

# SOY CHEMICALS FOR PAPER PROCESSING

## A MARKET OPPORTUNITY STUDY

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By:

Connie Howe

Robina Hogan

Steve Wildes



OMNI TECH INTERNATIONAL, LTD.  
2715 Ashman Street  
Midland, MI 48640  
Phone: 989.631.3377

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Connie Howe  
Robina Hogan  
Steve Wildes

## EXECUTIVE SUMMARY

This report has been prepared with three objectives:

- For the sponsoring United Soybean Board New Uses Committee to identify, evaluate and prioritize opportunities for expanded soy use in the pulp and paper chemicals industry as a guide for potential research investment.
- For the prospective soy researcher to provide an overview of chemical use in the pulp and paper industry as a guide to innovation of economic merit.
- For the prospective paper industry adopter to provide a view of soy technology currently available, under development or which can potentially be developed and commercialized.

Accordingly, this report is presented in sections for selective reference, depending on need.

The process of making paper, paperboard and tissues today is highly cost sensitive. The necessity for increasing productivity and quality, combined with environmental regulatory pressures, has resulted in an increased demand for pulp and paper chemical additives. The global market for pulp and paper chemicals is estimated to have been 51 million tons with a corresponding value of \$17.8 billion in 2010. It is projected to rise to 58 million tons or \$20 billion by the end of 2015. In North America, the demand for pulp and paper chemicals in 2010 was estimated to be 12.7 million tons or \$4.4 billion, increasing to 13.9 million tons or \$4.8 billion in 2015.

Pulp and paper continues to be the largest industry in demand for chemical additives. Even with the current economic downturn and the increasing reliance on electronic media curtailing paper use, specialty chemical consumption is still huge, leading to a very large opportunity for specialty chemical additives that impart strength/performance enhancements at a lower or equivalent cost of existing products. The industry has become very sensitive to the price stability of soy-based options compared to the volatility of existing petrochemical options and is seeking cost of use/performance data for new and innovative solutions for profitability in these markets. Basic pulp costs have also risen, leading to the need for alternate cellulose sources and greater use of additives to reduce wood pulp consumption without sacrificing performance.

Successful commercialization of soy-based products in pulp and paper markets will be driven by active programs within the United Soybean Board and strategic alliances with key paper manufacturers or paper chemical companies including Eka, Georgia Pacific and Ashland. Prime opportunities in sustainable paper additives are anticipated in three strategic areas:

1. Entrance into the market in established paper chemical segments that are commodity driven, but offer opportunities in very large markets. The potential usage indicated is based on what is considered to be a realistic targeted degree of penetration of the market segments.
  - Soy proteins as wet-end additives. Estimated potential - 120 million pounds.
  - Soy proteins as a sludge additive in the reclaim process. Potential - 200 million pounds.
  - Expansion of existing use of soy protein binders in paper and paperboard coatings to potentially double the demand if a more cost effective protein modification route could be identified. Potential - additional 25 million pounds. Soy protein binders for paper coatings are core strengths for Solae and Applied Protein Systems.
2. Increase knowledge and awareness of potential specialty applications that are niche markets but could have a high interest in innovative bio-based solutions or address unmet needs.
  - Soy hulls as an alternative cellulose source in pulps used in disposable wipes and nonwovens. Collaboration with manufacturers of cellulosic fibers for filament, staple and tow applications. Estimated potential – 1.2 million pounds.
  - Soy proteins as nonionic surfactants in paper coatings in the pulping process and in the deinking process.
  - Specialty coatings like grease proof, barrier coating and thermal papers that require hydrophobicity and heat stability of soy products such as waxes.
3. Expand existing commercial soy technologies into new paper markets by championing development work with paper chemical suppliers.
  - Soy-based methyl soyate and new soy solvents for cleaning and degreasing.
  - Transfer of UV curing resin technology in wood finishes to UV cured colored paper coatings.

The success of the above strategies hinge on the continuing support of the following:

- Collaboration with strategic large specialty chemical manufacturers and pulp and paper mills, specifically utilizing long standing relationships with the United Soybean Board in adhesives, fibers, coatings and plastics programs, including Ashland, Eka, Georgia Pacific, Cargill, ADM, Solae, Kimberly-Clark, Procter and Gamble and Polymer Group Inc.
- Continued effort to foster associated research and development projects involving fundamental protein behavior. This includes concurrent work to evaluate reactions of

soy derivatives in heated, aqueous environments rich in nutrients, enzymes and possible bacteria.

- Once proof-of-concept is established with the new soy-based technology sponsored by the United Soybean Board, assist in connecting resin companies with pulp, paper and paperboard companies.
- Publicize technical programs at technical conferences and Technical Advisory Panel (TAP) meetings in order to identify potential prospects for the new soy chemistry.

## **INDUSTRY OVERVIEW**

### **PULP AND PAPER CHEMICALS**

According to the Global Industry Analyst Report (GIA), the global market for all pulp and paper chemicals was estimated to be 51 million tons with a corresponding value of \$17.8 billion in 2010. United States demand for pulp and paper chemicals in 2010 was near 12.7 million tons or \$4.4 billion.

As an industry, the pulp and paper chemicals market is global, highly competitive and relies on very sophisticated technology to maximize quality and performance of paper products while keeping costs reasonable. Like most industries that rely on the economic health of consumers and businesses, a key indicator for demand is the Gross Domestic Product. The current recession has resulted in a substantial drop in some types of paper consumption, which was also exacerbated by a shift in paper demand caused by electronic media rise. This, in turn, has reduced demand for pulp and paper chemicals. Nevertheless, the paper market remains one of the largest markets for chemicals in the United States.

Logically, the consumption and demand for pulp and paper chemicals is a function of the demands for paper, paperboard, corrugated boxes and tissues. Pulp and paper manufacturing is one of the largest global industries with very high capital investments in mills producing paper on machines 10 meters wide at speeds in excess of 2000 meters per minute. The process involves very heavy use of resources including water, wood pulp and energy. Redirection in the pulp and paper industry in the last decade has been significant and can be attributed to both economic and environmental factors.

#### ***Economics Factors***

- Changes in the way information is recorded, stored, retrieved and disseminated have brought about permanent changes in paper use. The introduction of the internet and adoption of a variety of digital and electronic media transfer capabilities by the press of a button has reduced the demand for many kinds of paper including newsprint, catalogs, mailers, books and photos.
- With a growing segment of low cost, international alternatives, North American paper manufacturers are forced to reduce costs in order to retain market share. Profitability is improved by making the same quality goods from thinner paper stock at faster speeds. As expected, thinner paper is often lower in physical properties like opacity, brightness and reduced print quality. The cost/performance balance is achieved by the application

of low cost paper coatings and increased use of non virgin recycled/recovered fibers in the pulp.

- Even with the downturn in market pulp, the specialty pulp (dissolving and fluff used in nonwoven for personal care products) has continued to rise.

### ***Environmental Factors***

Pulp and paper mills have become highly regulated because of the high use of natural resources. The demand for cleaner, more efficient processes has brought about the following initiatives:

- The less harsh alkaline or neutral papermaking process has been adopted in the majority of United States paper mills over the last few decades. Different families of chemical additives were developed to perform at a higher pH range of 4.5 - 8.5.
- Wood resources for fibers have become costly and scarce. Cellulosic alternatives are constantly being evaluated. One significant trend is to reduce virgin fiber content by replacing it with inorganic fillers and recycled fibers. Recycled fibers are shorter and inherently produce weaker base sheets which results in a greater need for strength and performance additives. This has, in turn, driven the need for efficient and robust binders for diverse fillers in both the base sheet and specialty coatings.
- Water resources are at a premium. Paper mills are one of the highest water consuming industries of today, prompting legislation and regulation of effluents and energy constraints. For every one pound of wood pulp used to make a paper product, more than 99 pounds of water are required. During the production process, this water must be removed mechanically or by evaporation over heated rolls. Significant improvements in water consumption have occurred by the adoption of closed loop water recycle processes. Water consumption in closed loop systems is five cubic meters per short ton of paper compared to 125 cubic meters per short ton without water recycling. Effluent system recycling has greatly increased the demand for a wide variety of processing aids and deposition control.

### **PAPER MANUFACTURE**

The pulp and paper industry is one of the largest industries in the nation. The majority of manufacturing facilities in the paper industry are very integrated. Most paper mills begin with wood chipping at the front end, followed by pulping, bleaching, papermaking and recycling of post consumer products.

Wood logs are delivered to the mill where they are chipped and sent to pulping. The pulping process is used to break apart cellulose fibers by mechanical and/or chemical digestion to separate the fibers and optimize the resulting paper strength. If white pulp is desired, bleaching occurs at this stage. The resulting furnish is a highly diluted slurry of pulp, fillers and additives that are pumped into a pressurized headbox and extruded through a slit onto a moving screen. Water is continually removed by gravity or vacuum assist before moving to the wet-press section where the sheet is fed between felted nip rolls to remove remaining water. Further drying is accomplished by passing the supported sheet over metal cylinders heated by steam to dry the paper mat. If necessary, a calendering process is used to smooth the surface of the mat. The attributes of the sheet can be further modified by the application of coatings (either during the papermaking process or secondary operations) or adding multi-ply construction. If the paper is to be coated, in line, it generally occurs at this point before the sheet is wound on a take-off reel. The furnish mixing to the wet-press section is designated the “wet-end” of the process and the remaining stages as the “dry-end”. Paperboard (paper greater than 0.3 mm thick) and tissue can be run on the same equipment with modifications.

The paper industry has undergone significant changes due to mergers, acquisitions and restructurings in order to survive the competitive nature of the business. The process for making paper is very capital and resource intensive. Modifications to the process regarding chemical additives or processing conditions can be met with resistance. At the same time, the market is in need of innovation and creative solutions to improve profitability and performance.

