Semiannual Patents Review
January — June 2001
Marguerite Sykes and Julie Blankenburg

KEYWORDS
Chemical, Contaminant, Deinking, Enzyme, Patent, Reclaimed fiber, Recycling, Review, Stickies, Waste paper

INTRODUCTION
This review summarizes patents related to paper recycling that were issued during the first 6 months of 2001. Two online databases, Claims/U.S. Patents Abstracts and Derwent World Patents Index, were searched for this review. This semiannual feature is intended to inform readers about recent developments in equipment design, chemicals, and process technology for recycling paper and alternative products derived from post-consumer paper. Only brief summaries of individual inventions constitute this review. For more complete information, readers will need to access the full text of a specific patent.

The patents are organized into the following broad categories of recycling: equipment and related processes, chemicals and related processes, products made from recycled paper, and products designed to be more recyclable.

EQUIPMENT AND PROCESSES

Segregation/Shredding/Pretreatment
Critical to all recycling processes is good separation of the desired material. A new approach to separating mixed recyclable materials is described in a U.S. patent (1). Multiple rotating disc screens arranged at various angles and inclines form a screening pattern capable of segregating paper components from mixed recyclables.

A novel industrial shredder containing a specialized shredding head and stripper blades is claimed to prevent or reduce jamming during operation. The shredder is typically used to reduce industrial waste such as cardboard, paper, plastics, and rubber into small pieces prior to processing (2).

A fine-comb-type shredder has been designed to handle multi-layer packaging in preparation for recycling. This piece of equipment has a heavy-duty powered assembly that enables shredding heavy paper, plastic, and other materials (3).

A world patent (4) describes a process and assembly for totally immersing bales of paper or old corrugated containers (OCC) within a pool containing plungers that separate out heavy impurities. Removal of sand, metal, and other abrasive materials during this process prevents damage to the pulper mechanism; soaking also facilitates subsequent pulping.

Continuous processing is introduced into batch repulping of used paper with the addition of a rotating screw to the equipment assembly (5). The screw moves pulp at a constant volume and rate to another section within a rotating tubular reactor. A detailed description of the design of the equipment is included in the patent. Continuous flow of pulp is necessary for constant feed into the papermachine when papermaking is added at the end of a recycling line.

Screening
A novel pressure screening system has been awarded a world patent assigned to Valmet...
Fibertech. The screening apparatus accommodates heavily polluted pulp suspensions efficiently for improved yield. The apparatus does both coarse and fine screening; its design with pulsating pressure permits continuous operation even when any of the screen discs becomes clogged (6).

**Flotation**

Another recently patented process for deinking paper optimizes the flow of air bubbles introduced into the pulp slurry. Mixed papers are slushed by stirring, screened to remove foreign materials such as staples, and finally floated to remove inks, fines, and fillers. The flotation stage is based upon a stream of air bubbles recirculated through the pulp. Ink particles are carried along on the bubbles. A countercurrent flow of water also is recirculated and eventually carries away ink-laden bubbles, separating the clean fibers and fillers (7).

The combination of low- and high-intensity flotation stages offers to improve the removal of stickies and ink particles during recycling (5). According to claims in the patent, the low-intensity flotation works in the gravitational field and the high-intensity flotation in a centrifugal field. These complementary stages effectively eliminate contaminants of varied densities.

Wax-coated papers and containers have caused such major contamination problems during recycling that these materials are usually not accepted by recycling mills. A recently awarded patent for removing wax from fiber used for papermaking, however, may facilitate the reclamation of this fiber source. Cao and Heise (9) found that wax can be removed effectively by froth flotation following low consistency alkaline repulping and screening.

**Alternative Repulping Methods**

Two patents propose a different approach to conventional deinking and contaminant removal. In both instances, conventional process equipment is replaced by alternative equipment to produce recycled fiber. One novel approach is proposed by Chung (10). This process replaces disk refiners, beaters, and kneaders with agitators, then removes fibril fragments from cleaned and screened furnish with a fiber extractor while retaining the short and long fibers for papermaking. Dry-strength additives improve the strength of the final recycled paper.

Another patent features a washing machine as the primary equipment used to recycle cellulose fibers and plastic from discarded diapers (11). Diapers are washed in water, alkali, and soap, which separates the fiber from plastic materials; cellulose fibers are drained from the washer with the water, leaving the plastic in the washing machine. Fibers are pumped to another chamber for further cleaning. This process is also applicable for cleaning other products, such as newspapers, office waste paper, and wax-coated milk cartons and drink boxes.

Useful components from disposable diapers can be reclaimed by another approach described in a Japanese patent (12). The polymeric absorber, polyethylene film, and natural rubber constituents are separated from the fibers, ground, diluted, and sterilized. Solid residues are collected separately after dewatering. Recycling diapers diverts a large quantity of material from landfills as well as conserves useful fiber.

