic materials such as toluene 2,4-diisocyanate, but also produce toxic fumes when sprayed on flames at high temperatures. The use of waste vegetable oil could bring down the price of the bio-based product.

## **Glycerol (200,000 tons)**

Vegetable oils contain about 10-15 percent glycerine, or glycerol, by weight. Production of 10 pounds of fatty acids from 12 pounds of vegetable oil generates 1 pound of glycerol (and 1 pound of crude bottoms containing a mixture of low C number compounds). Glycerol recovery contributes about 20 percent of the raw material cost of esterification, the process of separating glycerol from the fatty acid part of the oil. Originally a byproduct of soapmaking, glycerol had little market value until World War II, when it was used in making cellophane, or nitroglycerine for dynamite. It now has a 200,000 ton annual market.

Interchem is establishing a facility to esterify vegetable oil, animal fat and/or waste vegetable oils from fast food processing facilities into a diesel substitute and glycerol. Every 100 pounds of vegetable oil esterified with 15 pounds of methanol and 1 pound of catalyst will yield 100 pounds of diesel fuel oil equivalent, 10 pounds of glycerol, and 5 pounds of methanol. All the catalysts are recycled in the process, and no additional wastes are generated.

Since crude glycerol has a value of 20-30 cents per pound, the revenues it generates will pay for some of the capital and operating costs of the plant. The diesel fuel replacement is expected to cost in these ranges: \$1.50-\$2.10 per gallon from vegetable oils, \$0.70-\$1.80 per gallon from animal fats, and \$0.70 per gallon from waste vegetable oil; in contrast to a cost of \$4.00-\$4.50 per gallon for the same product made from virgin soybean oil on an experimental scale.<sup>76</sup>

## **Furfural (50,000 tons)**

Furfural is an aldehyde, a substance that has two hydrogen atoms fewer than an alcohol. An amber-colored liquid that looks like tea and smells like almonds, furfural is derived from corncobs, sugar

cane bagasse, grain hulls (such as rice and oat hulls), and cottonseed hulls. The milling of one bushel of oats, weighing 32 pounds, generates 6.6 pounds of hulls, which yield 0.79 pound, or two-thirds of a pint, of furfural.

Furfural was very expensive when it was first discovered in 1821. In 1921, however, companies demonstrated that furfural could be produced from the huge stockpiles of oat hulls accumulated by oat milling operations. A pilot plant in Cedar Rapids, Iowa was built in 1922. Worldwide demand was 1 ton per year. The price dropped from 50 cents a pound in January, 1922 to 15 cents a pound in 1926.<sup>77</sup> Furfural now sells for about 75-80 cents per pound and has a market of about 40,000-50,000 tons per year.<sup>78</sup>

The bulk of the furfural produced in the U.S. is used in foundry sand binder or in the refining of lubricating oil. Furfural is also used in making cellophane, dye for living room carpets, coatings on golf balls, and magnetic audio tape. Between 1946 and 1961, Dupont produced adiponitrile, an intermediate chemical used in nylon manufacture, from oat hull-derived furfural. Quaker Oats Chemicals (QO Chemicals), the world's largest producer of furfural, sells FURCARB resin, a phenolic and urea-formaldehyde-based resin modified with 30 percent furfuryl alcohol, which can be used as a plasticizer in plastics and as a binder in the production of refractory products. The company is also working with consumers to formulate a new paint stripper that contains furfural-based materials. Other furfural products made by QO Chemicals include "no bake" resins; Tetrahydrofurfuryl plasticizers; QuaCorr resins, used to fabricate fire-retardant, fiberglass-reinforced plastics; Furan, an intermediate chemical used in insecticides and herbicides; Tetrahydrofuran, a solvent used in the manufacture of polyurethane coatings and vinyl films; and a glue extender for the plywood industry. Currently under development is a polymer concrete made with furfuryl alcohol resins for use in areas where salts, acids, and other solvents erode conventional concrete.