According to RISI, top United States manufacturers for each market are:

- *Wood Pulp* - Weyerhaeuser Company, Domtar and International Paper
- *Paper* - International Paper, Domtar and Abitibi Bowater Inc.
- *Paperboard* - International Paper and Rock-Tenn Company  
(acquired Smurfit Stone in 2011)
- *Tissues* - Koch (GP), Kimberly-Clark and Procter and Gamble

## **DOMESTIC PAPER MARKETS**

The selection of chemical additives is dependent on the application and function of the resulting paper or paperboard. One of the classifications of paper grades is shown in Figure 1. The full conventional designations can be found in Appendix I.

**FIGURE 1  
CLASSIFICATION OF PAPER GRADES**

Grade - 2009 Consumption	Types	Uses	Requirements
<b>Paper</b> <b>32 Million Tons</b>	Newsprint	Newspaper, Directories	Runnability , Low Cost
	<b>Uncoated</b>	Mechanical	Paperbacks, Catalog, Magazines
		Free	Printing, Writing, Copy, Books
	<b>Coated</b>	Free	Direct Mail, Reports, Magazines
		Specialty	Barrier, Thermal Papers, Label, Currency
	Industrial	Sack, Industrial Glassine, Greaseproof	Tear Strength, Barrier Properties for Various Fluids
<b>Board/Packaging</b> <b>26.4 Million tons</b>	Box Board	Food Carton, Paper Plates and Cups, Cardboard	Barriers, Burst and Dry Strength
	Industrial Converted	Fiber Drums, Tubes and Cores	
	Containerboard	Multi-ply Box, Linerboard	Crush Resist, Dry Strength
<b>Tissue-</b> <b>8 Million Tons</b>	Hygiene	Facial, Bath, Towel, Napkin, Wipes	Wet Strength, Softness. Low Basis Weight
	Absorbent	Diapers, Incontinence	Wet Strength, Absorbency, Retention of Fluids under Pressure, Comfort
<b>Runnability</b> - Ability to run through presses without breakage <b>Printability</b> - The ability to accept and preserve ink with minimum rub-off, set-off or show through <b>Appearance</b> - Optical qualities to include brightness, whiteness, cleanliness and opacity			

Printing and writing papers, magazines, catalogs and reports have strict appearance requirements such as opacity, brightness and print quality and account for most of the chemicals used in the papermill industry. These are high-quality, high-value paper grades that rely on the incorporation of fillers, pigments, coating chemicals and paper sizes to meet these requirements.

Specialty papers utilize chemicals for specialized applications such as barrier, grease resistance or thermal properties. While not substantial in size, they offer niche development opportunities to meet these specialized needs.

In paperboard applications, specialty additive use is most prevalent in boxboard where a large percentage involves bleached board for milk cartons, paper plates, cups and folding cartons.

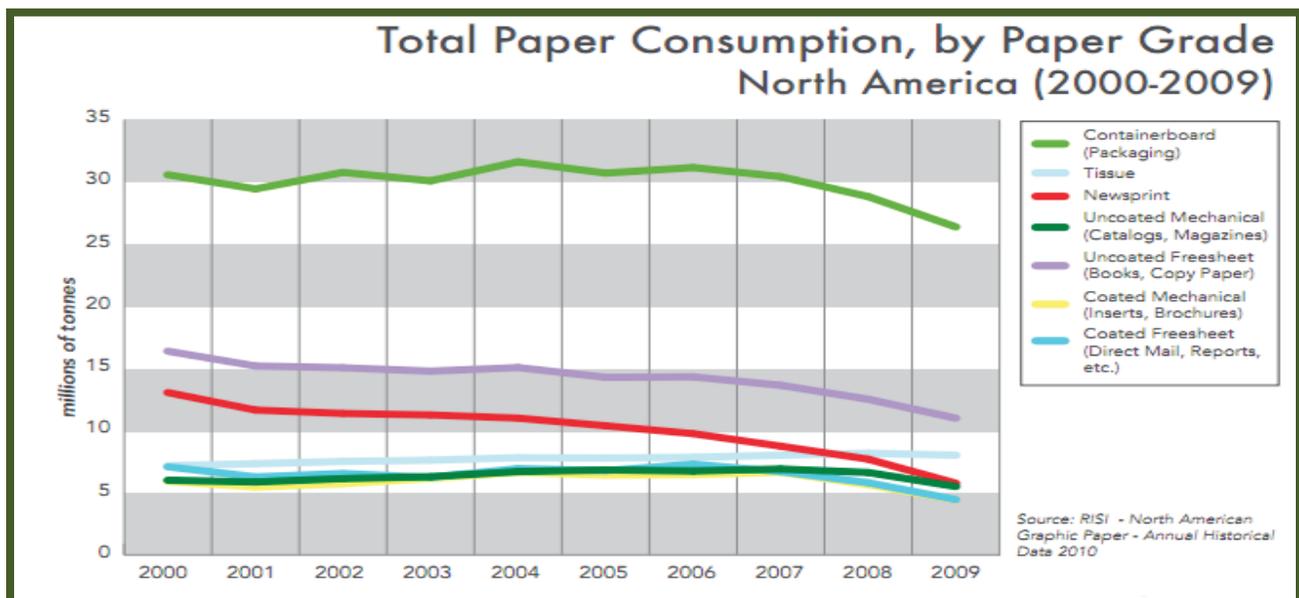
Tissues and nonwovens use dissolving and fluff pulps. Dissolving pulps are used in production of regenerated cellulose fibers to produce specialty paper products and nonwoven sheets. Fluff pulps are used as a raw material in the absorbent core of personal care products such as diapers, feminine hygiene products and air-laid absorbent toweling.

Figure 2 shows the consumption of paper in North America in 2009 as reported by RISI. The largest segment was containerboard which includes boxes for packaging with consumption of 26.4 million tons. The second highest in consumption is a segment that includes all uncoated paper from books, print and copy paper at 15.5 million tons. Tissue, one of the smallest in consumption at 8 million tons, is considered one of the potential growth segments.

Several studies have predicted that economic recovery will eventually boost manufacturing and commercial printing activity and increase demand for production of paper and paperboard. However, domestic paper producers will continue to face strong competition from China, India and South America, where low raw materials and labor costs lead to lower production costs.

It is expected that anticipated gains in packaging markets for containerboard and boxboard could be hampered by competition from plastic alternatives; however, it is possible that the trend toward sustainable products (paper-based) could temper the gain of market share from plastics.

**FIGURE 2**  
**NORTH AMERICAN PAPER CONSUMPTION**



Growing demand in nonwovens and other products using specialty pulp has led to increasing demand for dissolving pulp in textile type applications. The global demand for regenerated cellulosic in 2010 was estimated to be 4.5 million tons. Demand growth will continue at a rate of 3-7% per year. Global pulp production increased by 7% in 2010, which in turn increased the demand for wood raw-materials. As a result, prices for wood chips and pulp logs were up in most regions of the world according to the Wood Resource Quarterly. Variability in wood chip pricing and availability has prompted a serious search for alternate cellulose materials for these applications.

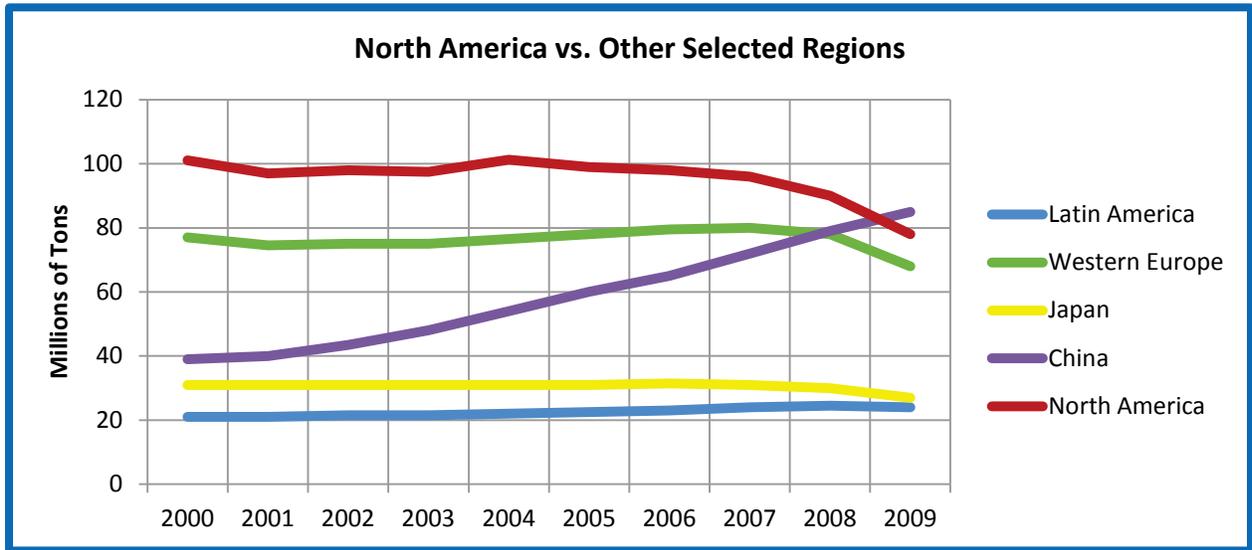
## **GLOBAL LANDSCAPE**

Today, many industries operate on a global scale. The pulp and paper chemical market is no exception. An understanding of the global trends and demand are an important part of assessing market opportunities in this industry.

The United States and Canada have historically been large consumers of the world's paper. North Americans consume 505 pounds per person, well above the world average of 121 pounds per person. Despite having only 5% of the population, North Americans consume over 17% of the world's paper. These demographics are beginning to change as developing countries continue to grow in wealth and population.

The total global consumption of paper was 370 million tons in 2009 with future gains expected to be primarily in Asia Pacific and Latin America. Figure 3 shows the onset of production loss in total paper and paperboard production occurring in 2004 in developed countries such as the United States, Canada, Japan and Europe. China, India and Latin America, increasing in population and technology, have seen gains in demand over this time period. North America, historically a dominant force in paper consumption, was eclipsed by China for the first time in 2009. It is expected that China will account for over 85% of the worldwide growth in demand for print and writing paper for the next 15 years.