**Water Clarification/Sludge Reclamation**

A world patent targets a critical element in recycling: minimizing fresh water required for processing. Process water used during recycling light packaging material is often contaminated by dirt, food particles, plastics, or metal particles. To minimize addition of fresh water to the system, water needs to be cleaned and clarified before it is recirculated. Cleaning based on multiple physical separation steps, followed by addition of chemicals, biological treatment, sedimentation, and/or flotation for final clarification, is disclosed (13). The closed water circuit requires fresh water intake only when the concentration of dissolved matter breaches a given threshold value.

Ciba Specialty Chemicals Water Treatments Ltd. GB and SCA Graphic Research (14) are the assignees of a process to separate solids from an aqueous suspension containing cellulosic fines and fibers by screening to remove the fibers. The resultant filtrate is floated in the presence of calcium and a flotation aid to reject the hydrophobic material in the froth. The accept fraction containing fines is subsequently concentrated.

Another wastewater clarification patent focuses on process water from deinking and bleaching of recycled fiber (15). This process is based on the addition of swellable polymers containing polymerized vinylamine units into the clarifier to adsorb watersoluble anionic compounds.

A patented process for reclaiming fillers and coating pigments found in sludge from coating plant
wastewater, deinking plants, or internal water treatment plants and for reusing these recovered materials in papermaking has been assigned to Alpha Calcitt (16). Recovered fillers, supplemented by fresh pigments or fillers, are milled together to form a powder and slurried together for reuse as coatings or fillers in subsequent papermaking.

A method for recovering calcium carbonate from waste material is offered by Betz and Blomquist in their recent patent (17). The pH of an aqueous slurry of carbonate-containing material is acidified to approximately pH 4 and later neutralized with a base to precipitate aluminum contained in the suspension. The liquid phase containing calcium is carbonized by the addition of sodium carbonate or bicarbonate to precipitate \( \text{CaCO}_3 \).

**Integrated Processing**

An efficient system for processing waste paper combines both the recycling and reforming of reclaimed fiber into corrugated sheets for linerboard within the same facility. This integrated recycling/packaging plant includes a corrugator and board machine to produce a new product on site (18).

Modeling of performance values that affect the target values for optimal pulp production and papermaking is the topic of a European patent (19). On-line measurements taken at each production stage are used to control chemicals, additives, and energy required based on values obtained through modeling. This patented tool can be applied to recycled paper processing.

**CHEMICALS AND PROCESSES**

**Deinking**

Perhaps the most innovative approach to deinking summarized in this review is the method and apparatus offered by the Xerox Corporation. The system scans a printed sheet, determines the location of printing, and deposits erasing material (typically a white toner) directly over the printing. The erasing material may remove marks from the sheet or may conceal marks with a colored opaque fluid (for inkjet printing) or powder. When a concealer is selected, its color matches the background color of the paper. Because the distribution of erasing material is confined to the printed areas, erasing material is minimized. Conventional copying systems can be easily adapted to accommodate this process (20).

A deinking process for improving ink removal is based on controlling the contact angle of the ink particles and bubbles during flotation with proprietary chemicals. The Kao Corporation has been assigned the rights to this invention, which uses a deinking agent to improve pulp wettability while preventing redeposition of ink particles on the fibers during the ink-stripping stage and a flotation aid that controls the contact angle of the ink particle:bubble interface during flotation (21).

The Oji Paper Company has developed a water-based coating using phosphoric esterified starch as its major constituent (22). The coating is used on newsprint containing deinked pulp, significantly reducing the vessel picking and thereby making the paper better for offset printing.

Nalco Chemical Company has recently been awarded a U.S. patent that covers a novel dispersant useful for controlling wax and other contaminants during paper or paperboard recycling (23). Comprised of a plasticizer, amionic dispersant, wetting agent, lecithin, and a pre-neutralized additive, this chemical mixture offers another option for improving the cleanliness of reclaimed fiber.

Another process and associated chemicals for removing non-impact inks and stickies from waste paper that includes the addition of both a densifying agent and an agglomerating agent to the repulped slurry has been assigned to Westvaco Corporation (24). These agents, added simultaneously or sequentially, precede conical cleaning of the slurry. This process can be used in addition to more conventional screening, flotation, centrifugal cleaning, and washing. If the densifying agent is magnetite, magnetic removal can be used.

Biodegradable nonionic surfactants consisting of both ketal and polyoxyalkylene groups are covered by a Japanese patent (25). They are useful as antifoamers, dispersants, deinking agents, and detergents. These new surfactants claim to be environmentally benign.