## Notes

### PART I

- <sup>1</sup>William Hale, *The Farm Chemurgic* (Boston: Alpine Press, 1934).
- <sup>2</sup>Williams Haynes, *Cellulose: The Chemical that Grows* (Garden City, New York: Doubleday & Company, 1953).
- <sup>3</sup>Fossil fuels are fossilized plant matter that has been stripped of its oxygen. These fuels contain carbon, hydrogen, and varying traces of other minerals that have been merged into these molecules over millions of years.
- <sup>4</sup>"Oil Plants," *Encyclopedia Britannica*, 1971 Edition.
- <sup>5</sup>Williams Haynes, *Cellulose: The Chemical that Grows*.
- <sup>6</sup>These first machines were compression molding machines, useful for thermoset plastics like Bakelite but not for more malleable thermoplastics like cellulose acetate. The invention of injection molding machines allowed for three times faster production. By 1939, 900 injection molding presses were operating. Haynes, *Cellulose*.
- <sup>7</sup>*Ibid.*
- <sup>8</sup>U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, Washington, D.C., 1976. Series L 166-177.
- <sup>9</sup>Cellulose and hemicellulose are differentiated by the kinds of sugars they contain. Cellulose has C<sub>6</sub> sugars, while hemicellulose has C<sub>5</sub> sugars. C<sub>6</sub> sugars are easily degraded into other short carbon chain chemicals; C<sub>5</sub> sugars are harder to degrade.
- <sup>10</sup>Quoted in Wheeler McMillen, *New Riches from the Soil* (New York: D. Van Nostrand Company, 1946).
- <sup>11</sup>Coal is about 80 percent carbon, 8 percent oxygen, and 4 percent hydrogen. Cellulose is 44 percent carbon, 49 percent oxygen, and 6 percent hydrogen. G.T. Austin, ed., *Shreve's Chemical Process Industries* (New York: McGraw-Hill, 1986).
- <sup>12</sup>U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, 122-137. Figures for wood are from 1869 and 1900.
- <sup>13</sup>*Ibid.*, 518, 590, 599, 818.
- <sup>14</sup>Before this, oil pools found on the ground were scooped up and the oil was separated.
- <sup>15</sup>U.S. Bureau of the Census, *Historical Statistics of the United States: Colonial Times to 1970*, Series M, 162-177.
- <sup>16</sup>Peter H. Spitz, *Petrochemicals: The Rise of an Industry* (New York: John Wiley and Sons, 1988).
- <sup>17</sup>G.E. Tong and R.P. Cannell, "The Economics of Organic Chemicals from Biomass" in *Organic Chemicals From Biomass*, ACS Symposium Series 476 (Washington, D.C.: American Chemical Society, 1990).
- <sup>18</sup>*Chemical and Engineering News*, June 10, 1991. American Iron & Steel Institute, Washington, D.C., 1992.
- <sup>19</sup>Institute for Local Self-Reliance, unpublished data, Washington, D.C., 1992.

### PART II

- <sup>1</sup>In 1925, 65 percent of all inorganic minerals used for industrial purposes went to make iron and steel. By 1989, iron and steel accounted for just 31 percent.
- <sup>2</sup>Municipal solid waste contains 10-15 percent yard waste by weight.
- <sup>3</sup>Some chemicals now derived from hydrocarbons will probably not be made in any significant degree from plant matter. For example, benzene, a widely used chemical, is a ring compound difficult to match with the straight chain chemicals derived from plant matter. Theoretically, one could produce benzene from plant matter. Five percent of wood consists of extractives, of which a small percentage, possibly 1/10th of 1%, is benzene. It is doubtful that benzene made from plant matter could become competitive with benzene made from hydrocarbons.

## PART III

### Surface Coatings

- <sup>1</sup>Luciano Caglioti, *The Two Faces of Chemistry* (Cambridge, Mass.: MIT Press, 1983).
- <sup>2</sup>Based on a 1.0-billion-gallon production figure for 1990 and an average paint density of 24 pounds per gallon. Paints weigh 20-30 pounds per gallon depending on type and color.
- <sup>3</sup>Typical solvents currently used in liquid paint formulations are predominantly petrochemically derived, and include volatile waxes, glycol ethers, amine compounds, alkylated benzenes, toluene, xylene, and naphtha.
- <sup>4</sup>William A. Finzel, "Use Low-VOC Coatings," *Chemical Engineering Progress*, November 1991.
- <sup>5</sup>Marc S. Reisch, "Higher Paint Sales Brighten Profits Outlook," *Chemical and Engineering News*, October 14, 1991.
- <sup>6</sup>"Regulators Putting the Lid on Paint," *Engineering & News Record*, October 5, 1989.
- <sup>7</sup>Raymond E. Foscante, "Tailoring The Optimum System," *Chemical Engineering*, vol. 97, no. 10, October 1990, 92-100.
- <sup>8</sup>Currently, the only surface coating product with a very low VOC content – 0.5 pounds per gallon – is a water-reducible vinyl coating system manufactured by Glidden Company and marketed only in Florida under the trade name "Rustmaster Pro." Vinyl coatings are based on polyvinyl resins derived from petrochemical feedstocks. Rustmaster Pro does not have a smaller proportion of hydrocarbon-derived resins than similar products in its class. Its low VOC level comes from replacing portions of the carrier solvent with water. However, in high humidity environments, this system tends to dry more slowly than similar conventional products. Glidden was recently purchased by ICI Chemicals.
- <sup>9</sup>*Fleet Equipment*, April 1990, 31-34.
- <sup>10</sup>"RadTech Report," *The Journal of RadTech International, North America*, Northbrook, Illinois, 1991.
- <sup>11</sup>*Ibid.*
- <sup>12</sup>E. H. Pryde and J. A. Rothfus, "Industrial and Nonfood Uses of Vegetable Oils" in *Oil Crops of the World*, ed. G. Robbelen, R.K. Downey, and A. Ashri (New York, McGraw-Hill, 1990).