**FIGURE 3  
GLOBAL PAPER AND PAPERBOARD CONSUMPTION**



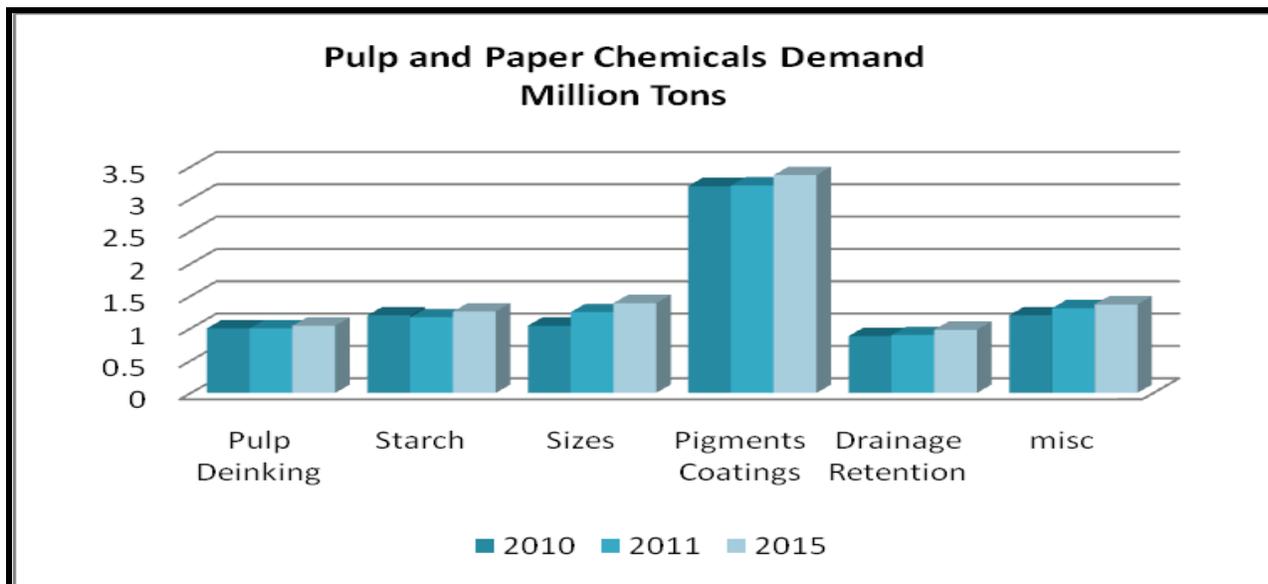
Source: RISI World Pulp Annual Historical Data 2010

### **PULP AND PAPER CHEMICALS MARKET OVERVIEW**

The global market for pulp and paper chemicals is estimated by Global Industry Analysts (GIA) to be 51 million tons with a corresponding value of \$17.8 billion in 2010 and is expected to rise to 58 million tons, or \$20 billion by the end of 2015. Japan and Europe are expected to be impacted similarly. The highest growth region will be in the developing nations in Asia Pacific and South America and many United States based chemical manufacturers will have a significant presence.

The United States market for pulp and paper chemicals in 2010 was estimated by GIA to be 12.7 million tons in 2010 and is expected to increase to close to 14 million tons by 2015. On a value basis, this correlates to \$4.4 billion and \$4.8 billion, respectively. Bleaching chemicals represent the largest volume with over a 30% share, translating to 3.9 million tons. However, pigment coatings dominate on a value basis, with a share of 25% or \$1.1 billion. Pigments and coatings chemicals are predominately (above 90%) calcium carbonate and clays.

**FIGURE 4  
PAPER CHEMICAL DEMAND BY TYPE**



Pigment coatings are used to compensate for lower basis weight paper where cost savings comes at the expense of appearance such as opacity and print performance. The addition of highly pigmented coatings is a low cost alternative that currently utilizes 25-30 million pounds of soy proteins every year.

While the majority of paper chemicals are commodity in nature, about 48% are specialty chemicals, including some that are polymeric from both synthetic and natural sources. In addition to soy proteins, bio-based additives are common in conventional paper and include starch, dextrin, carboxymethyl cellulose and casein.

It is not surprising to expect growing demand in additives that promote cost effective, high speed production of paper while providing the highest performance standards possible. This is achieved through intelligent use of fillers/fibers and specialty chemicals to aid in processing or performance requirements, particularly as they relate to recycle processes. The following strategies have been adopted to meet profitability demands and, ultimately, impact the growth of associated specialty additives in the pulp and paper market.

**FIGURE 5**  
**COST SAVING STRATEGIES**

<b>COST SAVINGS STRATEGY</b>	<b>OPTIMIZATION STRATEGY</b>	<b>COMPENSATION BY ADDITIVES</b>
Virgin Fiber Content Reduced	Recycled Fiber and Mineral Filler Substitution, Alternate Fiber Sources	Binder/Mineral Packages, Increased Use of Retention and Drainage Aids, Strength Aids, Pulping and Deinking
Basis Weight Reduction of Paper	Increase Use of Fillers and Pigment Coatings to Compensate for Lower Performance Characteristics	Stronger Resins in Sheet and Coatings, Better Binding of Fillers and Pigments
Faster Production Speeds	Higher Wet/Dry Strength to Prevent Breakage, Equipment Life Extension	Dry Strength Resins, Anti Pitch and Corrosion Control Aids
Reduction In Liquid Effluent	Reductions in Fresh Water Usage Via Recycling	Drainage/Retention Aids, Defoamers, Flocculants, Coagulants, Anti-Fouling

## **MARKET SEGMENTS**

The discussion of specialty chemicals will be defined in this report as they relate to three areas:

- **Pulp** - Wood and non-wood sourcing for fibers
- **Paper Chemicals** - Retention and drainage aids, dry strength agents, internal sizes and surface applied sizes and functional coatings
- **Recycle Chemicals** - Process aids for recycling of paper products and effluent water treatment

This study does not include discussions of commodity additives unless they influence the selection of potential soy-based alternatives.

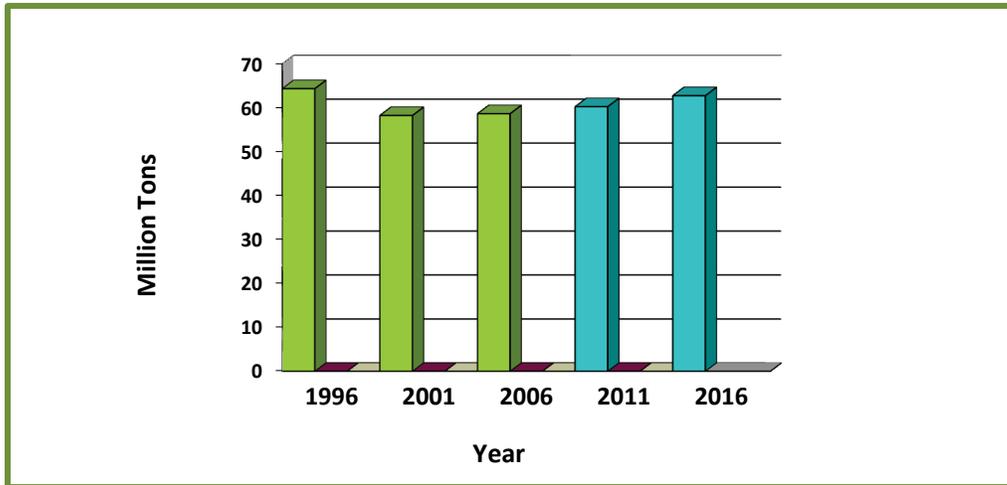
## **PULP**

### ***Pulp Feedstock***

Pulp is the starting material for all paper, paperboard and tissue products and comes from wood, agricultural residues or recycled fibers from post consumer paper waste. Wood is a natural resource rapidly being depleted due to high usage in many industries. Wood utilization

is optimized by significant and often mandatory recycled fiber programs, which limits the use of virgin wood in the paper industry. Even though a large percentage of pulp comes from plantations or reforested areas, there is still a significant need for more sustainable sources to offset availability, pricing and volatility of today's market and expected tightening of supply over the next five years.

**FIGURE 6**  
**WOOD PULP PRODUCTION**



In the United States, both hard and soft woods are major sources of fiber for wood pulp manufacturing and are chosen based on the application of the resulting paper product. The challenge is combining pulp sources to produce products of the highest quality at the most competitive prices within the industry.

- *Soft woods* - longer fibers provide strength in products such as paperboard
- *Hardwoods* - smoother, shorter fibers typically used in paper and printing applications
- *Cotton* - linters are used to give longevity to industrial papers such as currency stock
- *Plant Fibers* - rice, straw, jute, hemp and bamboo have longer fibers and are often used in filtration, tea bags and cigarette papers

Finding suitable sources for cellulose outside of wood has become a high priority given the increasing complexities associated with the cultivation, harvesting, processing and final cleanup of wood. There is currently a very high interest in developing processing methods and new products to support the commercial utilization of alternate cellulose. The potential for soy hulls or other recovered soy fiber in this application has been addressed in preliminary research studies.

## ***Wood Chips and Pulping***

The process of pulping separates the bulk components of the fiber source (wood chips, stems or other plant parts) into the constituent fibers. Pulp is made from a variety of wood species including softwood (spruce, pine, fir and hemlock) and hardwood (aspen, birch and eucalyptus) as well as non-woody plants, recycled or secondary fiber and deinked pulp. Because the pulping stage can be extensive and involves many commodity chemicals, the yield and supply source must be economically feasible to be commercially viable.

In general, wood pulp contains cellulose fibers, hemicellulose and lignin. Through the process of chemical and/or mechanical pulping, the cellulosic fibers are broken down and separated prior to making paper and paperboard. The structural integrity and performance of paper is directly related to the fiber type and quantity of entanglements of individual cellulosic fibers, so care in identifying proper pulp or pulp blends is paramount. Pulp can be manufactured using mechanical, semi-chemical or fully-chemical methods and is often bleached if the application requires bright, white pulp.