A dual surfactant process for flotation deinking is described in a recent patent. The nonionic surfactant used for liberating ink particles is a variation of an alkylene oxide adduct of a fatty acid and an alcohol. It is combined with a cationic compound, an amine, an acid salt of an amine, or an amphoteric compound during flotation for effective ink removal (26).
An interesting aspect of recycling and papermaking is addressed in a patent assigned to Praxair Technology, Inc. (27). Some grades of recycled fiber, especially corrugated, contain a residual aluminum sulfate carry-over from acid papermaking. Excess aluminum sulfate in a finished product reacts with moisture to produce sulfuric acid, which degrades fiber over time or causes flocs in the fiber suspension resulting in poor sheet formation. This patent describes the addition of carbon dioxide to the recycled pulp slurry to lower the pH to a level of acidity that dissolves the aluminum compound to eliminate potential problems.

Bleaching

One limitation to the recycling of mixed papers intended for printing and writing paper is the problem of dyed fibers that remain colored after conventional deinking processes. A new approach offered by Novo Nordisk Biochem of North America, Inc. (28) addresses this problem. Laccase enzymes, along with one or more chemical mediators, are used in the presence of oxygen to decolorize dyed fibers and to facilitate the release of ink from repulped paper furnish.

In a Japanese patent (29), a sterilization deinking method that uses ozone is proposed for recycling used paper. Ozone gas introduced into the pulp shortens deinking process time through the consolidation of pulping, bleaching, and sterilization. Fiberized paper is dewatered and fed into a series of reaction systems where ozone is injected. Conventional chemicals are not required, and the resulting deinked pulp remains stable during extended storage because microorganisms are inactivated and metal ions are already oxidized by the ozone.

Atypical deinking chemicals are proposed in a patent assigned to the University of Florida (30). Fiberized reclaimed paper is mixed with ammonium hydroxide and/or sodium bicarbonate and hydrogen peroxide, which react at the ink/fiber interface to dislodge ink particles from the fiber. Gas bubbles liberated from the reaction with peroxide carry ink particles to the surface for removal in the froth generated. This deinking method is claimed to result in high pulp yield and brightness.

A deinking agent with excellent ink dispersibility and moderate foaming has recently been developed and patented (31). The water-soluble polymer is obtained by graft polymerization of monoethylenic unsaturated monomer to polyether compound. The chemical can be used to effectively deink newspapers, pamphlets, copy paper, or magazines. The resultant regenerated paper has excellent printing characteristics.

An improved method for inhibiting the deposition of adhesive contaminants or hot melts onto the surfaces of secondary paper products and repulping equipment during the manufacture of waste paper products is proposed in a patent assigned to Vinings Industries, Inc. (32). The process is based on a water-soluble dispersant consisting of a hydrophobically modified hydrocolloid or an acrylic acid polymer. The dispersant, guar gum or sodium acrylic acid/maleic acid copolymer, improves product quality and papermaking equipment performance.

Another invention for stickie pacification in recycled fiber is based on multiple flotation steps for removing microstickies (33). A hydrophobized synthetic or natural mineral (zeolite or calcium carbonate) is added in powder form to the pulp slurry after initial flotation. Microstickies remaining in the pulp are absorbed by the mineral and removed in the deinking froth generated during secondary flotation prior to introduction into the paper machine.

PRODUCT DEVELOPMENT

Products Using Recycled Fiber

An interesting alternative to conventional deinking is based on altering preexisting patterns of ink on paper rather than removing the print (34). A chemical activator is applied to waste paper to diffuse the print into aesthetically pleasing patterns; additional inks may be added and further diffused across the paper. The final product can be used for wrapping paper, wallpaper or other decorative purposes.

Lusterless coated paper for gravure printing uses a recycled fiber base sheet (35). The sheet is coated with delaminated clay and a latex copolymer. The resulting paper is opaque, glossiness is under 45%, and printability is excellent.

A unique application for using fragments of waste paper currency is described in a Chinese patent for making a decorative packing box (36). Urea-formaldehyde resin is combined with pulverized waste paper money bits, emulsified with paraffin, cured by the addition of amine chloride, molded,
and pressed while heating electromagnetically. The patent claims that the resultant packaging is rigid, damp proof, and aesthetically attractive.

Recycled paper or cardboard is the material used to construct inexpensive, biodegradable pipes for venting industrial-scale compost heaps (37). The pipes have a series of air holes to meet air supply requirements. The patent claims that the paper pipes function more efficiently than plastic pipes and better withstand the high temperatures generated in the composting process. The desired service life of the tubes dictates the thickness of the pipe walls during construction.

The University of Huadong Science and Engineering has been assigned a patent for using waste paper as filler for plastic composites (38). Slurried waste paper pulp is dried, ground, and modified into a fiber-powder composition prior to being blended with plastic.