### Pigments and Dyes

- <sup>13</sup>D. O'Sullivan, "Strong TiO<sub>2</sub> Demand Draws DuPont to Europe," *Chemical and Engineering News*, January 22, 1992.
- <sup>14</sup>J. Shearman, "Color the Market Green," *Chemical Engineering*, September 1991, 53-55.
- <sup>15</sup>E.S. Lipinsky, "Using CO<sub>2</sub>: Complex Molecules from Simple Waste" (paper presented at the AAAS Conference, Washington, D.C., January 31, 1992).
- <sup>16</sup>*Ibid.*
- <sup>17</sup>C. Thieme and G. Aumann, "Precipitated Calcium Carbonate" in *Pigment Handbook*, ed. P.A. Lewis (New York: John Wiley & Sons, 1988). Its alkaline properties make PCC compatible as a filler in acid-free papers. New technology allows precipitation to occur within the pulp fiber, and eliminates the usual loss of strength associated with the use of titanium dioxide fillers. See G.G. Allan et al., "The Microporosity of Pulp: The Precipitation of Inorganic Fillers Within the Micropores of the Cell Wall," *TAPPI Journal*, January 1992.
- <sup>18</sup>Regarding cadmium oxide and cadmium pigments, see "Getting Rid of Cadmium: What's Holding It Up?" *Plastics Technology*, July 1991; and "Technology Meets Compliance: The Raw Materials Outlook," *Modern Paint and Coatings*, August 1991.

### Printing Inks

- <sup>19</sup>"Soy Ink Executive Summary," American Newspaper Publishers Association, March 1992.
- <sup>20</sup>A few years ago, black soy inks cost as much as \$4 per pound. The price reduction has been achieved mainly by cutting down on the resin content of the black soy ink, although this has also resulted in diminished drying quality. In general, black soy inks dry harder and rub off less than color soy inks.



<sup>21</sup>Graphic Arts Monthly, November 1991.

<sup>22</sup>Ibid.

<sup>23</sup>Stuart Ellis (Manager of Sales and Services, American Soybean Association, St. Louis, Missouri), personal communication, March 1990.

<sup>24</sup>American Newspaper Publishers Association, March, 1992.

<sup>25</sup>S. Ellis, "Soy Ink Flows Across the Nation," Internal Memo, American Soybean Association, St. Louis, Missouri, October 4, 1991.

<sup>26</sup>Keeler Cox, "The Ins and Outs," *American Printer*, June 1990, 44-47.

<sup>27</sup>C. Bloomfield, "Simple Steps Can Stem IAQ Problems," *Facilities Design and Management*, January 1991, 54-55.

<sup>28</sup>*De-inking of Soy Inks During Paper Recycling*, Final Report, Western Michigan University, 1991.

### Soaps and Detergents

<sup>29</sup>M.M. Hamilton, "Cleaning up the Country With Less," *The Washington Post*, April 26, 1992.

<sup>30</sup>Luciano Caglioti, *The Two Faces of Chemistry* (Cambridge, MA: MIT Press, 1983).

<sup>31</sup>Half of all phosphates present in sewage come from soaps, laundry detergents, and other industrial cleaning agents. Two loads of laundry done with a typical detergent containing 14.7 percent phosphates discharge an amount of phosphates equivalent to that found in the average ton of sewage.