Chemical pulping degrades the lignin and hemicellulose which can then be separated from the cellulosic fibers. The best papers are made from highly separated fibers, with none of the weaker lignin or hemicelluloses remaining. Two prominent chemical processes are Kraft and Sulfite:

- Kraft or Sulfate processes use sodium hydroxide and sodium sulfide. These principal organic sulfides cause the characteristic sulfur smell and additional environmental concerns. This process makes higher strength pulp with a wide variety of wood species. The Kraft process is 80% of the world production with corresponding yields of 50-55%.
- The Sulfite process uses a mixture of sulfurous acid and bisulfite ion. Sulfite pulp is easy to bleach, brighter when unbleached, higher in yield and easier to refine but produces weaker sheets. Only 10% of the world production is with this process at yields of 45%.

In mechanical pulping, pulpwood is debarked and shredded with rotating grindstones. There is no chemical separation of the lignin or hemicellulose, resulting in lower strength and the characteristic brown color in unbleached pulp and papers. For this reason, the pulp yields are significantly higher at 95%. This is a very energy intensive process.

Hybrid pulping methods use a combination of chemical and thermal treatment, followed by a mechanical treatment to separate the fibers. These hybrid methods include thermomechanical and chemithermomechanical pulping and are used to reduce the amount of mechanical treatment, reducing the loss of fiber strength that occurs in purely mechanical pulping

methods. In bio-pulping, the wood chips are treated with lignin degrading fungi under controlled conditions.

### ***Pulp Processing***

During production, the pulp feedstock includes the cellulose source and a large amount of primarily high volume commodity chemicals such as acids, alkalis, chlorine and sulfate bleaching chemicals, defoamers, dispersants and descaling compounds to aid in the following process steps prior to papermaking:

1. Digesting or cooking removes the lignin.
2. Defibrillation ensures that the fibers are separate after cooking.
3. Deknotting removes any uncooked wood chips.
4. Brown Stock washing to remove residual cooking liquor.
5. Delignification and bleaching if required to obtain bright, white papers.
6. Screening, cleaning and thickening prior to pump storage, blending, drying and packaging in sheets or rolls if not immediately used in papermaking.

### ***Pulp Types***

**FIGURE 7  
GRADES OF PULP USED FOR DIFFERENT APPLICATIONS**

<b>PULP GRADE</b>	<b>APPLICATION</b>	<b>MARKET SIZE - 2010 Million Tons</b>	<b>COST - 2010 Metric Ton</b>
Market	Paper	45	\$900 - \$1,000
Dissolving	Acetate and Rayon Fibers	5.1	\$2,000
Fluff	Absorbents	5.1	\$1,050
Eucalyptus	Print and Writing, Towel and Tissue, Acetate Fibers	15	\$730
De-inked	Newsprint, Writing, Tissue	40 - 50	\$425 - \$600

A current research project sponsored by the United Soybean Board is aimed at defining the potential value of soy hulls as a cellulose source for dissolving pulps because of the high alpha content and short fiber length. Dissolving pulps typically come from the sulfite process, are bright white in color and used in the production of regenerated cellulose for textiles, cellophane, various acetates and cellulose derivatives including carboxymethyl cellulose. Specialty filter papers and tea bags are also made from these pulps.

Fluff pulps primary come from softwoods and are highly bleached and used where bulk and absorbency are important properties, as in personal care products. These markets are huge and growing but utilize a large amount of synthetic super absorbents based on polyacrylic acid and may not be an optimum place for soy products.

### ***Cellulose Fiber Applications***

World dissolving pulp demand reached 5.1 million tons in 2010, an increase of 16% over the previous year when world demand for all textile fibers jumped 12%. In the second quarter of 2011, eleven new dissolving pulp start-up projects were announced, totaling an additional 1.2 million tons of capacity. Half of this new capacity comes from one mill in China. The United States production of pulp for specialty cellulose applications is estimated at 3.0 - 4.5 million tons per year. The estimated average value is \$.80-1.00 per pound and total market of \$6 billion per year.

The specialty cellulose market is actively looking for new and innovative sources of these grades of cellulose, which may make the high alpha cellulose content of soy hulls an ideal starting material for dissolving pulp. The supply of appropriate grades of cellulose raw materials has had significant issues such as:

- Material shortages and rising prices – The average price for standard grade dissolving pulp for 2010 was \$2,000, but had climbed to near record levels of \$4,500 per ton for the first quarter of 2011.
- Rising demand for cellulose-based materials in nonwovens, personal care products and for substitution in textiles. Demand will continue to grow between 3 - 7% per year.

Cellulose-based textile fibers are used in applications such as filtration, nonwovens and clothing. The cellulosic man-made fiber industry is primarily manufacturing rayon and acetate fibers in the form of monofilament, yarn, staple or tow.

Cellulosic man-made fiber lost ground in the late 1990s to synthetic fiber, falling to less than 6% of total United States and worldwide man-made fiber output in 2002. According to the *Fiber Economics Bureau's World Surveys of Manufactured Fiber Production*, the demand for cellulosic fibers has rebounded in 2009 to 3.8 million tons making cellulosic fibers 7.7% of the man-made fiber market in 2009 and 5% of overall fiber demand.

- Worldwide filtration products use is approximately 290,000 – 300,000 tons of softwood (60%) and hardwood (40%) cellulose fibers and approximately 80% are from North

America and Europe. The major United States manufacturers are Celanese, Eastman and Lenzing.

Rayon accounts for roughly 90% of the cellulosic man-made fiber production. Acetate, which is primarily used to create apparel, home furnishings and cigarette filters, accounted for less than 6% of production in the early 2000s. Lyocell (brand name: Tencel) is a new, third-generation cellulosic fiber that is similar to Rayon. Total industry shipments increased from \$1.66 billion in 2007 to \$1.79 billion in 2008. See Appendix 2 for manufacturers of cellulose textile fibers.

- United States production of cellulose staple in 2009 was 2.7 million tons.
- The market size for various fibers in 2009 was 70.5 million tons.

Based on this data, the market volume potential for soy hull cellulose is described below based on share of market.

**FIGURE 8  
POTENTIAL UNITED STATES MARKET VOLUMES - ESTIMATES OF SOY HULL UTILIZATION**

<b>% OF SPECIALTY CELLULOSE MARKET</b>	<b>CELLULOSE USAGE (MM LBS.)</b>	<b>POUNDS OF HULLS UTILIZED (MM LBS.)</b>	<b>ANNUAL HULL PRODUCTION (MM LBS.)</b>	<b>% OF AVAILABLE HULLS UTILIZED</b>
1.0	80	120	8,000	1.5
5.0	400	600	8,000	7.5
10.0	800	1,200	8,000	15.0
15.0	1,200	1,800	8,000	21.5

Enzymes also can play a significant role in pulp and paper manufacturing in the bleaching and deinking process by reducing the use of chlorine bleach. The use of enzymes to hydrolyze the cellulose is predicted to see growth for this reason. Enzymes are extremely attractive “green” technologies.

- Enzymes will assist in widening the refining window, allowing paper quality specifications to be met and/or production costs to be reduced.
- The soy enzyme lipoxygenase is used as natural bleach in bread dough at 0.7 - 1%. The potential of this type of technology for pulp bleaching has yet to be evaluated.

## PAPER CHEMICALS

Chemical additives can be added to the papermaking process at the wet end, at the size press, or in a coating after the paper has been through the drying stage. Figure 9 highlights the relevant papermaking chemicals that could potentially involve introductions of soy-based alternatives. The effective use of these chemicals requires knowledge of pH, conductivity and details on addition sequence and other components in the furnish.

The following section reviews relevant polymers used in paper manufacture. In particular, the specialty chemical families that could potentially contain soy protein based counterparts are broken down below. Additives are evaluated on the cost of use but those values for soy proteins have not yet been generated.

**FIGURE 9  
SPECIALTY CHEMICALS IN PAPERMAKING**

2010 U.S. DEMAND	WET END AIDS	CHEMISTRY
Sizes - Internal 0.8 Million Tons	Controls penetration of water to improve coatings and ink deposition.	Rosin, AKD, ASA. Cationic Starch, CMC, PVOH
Retention/Drainage Aids 0.9 Million Tons	Allow maximum drainage for high speed processing. Retaining fines and fillers for pitch and deposit control and uniform distribution of fillers for better print surface.	Coagulants, Flocculants and Microparticle Systems using DADMAC, PAM, PAC, PVF, PVAm and PEI usually as a hybrid system
Dry Strength Resins 0.6 Million Tons	Increase strength of sheet during wet and dry process to prevent breakage.	Cationic Starch, Acrylamide Copolymers, Guar and Carboxymethyl Cellulose
DRY END AIDS		
Surface Sizes 0.4 million tons	Surface modifications inhibit penetration of water and control spread of coatings and inks.	Polymeric sizes include SMA, SAE, SAA and Polyurethanes, Starch
Coatings 3.2 million tons	Binders compensates for thinner paper stock by bonding to fillers for improved optical and print quality.	Starch, Styrene-Butadiene Latex, Dextrin, Proteins

### ***Internal Sizing Agents***

Internal sizing agents act to impart a surface optimized for print sharpness by controlling penetration of liquids by changing the contact angle of the surface. Internal sizing agents also improve the surface strength and internal bond values. Sizing agents can be added to the papermaking stock (internal) or applied as a surface coating at the size press located in the middle of the dryer sections. Internal sizing agents can be:

- *Natural rosins* have been used in the acid process for over a hundred years and frequently require a fixative such as aluminum sulphate or PAC (polyaluminium chloride). Rosins are most effective in the acidic pH range from 4-7.5 (with PAC). Cationic Rosins are made using cationic starch or PAC.
- *ASA - Alkenyl succinic anhydrides* contain an anhydride ring to impart hydrophobicity and have a high reactivity with cellulose.
- *AKD -Alkyl ketene dimers* have been used commercially for 40 years, and are synthesized from fatty acids. They are much less reactive than ASA.
- *Cationic starch* is often used in small percentages (1%) in the wet-end to impart strength. Several modifications of starch include cationic, hydroxyl alkyl, oxidized starches and starch acetates. Starch performance is enhanced when poly aluminum chloride is present in the furnish.