A biological approach is employed in a patent for converting recycled paper sludge liquids into a growth stimulant and soil conditioner for vegetable and fruit cultivation (39). Photosynthetic bacteria deodorize and process the waste material simply and efficiently. An enzyme formulation added to the waste material stimulates production of organic acids that enhance the bacterial culture solution. The resulting solution contains bioactive components such as vitamins and pigments claimed to stimulate plant growth and to condition soil.

A unique application has been patented for treating offensive odors from animal stalls, waste deposits, or other contaminated air through biological action on moist waste paper (40). Foul air is passed through a moving bed or screen made from waste paper that supports microorganisms capable of removing odors. A rotating drum-like vessel with a smooth internal surface has a central hole for intake pipes and removal of decontaminated air. High-odor components are successfully removed from exhaust air by biodegradation.

**Miscellaneous Products**

Waste paper is crushed, mixed with a thermoplastic resin, heated, and kneaded to form waste paper pellets used for molding. In one patent, pelleting the compressed materials provides enhanced fiber/resin conformability and permits feeding of the material into the processing equipment at high speed (41). Another product combines recycled paper pulp and special additives to produce a strong molded shoe support (42). An alternative raw material for constructing dwelling modules is produced by mixing equal proportions of paper or plastic wastes with cement (43).

A household gate constructed from recycled fiber is described in a recent patent (44). An inexpensive gate for wall openings is constructed with parallel board panels made from chipboard or plywood. Glued recycled fiber is used for the honeycomb structure between the panels.

Marcel Paper Mills, Inc., has licensed the patent for an absorbent granular product consisting of kaolin clay and waste cellulose fibers (45). The granules can be used to absorb liquids spilled on floors and are crushable when walked on, which prevents slipping.

**Products Designed for Recyclability**

The Campbell Soup Company has licensed a patent for a specialized container for shipping and storing food products (46). The container has two separate chambers: an outer casing and an insulated temperature-controlled container. Dry ice may be placed in the insulated portion to maintain desired temperature during shipment. The patent also covers a method to recycle the shipping and storage containers for individually packaged meals. Empty containers are returned to the provider of the packaged meals, where they are sanitized and reused; damaged containers are sent to the container manufacturer to recycle the outer casing and insulating material.

A world patent offers an alternative for waxed paper packaging suitable for food products. An inside layer of dispersed wax, paraffin, and a copolymer is paired with an exterior coating of kaolin and limestone (47). The patent claims problem-free recycling, low cost, and good grease and moisture resistance. The coatings comply with standards for materials used in direct contact with foods.

A reusable, recyclable corrugated container featuring removable paraffin and varnish layers has been developed (48). The paraffin and varnish layers are attached with a special adhesive tape that permits the layers to be completely peeled off after use. The formulation of the varnished surface contains ethyl alcohol, amino alcohol, glycol, plastic, and a silicon additive.

A recyclable release paper that also claims superior surface smoothness, barrier properties, and...
good adhesion to the silicone-based release film has been developed by a Japanese company (49). A coated film is formed on the surface of a thin, porous-base material for a silicone-based release film. The coating uses a polyvinyl alcohol-based resin as its major constituent and contains an adhesive component. Because the resin displays no thermoplasticity below 150°C, the adhesive can be removed by screening when recycled.

PATENTS CITED


5. Bender, M; Langen, M.; Wulf, G. Tubular reactor for batches of used paper materials from a pulper. WO 200126804 (April 19, 2001).


17. Betz, G.; Blomquist, M. Method of recovering calcium from waste material. US 6193945 (February 27, 2001).


25. Asahi Denka Kogyo K.K. Nonionic surfactants with high biodegradability and cleaning ability without environmental problems bearing ketone polyoxyalkylene groups. JP 2000192076 (July 11, 2000).

26. Iranatsu, Y.; Miyauchi, Y.; Takahasi, H. Wastepaper deinking method using amine or acid salt or amine in the flotation stage. Assigned to Kao Corp JP. US 6251220 (June 26, 2001).


37. Umwelt-EltronikGMBH & Co Ing KG. Industrial scale compost heap comprising a ventilating air supply from biodegradable paper or cardboard pipes. DE 20103750 (May 17, 2001).


43. Sampio Dos Santos. Dwelling construction module ... BR 9803115 (September 19, 2000).

44. Guter, A. Gate for a wall opening which resists torsion forces and is inexpensive. Assigned to Torbau Schwaben. EP 1092830 (April 18, 2001).


47. Novak, I. Material for packing frozen and/or fatty foodstuffs. WO 200121893 (March 29, 2001).

48. Belpack KK. Reusable, recyclable corrugated cardboard box has peeling-off varnish and paraffin to which adhesive tape is affixed. JP 2001080636 (March 27, 2001).