<sup>32</sup>Some tertiary plants in Europe and Canada make use of microorganisms that store the phosphate within their cells, resulting in increased removal of phosphates at lower costs. Water authorities in Europe charge a fee to detergent companies based on their annual sales of phosphate-based soap or laundry detergent products. This fee structure actually has led governments to encourage the use of phosphate-based detergents to help pay for the operating costs of these plants. D. Hunter and D. Rotman, "Phosphate Use Continues to Take Its Lumps," *Chemical Week*, January 30, 1991.

<sup>33</sup>"Environmental Concerns Continue to Erode Phosphates Market," *Chemical And Engineering News*, January 20, 1992.

<sup>34</sup>G.T. Austin, "Soaps and Detergents" in *Shreve's Chemical Process Industries* (New York: McGraw-Hill, 1986).

<sup>35</sup>An ion is any chemical element, such as magnesium or calcium, that is in a highly reactive, electrically charged state which will react with an oppositely charged molecule. The static at the end of a laundry drying cycle is a result of the presence of high concentrations of such ions that have been generated during the wash cycle and have not been neutralized.

<sup>36</sup>These prices have come down from a production cost of over \$2.00 per pound for zeolites in the late 1970s.

<sup>37</sup>D. Rotman, "Enzymes: Tough Market with a Bright Future," *Chemical Week*, January 30, 1991, 46-47.

<sup>38</sup>About 2.0-2.5 ounces of enzyme-based compact detergent are needed to wash one standard-sized load of laundry, compared with 3.0-3.5 ounces of regular phosphate-based detergent. (Proctor & Gamble claims that a 42-ounce box of Ultra Tide detergent can wash 18 standard-sized loads of laundry.) We arrived at our cost conclusions in the text based on an average of 2.3 ounces of ultra detergent per load versus an average of 3.2 ounces of regular detergent per load.

### Adhesives and Glues

<sup>39</sup>R. Mullin and M. Roberts, "Adhesives and Sealants: Innovating Under Pressure," *Chemical Week*, March 11, 1992.

<sup>40</sup>Peter Coombes, "Adhesives Find New Strength in Diversity," *Chemical Week*, March 13, 1991.

<sup>41</sup>B.J. Feder, "Making Things Stick in the Age of Plastic," *The New York Times*, May 31, 1992.

<sup>42</sup>"Chemical Prices," *Chemical Marketing Reporter*, March 9, 1992.

<sup>43</sup>U.S. Congress, Office of Technology Assessment, "Agricultural Commodities as Industrial Raw Materials," OTA-F-476 (Washington, D.C.: Government Printing Office, May 1991).

<sup>44</sup>R.A. Northey, "Low-cost Uses of Lignin" in *Emerging Technologies for Materials and Chemicals from Biomass*, ed. R.M. Rowell, T.P. Shultz, and R. Narayan, ACS Symposium Series 476 (Washington, D.C.: American Chemical Society, 1990).

<sup>45</sup>*Wood Adhesives: Chemistry and Technology*, ed. A. Pizzi (New York: Marcel Dekker, 1989); and *Adhesives from Renewable Resources*, ed. R.W. Hammingway et al., ACS Symposium Series 385 (Washington, D.C.: American Chemical Society, 1990).

### Plastics and Resins

<sup>46</sup>B.F. Greek, "Plastics Producers Look For Turnaround by Year's End," *Chemical and Engineering News*, vol. 69, no. 23, June 10, 1991, 39-68.

<sup>47</sup>This represents crude oil equivalent utilized for both the raw materials and the energy requirements of the plastic and resin production processes.

<sup>48</sup>In 1990, total U.S. petroleum consumption for both fuel and industrial uses combined was 6.2 billion barrels. U.S. Bureau of the Census, *Statistical Abstract of the United States: 1991*, (111th Edition), Washington, D.C., 1991.

<sup>49</sup>Production of polymers from basic raw materials involves numerous intermediate processing steps and intermediate chemicals. These estimates are based on overall utilization of fossil fuels in the production of both intermediate precursors and end plastics in the United States as shown in the 1990 production figures of major plastic categories.

<sup>50</sup>A. Kagan, "Specialties are Holding Up Well," *Chemical Week*, July 24, 1991.

<sup>51</sup>K. Johannes (President, Missouri Soybean Association, Jefferson City, Missouri), personal communication, October 1991.