### ***Retention and Drainage Aids***

Retention and drainage aids are used to anchor papermaking stock components in the sheet during the forming process, while at the same time promoting the free drainage of water. It is the fines, short fibers, fillers and other wet end chemicals which have a tendency to be washed out as the water drains from the paper mat. In a balanced system, water is released from the stock improving machine speeds and reducing drying costs resulting in a more stable process and a reduction in fines lost to effluent. The success of a retention system depends on several factors including furnish type (virgin or secondary) amount of filler and broke (scrap paper recycled within the mill), conductivity and machine speed. Closed systems produce higher conductivity and greater chemical concentrations.

Retention aids can be based on organic or inorganic chemicals and often multi-component packages. Flocculants adsorb on particles and cause destabilization mainly by bridging or by creating patches of positive charge on the solid surfaces. They carry active groups which counterbalance the charge of the particles. Retention aids from inorganic components are based typically on either aluminum species, on montmorillonite clays or on polysilicate materials. The

aluminum compounds, such as aluminum sulphate (alum), have a coagulating and a charge neutralizing action. The three main types are:

- *Single Component* - Medium to high molecular weight polyacrylamide, alum or PAC may be the single component.
- *Dual Component* - A cationic and an anionic component are added separately. The cationic component can be starch, synthetic polymer or guar gum and the anionic component can be an anionic polymer or a microparticle. The most common synthetic polymers are those based on polyacrylamide. Polyvinyl amines, polyethylene-imines, polyamides-amines, polyamines, polyethylene-oxide and sulfonated compounds are utilized to a much smaller extent.
- *Multi-Component* - Polyaluminium chloride (PAC), polyDADMAC or a cationic resin is added to neutralize anionic substances which can interfere with the retention. Enzyme systems based on cellulase or hemicellulase are also used.

### ***Dry Strength Resins***

Dry strength resins increase the internal bond strength and tensile strength of paper by increasing bonding sites on fibers or by providing stronger bonds. These include:

- Cationic starch - has a greater affinity, being positively charged to negatively charged fibers under standard papermaking conditions. Typical additions in the wet-end of 0.5 - 1.5%.
- Amphoteric starches - are frequently used in multi-component furnishes and are effective over a higher pH range. Starch also is used to improve drainage and retention.
- Synthetic aids - like low molecular weight polyacrylamides increase the strength of the fiber-fiber bond when added at 0.2 - 0.5% dry basis on fiber. These can be cationic or anionic in nature.
- CMC - carboxymethyl cellulose can be used alone or in conjunction with another dry strength aid. CMC increases the negative sites on the fiber which makes it more receptive to cationic starch in later additions. CMC is added in the pulp at levels that are 0.3 - 0.5% per dry basis on fiber.

### ***Surface Treatments***

Sizing agents are used to fill surface voids to optimize the penetration of ink. Surface sizes are applied during the dryer stage. In contrast to internal starch, surface starch, that is applied at the size press, is cheaper (corn-based) but requires more (5%) to reduce viscosity which allows for greater surface coverage. Ethoxylated or oxidized starches and blends of starches with non-

cationic, linear film forming polymers, such as carboxymethyl cellulose, hydroxyl ethyl cellulose, sodium alginate and polyvinyl alcohol are common as is Styrene Maleic Anhydride (SMA), Styrene Acrylic Emulsion (SAE), Styrene Acrylic Acid (SAA) and Polyurethane (PUR).

**Specialty Coatings**

Specialty coatings can contain pigments to impart color or make up for lower performing fibers in sheet stock. Kaolin, ground and precipitated carbonates, titanium dioxides, colloidal silica and borosilicate based microparticles are all commonly used as well as clay varieties such as bentonite. Particle geometry and charge impacts choice and effectiveness of binder to disperse and bind particles for even distribution and maximum loading. Soy proteins are effective binders for a variety of fillers and pigments. Starch, styrene-butadiene rubber latex and dextrin are also used as binders.

Soy proteins can potentially work in the above applications, particularly as part of a dual system to maximize performance. The specialty chemical families that could potentially contain soy protein-based counterparts are broken down in Figure 10.

The cost of use of soy protein as a wet-end aid is currently being evaluated, but the price per dry pound comparisons are shown below.

**FIGURE 10  
PRICE OF EXISTING PAPER CHEMICALS**

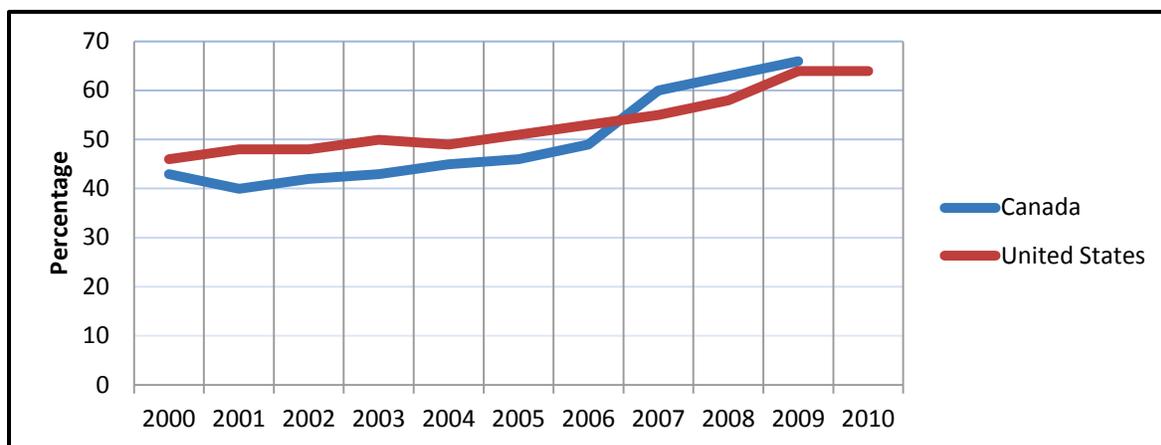
FUNCTIONAL CHEMICAL	PRICE PER DRY POUND	USE
Starch	\$0.20 - \$0.40	Majority of market for strength aid
Polyacrylamide, Modified	\$1 - \$4	Major synthetic strength aid
Polyvinyl Amines	\$5 - \$7	Minor synthetic strength aid
Styrene-Butadiene Latex	\$0.80 - \$1.10*	Major binder in coatings
Soy Protein	\$0.60 - \$2.00	Binders, possible dry strength aid

\* Latex priced at 50% solids

## RECYCLING

The growth of paper recycling has become one of the most significant recent trends in the paper industry creating rising demand for recycled fibers and specialty chemical additives. This is being driven by increasing environmental, regulatory and ecological pressures. In 2009, the paper recovery rate was 63.4% in the United States, 66% in Canada and 72.2% in Europe. About 75% of United States paper mills utilize recovered fiber and 200 mills run totally on recovered paper fiber. However, the percentage of total United States pulp production using recovered paper fiber has plateaued at 37% for the past decade. In 2009, approximately 44 million tons of paper were recovered in the United States with about 25 million tons recycled and 19 million tons exported (RISI World Pulp Annual Historical Data 2010).

**FIGURE 11**  
**CANADA AND UNITED STATES PAPER RECOVERY RATES**



Sources: AF&PA, (United States) Paper Recycling Association (Canada)

The pulp and paper industry is heavily regulated due to the sizable use of chemicals, raw material resources and water. The primary environmental regulations affecting the industry include the Clean Air Act, especially the 1998 “Cluster Rule”, the Clean Water Act, the Resource Conservation and Recovery Act and the “Superfund” Act. These regulations emphasize air emissions and water discharges, especially in pulping and recycling operations.

The use of recycled or recovered paper fiber provides numerous ecological and economic benefits. Recycling reduces demand for virgin tree fibers and tree harvesting. Recycling one ton of newsprint saves about one ton of wood while recycling one ton of printing or copier paper saves about two tons of wood. This is because Kraft pulping requires twice as much wood fiber, since it removes lignin, to make higher quality fibers than mechanical pulping.

Energy consumption can be reduced by up to 65% by using recycled pulp according to the Bureau of International Recycling. Water use by the paper industry is vast but can be reduced by about 50% using recovered paper and by closed-loop recirculation of wastewater. Producing paper from recycled pulp is generally a cleaner manufacturing process which reduces chemical use and cuts the generation of waste. Copy paper made from 100% recycled paper fiber, versus 100% virgin wood fiber, reduces wastewater and solid waste by 50% and particulate emissions by 41%. The recycling of waste paper also saves landfill space and reduces greenhouse gas (methane) emissions from land filled paper by about 38%.

### **Sources of Recycled Stock**

There are three categories of paper waste that are recycled to produce “recovered” paper:

- Mill broke is paper trimmings and other scrap from the manufacture of paper that is recycled internally in a paper mill.
- Pre-consumer waste includes scraps created in a paper mill after the initial papermaking process as well as scraps from paper converters and printers.
- Post-consumer waste includes old corrugated cartons (OCC), old newspapers (ONP) and office/residential mixed paper (RMP).

### **Recycling Process**

Recycling starts with the sorting of waste paper by type: newsprint, magazines, etc. Each type is processed differently as determined by waste (scrap) paper composition and the recovered paper product that will be produced.

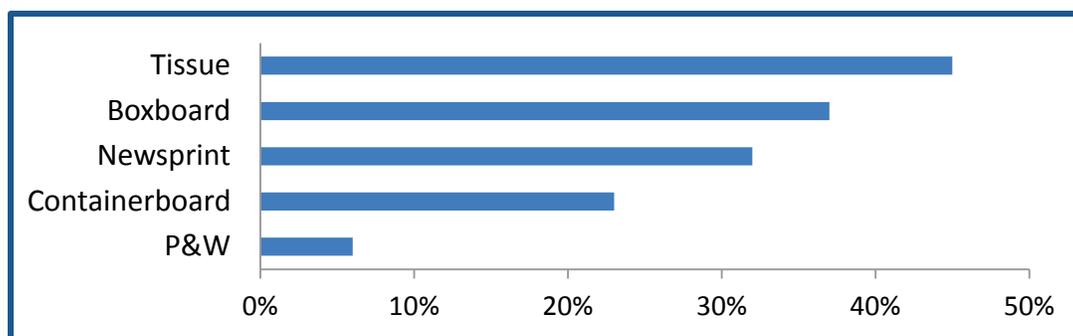
**FIGURE 12**



Recycle processes generally include the following steps:

1. Pulping – Waste/scrap paper is soaked in water and chemicals in a giant blender called a pulper. This breaks the paper down into finer fibers.
2. Screening – The pulp is forced through coarse and fine screens to remove contaminants like clays, wood, plastics, dirt, glass and metals.
3. Centrifugal cleaning – pulp is then spun in centrifuge cones to further separate smaller contaminants from pulp fibers.
4. Deinking – This step involves the removal of printing inks and “stickies” such as glue residues and adhesives by a combination of mechanical action (kneading) and chemical (flotation) processes. With flotation, paper pulp is fed into flotation cells where air and surfactants are injected into the pulp. Ink particles and stickies are dislodged from the pulp fibers and entrained by the air bubbles and float to the surface for removal.
5. Refining, color stripping and bleaching – During refining, the pulp is beaten and washed to make the fibers swell and separate. If the recovered paper is still colored, chemicals are added to remove dyes. A white recovered paper is produced by bleaching with peroxides or chlorine dioxide.
6. Recovered papermaking – Now the cleaned pulp is ready to be made into recovered paper. The recycled fiber can be used alone or blended with virgin wood fibers to provide extra strength or smoothness. Recovered wood fibers can be used five to seven times before becoming too short to be useable in new paper products. Recovered paper with long cellulose fibers provide more flexibility and value for making numerous types of recovered paper. A growing number of mills utilize both recycled and virgin fiber due to consumer demand, environmental awareness and economics. About 75% of United States paper mills utilize recovered paper.

**FIGURE 13**  
**UTILIZATION OF RECYCLED FIBER IN UNITED STATES PAPER PRODUCTS BY SECTOR, 2005**



Sources: RISI 2006 and AF&PA 2005

### ***Chemicals Used In Paper Recycling***

- Pulping
- Deinking
- Stickies removal
- Waste water treatment

### ***Pulping and Deinking***

Chemicals used during pulping and flotation deinking include sodium hydroxide (alkali), sodium silicate, hydrogen peroxide, surfactants and soaps, chelating agents and fatty acids. The alkali helps swell fibers and assists in detaching ink particles from fibers. Hydrogen peroxide is added to overcome alkali yellowing of the fiber interacting with lignin present in the pulp. Chelating agents are used to prevent peroxide decomposition by metals. Surfactants and soaps are used to help agglomerate ink particles so they can be attached to air bubbles and be removed by flotation. Sodium silicate keeps the ink particles from reattaching onto the fibers and also acts as a dispersant and pH buffering agent. Fatty acids (oleic and stearic) additives act as coagulation collectors to assist flotation separation of ink and stickies.

### ***Stickies Removal and Control***

The recycling of paper continues to be plagued by sticky contaminants that cause numerous process problems including deposition on mill equipment surfaces and recovered paper quality problems such as spots and holes in paper sheets. Sticker contaminants are classified into three broad classes by particle size:

- Macrostickies are solid particles exceeding 100 microns resulting from disintegration during repulping. They can generally be removed by coarse and fine screening and cleaning. Major contaminants are hot melt and pressure-sensitive adhesives.
- Microstickies are particles with a size in the 1-100 micron range. Primary sources are small adhesive particles, coating binders and ink resins. Microstickies are generally removed by washing and froth flotation. Seventy percent removal is typical.
- Colloidal stickies have particle sizes below 1 micron and typically consist of insoluble wood resins, styrene butadiene rubber, polyvinyl acetate, latexes and emulsified oils. They are very difficult to remove by traditional mechanical or chemical processes.

**FIGURE 14  
POTENTIAL CONTAMINANT SOURCES IN PAPER RECYCLING MILLS**

<b>Adhesives: Pressure-Sensitive/Hot Melts</b>	<b>Coating Binders</b>	<b>Printing Ink Residues</b>	<b>Deinking Chemicals</b>	<b>Wood Resins, Rosin, Wet Strength Resins</b>
SBR, PVA	SBR	Mineral Oils	Resins	Resin & Fatty Acids
PBD, PIP	PVA, PVOH	SBR,PVA	Fatty Acids	Rosin
EVA	Polyacrylates	Styrene-Acrylates	Metal Soaps	Alum
Polyacrylates	Starch	Polyacrylates	Nonionic Surfactants	Urea-Formaldehyde
PE, PP	Casein	Epoxy Acrylates (UV Cured)	Polyacrylates	Melamine-Formaldehyde
Tackifying Resins	CaCO <sub>3</sub>		Hydrocarbons	
Petroleum Waxes	Clay, TiO <sub>2</sub>			

SBR – Styrene-butadiene copolymers  
PVA – Polyvinyl acetate  
PBD – Polybutadiene  
PIP – Polyisoprene  
EVA – Ethylene vinyl acetate  
PVOH – Polyvinyl alcohol

Since most of the larger particle macro and micro stickies are removed by screening and flotation, colloidal sticky residues remain to be removed or controlled in the recycle process to prevent deposition and clogging of equipment.

Nonionic surfactants are used as dispersants to break up ink and stickies into finer particles during the pulping process to prevent build up on surfaces.

Cationic polymers are used as fixation agents for the anionic sticky contaminants that have previously been dispersed onto fibers. The stickies are also de-tackified to prevent further attachment to machine surfaces.

***Water Treatment***

The paper industry is the largest water user per ton of product of all industrial processes in the United States. Efficient water utilization by treating and recycling process water reduces energy use, improves process performance and product quality. This applies to all phases of paper manufacturing including paper recycling. The use of process chemicals for deinking and stickies control and removal described above improves water reuse quality and concentrates

solid waste (sludge). The increasing use of “closed loop” mill processes will require the use of new, more effective specialty chemicals.

The paper industry uses a variety of cationic and anionic polyelectrolytes for fiber retention, sheet strength, contaminant control and dewatering. The primary polyelectrolytes used are petro-based cationic and anionic polyacrylamides and poly DADMAC (polydiallyldimethylammonium chloride). These additives, especially cationic polyacrylamides (C-PAMs), are used to agglomerate fine fibers and anionic contaminants (small particle stickies) and paper sludge dewatering.

### ***Paper Recycling Chemicals Market Summary***

Growing demand for recycled/recovered paper presents some hope for a depressed United States pulp and paper chemicals market. Recovered paper offers significant cost savings compared to virgin wood fibers as well as numerous environmental benefits. However, lower paper strength of recovered paper requires the use of higher levels of specialty chemicals such as dry and wet strength additives, deinking chemicals and drainage and retention aids.

### ***Pulping and Deinking Chemicals***

- PULPING:
  - Caustic Soda
  - Hydrogen Peroxide
  - Chelating Agents
- DEINKING CHEMICALS:
  - Nonionic Surfactants
  - Sodium Silicate
  - Metal Soaps
  - Chelating Agents
  - Fatty Acids – Oleic, Stearic
- STICKIES CONTROL AND REMOVAL:
  - Nonionic Surfactants
  - Cationic Polyacrylamides (C PAMs)
  - DADMAC (Polydiallyldimethyl ammonium chloride)
- CLEANING AND DEGREASING:
  - Chlorinated and petroleum solvents

**FIGURE 15**  
**MARKET DEMAND FOR PULPING AND DEINKING CHEMICALS**

BILLION POUNDS PER YEAR				
	UNITED STATES		WORLD	
	BILLION POUNDS	% CHANGE	BILLION POUNDS	% CHANGE
2000	4.16		11.5	
2005	4.26	2.4	12.33	7.2
2007	4.34	1.9	12.85	4.2
2008	3.3	-24.0	11.05	-14.0
2009	2.12	-35.7	8.29	-25.0
2010	2.02	-4.8	8.15	-1.7
2015	2.07	2.5	8.75	7.4

The largest volume chemicals used in this product category are the inorganic commodity chemicals used in pulping and beaching of recycled paper - caustic soda, hydrogen peroxide at low concentrations of 1 - 1.5% per ton of dry paper. For deinking and stickies removal and control, sodium silicate is the largest volume chemical used. Nonionic surfactant use concentrations are small at about 0.15% per ton of dry paper, but industry surfactant use volume is considerable.

***Primary Chemicals Used in Paper Recycling for Deinking and Stickies Control***

The use of chemicals in paper recycling is a major operating cost factor and there is widespread industry concern for the drastic escalation and instability of chemical prices, especially petrochemicals. Many of the critical products used in the recycle process are petroleum-based and they have generally doubled in price since 2005. Some examples of these petrochemicals are:

**FIGURE 16**

CHEMICAL	APPL. RATE (LBS/TON OF DRY FIBER PULP)	USE VOLUME MM LBS U.S. EST. 2010	PRICING \$/ LB
Nonionic Surfactants	8-10 lbs/T.	200	1.50-1.70
PAM (Mostly Cationic Polyacrylamide)	1-4 lbs/T.	60	2.00-2.25
Fatty Acids * (Stearic & Palmitic)	2-4 lbs/T.	65	0.70-0.80

## PULP AND PAPER CHEMICAL SUPPLIERS

Top United States suppliers of pulp and paper chemicals are included in Figure 17. The suppliers have a large international presence so global demand will influence the United States based chemical additives. Additionally, global research programs are increasing innovative expansions of specialty chemical use into packaging and other markets.

**FIGURE 17**

CHEMICAL COMPANY	CORE PRODUCT
Akzo Nobel Eka Chemicals	Pulp, Paper, Coatings and Finishing
Ashland Hercules	Paper
BASF/Ciba	Paper, Coatings and Finishing
Kemira	Pulp, Paper
Nalco Holding	Paper
Clariant	Paper

**Akzo Nobel - Eka Chemicals** is a Netherlands based leader in specialty chemicals, paints and coatings with annual sales of \$19 billion in 2009. North America accounts for 20% of sales. Eka Chemicals Inc., within Akzo Nobel, handles pulp and paper chemicals. Eka Chemicals, based in Marietta, GA is the world's leading producer of bleaching chemicals. Eka offers products in almost every segment in pulp and paper additives including EKA RF Series, S-Quad<sup>®</sup>, Eka PAM<sup>®</sup>, Compozil<sup>®</sup>, Purate<sup>®</sup>, Dissolvine<sup>®</sup> and Alcosperse<sup>®</sup>.