<sup>52</sup>R. Narayan, "Compatibilization of Lignocellulosics with Plastics" in *Emerging Technologies for Materials and Chemical from Biomass*.

<sup>53</sup>K. F. Lindsay, "Truly Degradable Resins are Now Truly Commercial," *Modern Plastics*, February 1992.

<sup>54</sup>NOVON Product Update, vol. 2, no. 1 (Morris Plains, N.J.: NOVON Products Group, Warner-Lambert Company, November 1991).

<sup>55</sup>S.A. Mojo (Director, Market Development and Product Positioning, NOVON Products Group, Morris Plains, N.J.), personal communication, February 1992.

<sup>56</sup>D. Loepp, "Novon Debuts Two Degradable Resins, Begins Building Plant," *Plastics News*, June 18, 1991.

<sup>57</sup>*Business Week*, August 19, 1991.

<sup>58</sup>Personal communication, and "Product Report: PHBV Biodegradable Polyesters," ICI Americas Inc., Wilmington, DE, March 1992.

<sup>59</sup>W. Luzier (North American Commercial Manager for Biopolymer Division, ICI Americas Inc, Wilmington, DE), personal communication, March 1992.

<sup>60</sup>Ibid.

<sup>61</sup>T. Studt, "Degradable Plastics: New Technologies for Waste Management," *R&D*, March 1991.

<sup>62</sup>R. Mueller, et. al., "Lactic Acid Production from Liquefied Corn Starch Using *Lactobacillus amylovorus* and Newly Isolated *Lactobacilli*," Proceedings of Corn Utilization Conference III, June 15-18, 1990.

### Intermediate and Specialty Chemicals

<sup>63</sup>A. Kagan, M. Ward, and D. Hunter, "Specialties Are Holding Up Well," *Chemical Week*, July 24, 1991.

<sup>64</sup>G.T. Austin, ed., "Wood-Derived Chemicals" in *Shreve's Chemical Process Industries* (New York: McGraw-Hill, 1985).

<sup>65</sup>G. Robbelen, R.K. Downey, and A. Ashri, eds., *Oil Crops of the World* (New York: McGraw-Hill, 1990).

<sup>66</sup>B.F. Greek, "Sales for Detergents Growing Despite the Recession," *Chemical and Engineering News*, January 28, 1991.

<sup>67</sup>"Surfactants Aim for Niche Markets," *Chemical Engineering*, vol. 99, no. 2, February 1992.

<sup>68</sup>"Chemical Prices," *Chemical Marketing Reporter*, March 11, 1992.

<sup>69</sup>"Specialty Surfactants, A Changing Environment," *Chemical Week*, September 4, 1991.

<sup>70</sup>The consumption of vegetable and wood oils (especially tall oil from pulp mills) was expected to double in 1990, when several natural oil processing plants came on line.

<sup>71</sup>"World Chemical Outlook," *Chemical and Engineering News*, December 9, 1991.

<sup>72</sup>The oil derived from this process is similar in viscosity to No. 4 fuel oil, but the product must be marketed as No. 6 fuel oil since there is no market for No. 4.

<sup>73</sup>P.W. Bergeron and N.D. Hinman, "Technical and Economic Analysis of Lignin Conversion to Methyl Aryl Ethers," *Applied Biochemistry and Biotechnology*, vol. 24/25, 1990, 1115-1129.

<sup>74</sup>W.M. Doane, "Promising New Products and Processes from Corn," *Annual Agricultural Outlook Conference*, November 27-29, 1990 (Washington, D.C.: U.S. Department of Agriculture, 1991).

<sup>75</sup>Geoff Cohen (President, Ecotek Holdings, Ltd., Lions Bay, B.C.), personal communication, October 1991.

<sup>76</sup>Donna Johnson (Program Director, Interchem Industries, Leawood, Kan.), personal communication, September, 1992.

<sup>77</sup>Wheeler McMillen, *New Riches from the Soil*.

<sup>78</sup>*Chemical Marketing Reporter*, February, 1992; and *Chemical Economics Handbook* (Boca Raton, Fla.: CRC Publishing Company, 1986).

Subscribe to  
*The Carbohydrate Economy*  
Voice of the Plant Matter Revolution

Contact:

**Institute for Local Self-Reliance**

1313 5th Street Southeast

Minneapolis, MN 55104

(612) 379-3815

[www.carbohydrateeconomy.org](http://www.carbohydrateeconomy.org)



RECYCLABLE



RECYCLED