**BASF** is based in Germany and New Jersey, had global sales of over \$70 billion in 2009, \$13 billion of which were attributed to North America. The UNITED STATES pulp and paper chemicals group of BASF is part of the Performance Products division with \$1.8 billion in sales from paper chemicals including Luredur<sup>®</sup>, Basoplast<sup>®</sup> and XSB<sup>®</sup>. BASF is a significant supplier of pigments. Specialty additives are also available from BASF through Ciba Holding, a Switzerland based paper chemicals group.

**Kemira Oyj** is a Finnish pulp and paper chemicals supplier with sales in excess of \$3.5 billion, \$803 million of which were North American sales in 2009. Kemira Chemicals Inc. is located in Kennesaw, GA and provides a wide array of specialty chemicals such as Fennobond<sup>®</sup> 400S

strength additive, Lionsurf<sup>®</sup>, Hydrores<sup>®</sup> AS, efficient ASA-based sizing technologies and Hydrores<sup>®</sup> Gamma, a technology that combines AKD and rosin size.

**Ashland** is based in Covington, KY and had 2010 sales of \$9,012 million. Aqualon and Hercules Water Technologies groups provide expanded paper chemical offerings in many process, functional and water management chemistries such as flocculants, dispersants, antiscalants, strength resins, Kymene<sup>®</sup>, Ameristat<sup>®</sup>, Biosperse<sup>®</sup> products DrewfaX<sup>®</sup> and DrewslipS<sup>®</sup>.

Other Companies of Interest:

**Koch Industries** in Wichita, KS with an estimated 2008 sales of \$100 billion, is the largest privately held company. Georgia Pacific LLC is a subsidiary based in Atlanta, GA. Georgia Pacific is one of the world's leading manufacturers and distributors of tissues, toweling, printing and writing paper, linerboard and food packaging. Top brands include Quilted Northern, Dixie and Brawny paper towels. Paper chemical products include internal and surface sizing agents, dry and wet strength resin brands Ambond<sup>®</sup>, Amres<sup>®</sup> and Novaflow<sup>®</sup>. They also provide GP Chemicals LLC performance chemical additives used in the papermaking process. These include rosin based sizes, creping and draining aids and products primarily used in bleached paper and paperboard grades. GP has building products and bleached pulp divisions.

**Buckman Labs** in Memphis, TN is a subsidiary of Bulab Holdings, a leading producer of specialty chemicals to include scale and corrosion inhibitors, defoamers, dispersants, flocculants, retention/drainage, surface sizes, the Mosaic<sup>®</sup> microparticle system, enzymatic fiber modification and Bubond<sup>®</sup> 408 dry strength resins.

**Solae**, a joint venture between DuPont and Bunge, markets soy protein-based polymers under the brand name of DuPont Pro-Cote<sup>®</sup> and is active in supplying the paper industry with soy-based resins for paper coatings.

## **CURRENT SOY MARKETS AND RESEARCH**

### **SOY PROTEINS**

Soy proteins are made up of 18 amino acids that are covalently linked through peptide bonds to form linear polymers with molecular weight range between 150,000 and 600,000 Da. The chemical moieties in the amino acids - carboxy, thiol, hydroxyl and amine groups - give rise to an entangled, globular three-dimensional arrangement of helical coils, beta sheets and folds known as the tertiary structure. In the natural state, polar and charged amino acids are likely to be hydrated at the surface of the globular protein, whereas the non-polar residues stick to each

other and form the core of a protein. However, when subjected to shear, heat, salts and pH variations, a disruption of the 3D structure occurs and the charge distributions can be altered for different behavior. This is known as denaturing and it is essential to have a thorough understanding of this phenomenon to fully appreciate the ability to tailor properties for specific applications. The protein has an isoelectric point of 4.5. Above that pH, soy proteins exhibit a slightly negative charge from carboxy groups, but at lower pH, carry cationic tendencies.

Additional properties of soy proteins that offer opportunities in pulp and paper applications include:

- Strong film forming polymers give strength and heat resistance to product
- Strong cohesive and adhesive bonds formed between cellulose, pigments and minerals
- Amphoteric behavior – possess both cationic (positive) and anionic (negative) charges
- High water holding capabilities
- Ability to function as a protective colloid

Many of these properties have been utilized for years in paper and paperboard applications. Pro-Cote, a soy protein polymer family from DuPont, has been used in coating formulations to improve the flow characteristics, which in turn improves print quality. They are also stiffer, more dimensionally stable and heat resistant binders that can tolerate high speed production.

Extensions of soy protein applications are being utilized in the wet-end of pulp and paper as strength aids and potential dewatering agents for sludge treatment. Existing projects being funded by the United Soybean Board, which address the use of soy-based components in pulp and paper applications, are shown below.

The combination of adhesive strength, stiffness and heat resistance could make modified soy proteins very effective dry strength resins when used as part of a hybrid system in the wet-end of paper and paperboard manufacture.

- USB #0490 - *Soy-Based Paper Mat Wetting Agent*, North Carolina State University. Work has shown promise in the addition of soy proteins in the paper mat during the wet-end of the papermaking process to improve water drainage and resulting paper strength, impacting the expanded use of recycled fibers and water. It is possible that soy protein, in conjunction with other materials, could provide an alternative to the polyelectrolytes based on starch or acrylamides that are currently in use but a more widespread adoption has been limited by price.

The amphoteric nature of protein could expand the capabilities further by modifications of charge densities to impact the retention and drainage of paper mat. These same functions also promote the use of soy proteins for sludge treatment.

- USB #1439 - *Evaluating Soy Protein Polymers for Paper Chemical Applications*, Georgia Tech, Institute of Paper Science & Technology. Working on developing cationic soy protein polymers to replace petrochemical polyacrylamides and DADMAC for fiber fines retention, sludge dewatering and stickies control.

Soy proteins have emulsification and dispersability properties that could be advantageous in surfactants for paper coatings, pulping and in the deinking process for the removal of stickies and ink particles. Soy-based materials would replace a range of nonionic surfactants, amine-based surfactants and polymeric surfactants/dispersants that are currently used in these applications.

- USB #1424 - *Soy Protein Fragments as Hydrophilic Components in Non-Ionic Surfactants*, TensTech Inc. Research on developing a soy protein product to compete with non-ionic surfactants produced using petroleum.

Projects involving *new protein modification processes could produce soy isolates more economically*, resulting in an increased use in pigment coating applications. An additional 25-50 million pounds of soy protein isolates may be possible. Styrene butadiene latex is one of the synthetics used as binder in coating applications. Wildly erratic butadiene pricing may prompt more interest in soy protein substitution in these applications.

## **SOY HULLS/FIBER**

The high alpha cellulose found in soy hulls has the potential to be a cellulose fiber replacement for dissolving pulp applications. Initial research is encouraging, but more data and verification is needed on pulping and fiber properties. Additional pulp opportunities in fluff pulp and market pulp blending may show merit but need to be evaluated for proof of concept.

- USB #1491 - *Utilization of Soy Hulls in the Preparation of High Value Cellulosic Forms*, Custom Solutions Builders. Soy hulls as a source of alpha cellulose for potential applications in dissolving pulp and cellulose fibers.

## SOY OIL DERIVATIVES

Soy-based methyl soyate and new soy solvents for stickies removal and cleaning and degreasing paper machine equipment to replace chlorinated and petroleum solvents.

- USB #2412 - *Soy Methyl Esters Used in Recycled Paper Pulp Cleaning Systems*, Cesco Solutions, Inc. Cesco developed Purrg 200 to remove stickies and Purrg 100 for deinking. Purrg 200 is being marketed in Latin America, China and the Middle East.

Soy oil waxes can provide non-stick and barrier properties for packaging of aqueous products.

Transfer of UV curing resin technology based on chemically modified soybean oil for wood finishes to paper processing. At present these new soy coatings are unpigmented. It is probable that these clear soy resins could be pigmented and used for UV cured colored paper coatings. United Soybean Board funded work at Lehigh and Northampton Community College.

## ENVIRONMENTAL AND REGULATORY

The United States Environmental Protection Agency (EPA) issued national regulations that set pollution prevention standards for the pulp and paper mills in the 1990s. These "Cluster Rules" link two major sets of standards for air and water which restrict pollution by industries that have high effluent/emission volumes. These rules have significantly changed the way pulp can be treated. The Clean Air Act in 1997 mandated chlorine restrictions in bleaching and chemical pulping mills. Elemental chlorine use has been banned and the industry has switched to alternate bleaching and pulping processes involving chlorine dioxide. Maximum Achievable Control Technology (MACT), which limits air discharge of vented gas, has caused conversion to oxygen delignification processes.

Water recycling expectations of mills have emphasized two potential methods. ZEF (Zero Effluent Mill) is a closed loop water system where a complete balance exists between input and output - all water is recycled, reused and cleaned. In contrast, the TEF mills (Total Effect Free) produce effluent, but the wastewater has been treated to meet water pollution standards without the large expenditure required for ZEF.

The 2008 proposed ban on perfluorooctanoic acid (PFOA - Teflon) has prompted research into alternative materials to impart grease and oil resistance to paper and packaging application such as pizza boxes, disposable food containers and pet foods bags. Ashland has been successful in marketing alternatives with no detectable PFOA.

Agenda 2020 created in 1994 as a partnership between the American Forest and Paper Association and the Department of Energy's Industrial Technologies Program (ITP) has the objective of accelerating the research and development of new technologies in the paper industry. Emphasis is on developing processes and technologies that can cut energy use, minimize environmental impacts and improve productivity in industry. Bio-based alternative technologies are sought for evaluation.

## UNMET NEEDS

- Innovative and sustainable alternatives with stable pricing over the long term. The commodity nature of paper markets demands high quality at very slim profit margins. The volatility of petrochemical pricing puts a great risk on profitability from day to day in an industry that requires huge capital investment to maintain and advance pulp and paper processing.
- Alternative sources of cellulose are needed as wood resources become scarce and costly. The high alpha cellulose content of soy hulls makes an ideal starting material for dissolving pulp. Demand growth is forecasted to continue between 3-7% per year.
- Dry strength and dimensional stability additive improvements from cost saving measures such as increasing recycled fiber content and/or thinner base sheet. Stronger resins with enhanced binding abilities in wet-end or coating applications can compensate for strength reduction with recycled fibers.
- Optimization of water resources using effective drainage and retention aids.
- Optimize wet-end components to maximize fiber retention and water removal ahead of dry end for more efficient drying. Existing petro chemicals such as polyacrylamides and polyampholytes are costly.
- Increased deinking mill production capacity. Demand for recycled paper fiber is growing but industry deinking mill production is not keeping pace. The use of recycle pulp varies widely from 45% in tissue products to only 6% in printing and writing papers. There are 17 major deinking mills in the United States that are running at 90% of capacity currently in the face of this rising demand. Additional capacity and better quality fiber production is required to supply recovered paper pulp to more finished paper grades that could use it. This will require the utilization of more effective chemicals to deink and remove stickies from recycled fiber.
- More effective stickies removal processes. Recycle fiber is being recovered at a rate of 44 million tons annually in the United States. Currently, 75% of paper mills utilize recovered fiber and 200 mills are 100% recycle. It is estimated that the economic impact of stickies on paper industry production is \$700-800 million per year. The cost

impact of stickies will continue to rise as lower quality recycle fiber is used to meet growing demand for recovered paper fiber.

- Paper recycling process cost control. The use of recovered paper fiber is more cost effective than using virgin fiber. However, the recycling process requires more effective technologies to produce better quality fibers, improve mill efficiency and reduce energy, water, waste disposal and chemical additive costs.

## **BARRIERS TO ENTRY**

Paper chemical companies handle most paper mill development, as in-house R&D has all but disappeared. A very sophisticated and complex chemical mix from pulping to paper furnish has cultivated a reliance on chemical suppliers for R&D and plant support. Success for a new soy entry would rely on a major pulp and paper chemical supplier to champion the product.

- Bio-based materials make up a significant portion of the existing market. New alternatives must be effective at a reasonable cost of use.
- Large scale processes exhibit a great deal of inertia which resist change. Because of the multi-million dollars in capital equipment and high production speeds, failures can be very costly resulting in a very risk-averse industry.
- Commercial trials can be lengthy and difficult, particularly because a fundamental understanding of all of the factors in papermaking is lacking. An in-depth knowledge of the chemical interactions of solids, colloids and solubles as well as the process dynamics of high speed sheet formation is required in order to meet the chemical and physical demands of continuous wet mat formation.
- Pulp and paper chemical environment involves heated, aqueous slurries with potential for mold growth. Data must be collected to test for and prevent contamination.
- Collection of soy hulls in quantity may prove to be difficult to meet the needs of the industry for alternate source of cellulose, especially as other options may be more readily available. The penetration into some of these markets may be a lengthy and costly process. Cellulose derivatives for tow fiber applications are highly regulated.

## **COMMERCIALIZATION STRATEGIES**

Based on the nature and size of the paper industry, the recommended approach to commercialization of soy products involves three key strategies: the larger commodity markets of paper additives, niche markets and crossover technology transfer.

1. Entrance into the market in established paper chemical segments that are commodity driven, but offer opportunities in very large markets. The current competitive products are both bio-based (starches) and synthetic. The potential usage indicated is based on what is considered to be a realistic targeted degree of penetration of the market segments.
  - Soy proteins as wet-end additives to increase strength and improve other properties of the base sheet. This would most likely involve modified soy proteins in a hybrid system. Estimated potential is 120 million.
  - Soy proteins as a sludge additive in the reclaim process. Potential of 200 million.
  - The additives above would benefit by collaboration with large paper chemical suppliers currently involved in other United Soybean Board technologies including Eka, Georgia Pacific and Ashland. Soy proteins as binders in paper and paperboard coatings. Existing use of proteins for this application could see a two fold increase in demand if a more cost effective protein modification route could be identified. Additional 25 million pounds potential if more economical isolate could be marketed. Soy protein binders for paper coatings are core strengths for Solae and Applied Protein Systems.
2. Increase knowledge and awareness of potential specialty applications that are niche markets but could have a high interest in innovative bio-based solutions or address unmet needs.
  - Soy hulls as an alternative cellulose source in specialty pulps used for disposable wipes and nonwovens. Collaboration with manufactures of cellulosic fibers for filament, staple and tow applications to assess new bio-based alternatives to wood pulp. Estimated potential is 1.2 million pounds.
  - Soy proteins as nonionic surfactants in paper coatings, pulping process and in the deinking process.
  - Specialty coatings like grease proof, barrier coating and thermal papers that benefit from the hydrophobicity and heat stability of soy products such as waxes.
3. Expand existing commercial soy technologies into new paper markets by championing development work with paper chemical suppliers.
  - Soy-based methyl soyate and new soy solvents for stickies removal and cleaning and degreasing paper machine equipment to replace chlorinated and petroleum solvents.
  - Transfer of UV curing resin technology in wood finishes to UV cured colored paper coatings – Lehigh and Northampton Community College.

The success of the above strategies hinge on the continuing support of the following:

- Collaboration with strategic large specialty chemical manufacturers and pulp and paper mills, specifically utilizing long standing relationships with the United Soybean Board in adhesives, fibers, coatings and plastics programs including Ashland, Eka, Georgia Pacific, Cargill, ADM, Solae, Kimberly-Clark, Procter and Gamble and Polymer Group Inc.
- Continued effort to foster associated research and development activities on the interfacial and colloidal interaction mechanisms of soy-based components that occur during paper formation. This includes concurrent work to evaluate reactions of soy derivatives in heated, aqueous environments rich in nutrients, enzymes and possible bacteria.
- Once proof-of-concept is established, assist in connecting resin companies with pulp, paper and paperboard companies with the new soy-based technology sponsored by the United Soybean Board.
- Publicize technical successes at technical conferences including the United Soybean Board sponsored Technical Advisory Panel (TAP) meetings in order to identify potential prospects for the new soy chemistry.

### **PRINTING GRADES**

**Newsprint** - Machine finished paper composed mainly of mechanical pulp, commonly used for printing newspapers.

**Catalog** - Basically lightweight newsprint, but usually contains fillers.

**Rotogravure** - Usually refers to uncoated newsprint type sheet that is highly finished.

**Publication** - Supercalendered and coated magazine papers. Raw stock is composed mainly of mechanical pulps but the best grades use chemical pulp.

**Banknote, Document** - High-grade permanent paper usually made from rag furnish.

**Bible** - Lightweight, heavily loaded paper made from rag or chemical pulp furnish.

**Bond, Ledger** - High quality paper used for letterheads and records. Furnish is either rag or chemical pulp.

**Stationery** - Relatively soft and bulky paper of good appearance. Furnish is usually chemical pulp, but highest quality uses rag.

### **INDUSTRIAL GRADES/ Packaging. Thicker than .3 mm**

**Rag** - High strength paper usually made from highly refined unbleached softwood kraft.

**Linerboard** - Lightweight board commonly used as the liners for corrugated board. Also used for wrapping paper. Formed from high yield, unbleached kraft with a better quality top layer for printing.

**Corrugating Medium** - Used for the fluted inner plies of corrugated board. Usually prepared from high-yield semi-chemical hardwood pulp at nine point thickness.

**Construction Paper** - Newsprint type sheet produced at higher grammage and bulk typically used for kindergarten cutouts and artwork.

**Greaseproof** - Dense, nonporous paper made from highly refined sulfite pulp.

**Glassine** - Produced from greaseproof paper stock by dampening and heavy pressure during subsequent supercalendering. This glossy transparent sheet is used for special protective wrappings and is converted to wax paper.

### **TISSUES**

**Sanitary Tissues** - This classification includes facial and toilet tissues, sanitary products and table napkins. The primary feature is softness and absorbency.

**Condenser Tissue** - Lightweight, well formed tissue (5g/m) made from highly refined kraft, used as capacitor dielectric. Basically the same product is used as raw stock for carbonizing grades and tea bags (with wet strength treatment).

**Toweling** - Creped absorbent paper usually made from lightly refined kraft with the addition of mechanical pulp. Fast absorbency and water holding capacity are prime requisites. Sometimes treated with wet strength resins to prevent disintegration during use.

**Wrapping Tissue** - This designation covers a variety of tissues made for wrapping and packaging merchandise. The general requirements are strength, good formation and cleanliness. Grammage is in the 16-28 g/m range.

## **APPENDIX II**

### **CELLULOSIC FIBER MANUFACTURERS**

#### **Acetate**

Celanese  
Rhodia Acetow  
Eastman Chemical

#### **Lyocell**

Lenzing  
Formosa Chemicals & Fibre Corp. (FCFC)

#### **Modal**

Lenzing  
Century Rayon  
Grasim Industries Limited  
Formosa Chemicals & Fibre Corp. (FCFC)

#### **Rayon**

Lenzing A.G

## REFERENCES

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Freedonia- Focus on Pulp and Paper Chemicals, January 2011

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Environmental Paper Network - State of Paper Industry, 2011

Soybean conversion factors used in this study obtained from

<http://ussec.org/resources/conversions.html>

1 bushel of soybeans	= 60 pounds = 10.7 pounds of crude soy oil = 47.5 pounds of soybean meal = 39 pounds of soy flour = 20 pounds of soy protein concentrate = 11.8 pounds of isolated soy protein
1 metric ton of soybeans	= 36.74 bushels
1 short ton of soybeans	= 33.33 bushels = 0.907 metric tons
1 long ton of soybeans	= 37.33 bushels
1 metric ton of soybean meal	= 46.39 bushels of soybeans
1 short ton of soybean meal	= 42.08 bushels of soybeans
1 long ton of soybean meal	= 47.13 bushels of soybeans
1 metric ton of soybean oil	= 206 bushels of soybeans
Soybeans	= 79.2% soybean meal = 17.8% soybean oil = 3.0% hulls and waste