Semiannual Patents Review  
July 2001 - December 2001

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KEYWORDS
Chemical, Contaminant, Deinking, Enzyme, Fiber, Patent, Recycling, Review, Stickies, Wastepaper

INTRODUCTION
This review summarizes patents related to paper recycling that were issued during the last six months of 2001. Two on-line 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 postconsumer paper. Only brief summaries of individual inventions are given in this review. For more complete information, readers will need to access the full text of a specific patent.

EQUIPMENT
Numerous patents have been granted for pulping methods and equipment that are meant to enhance contaminant removal from the recovered paper while minimizing the size reduction of contaminants. The first of these recently issued patents (1) describes a pulping system that minimizes the size reduction of tramp material such as glass, stone, metal, and plastics. The pulping vessel is designed with a helical, downward sloping reject chute along the outside circumference of the pulper wall and at a slightly lower level than the pulping rotor. Centrifugal forces direct the tramp material into this chute and away from the rotor area, preventing any further size reduction. The reject material is continuously removed from the reject chute by a coreless conveyor screw.

The difficulty of recycling polymer and plastic coated papers, UV cured inks, and adhesive containing papers, such as milk and ice cream cartons, can be eased according to this recent patent (2). The pulping occurs in a pressurized, drum shaped vessel. The vessel rotates around a slightly angled longitudinal axis. The recovered papers, water, and chemical aids are agitated by rotation of the drum while at an elevated temperature and pressure caused by the application of steam. The polymeric materials are separated from the fiber and agglomerate due to repeated contact. Small contraries, such as inks and adhesives, are captured by the agglomerating polymer and scavenged from the pulp. This process entails fewer steps and generates less downstream wastes.

The apparatus and process for removing fine impurities from a fibrous suspension involves a sorting device that accepts only desirable fibers and rejects impurities (3). The accepts portion is resorted, segregated further by flotation, and ultimately subjected to a finishing device.

Another patent (4) extends separation even further by segregating white and brown fibers after pulping. A screen drum separates the white fibers that then continue processing by screening, cleaning, deinking, and bleaching. Brown fibers are separated in a second screen drum and are processed separately by screening, cleaning, and bleaching.

A related approach is described in another patent (5). This process can treat baled recovered papers in a pressure vessel in the presence of causticizing agents and deinking chemicals. The intent is to cause the swelling, fiberization, and deinking of the paper prior to transfer to a standard pulper. The pressure vessel can be evacuated prior to the chemical addition to promote the flow of chemicals into the bale. After chemical addition, the vessel can be pressurized with air to promote the penetration of the chemi-
cal agents into the fibers. After sufficient time, the causticizing agents, deinking agents, and released inks are drained from the vessel. The treated recovered papers can be transferred to a normal pulper for further processing. These pressurization steps can also be conducted on partially fiberized pulp in later stages of the recycling system. The potential benefits include reduced bleaching, decreased fiber damage, and minimal or no flotation.

A unique pulper with low operating costs and energy consumption is disclosed in this French patent (6). The cylindrical pulper is divided into a wetting zone, a shredding zone, a fiberization zone, and a clump-breaking zone, top to bottom, respectively. Each zone has an independent rotor and drive at its respective level in the tank and is separated from the adjacent zones by stator elements. The recovered paper bales are loaded into the wetting zone where piston devices break open the bale. The paper travels downward through the different zones before it is extracted out the bottom of the vessel in a fiberized state.

A method for recycling old corrugated containers (OCC) uses flotation and kneading (7). After fines and ink are removed by flotation, pulp accepts are kneaded to further enhance the cleaned fiber. The resulting fiber has improved strength and drainage similar to that of unbleached virgin kraft pulp.

**PAPER SORTING**

Two European patents provide methods for sorting dry, shredded papers via air classification. The apparent intent of each method is the separation of heavily coated papers and foreign matter from the lighter weight papers that will be used for producing deinked pulps.

The equipment and processing steps of the first patent (8) include agitation and mechanical screening stages, size reduction, and air classifications in conical or zig-zag types of air classifiers. The screen sizes and airflow rates are varied at different stages to affect the separation of the desired materials. The size reduction stages are carefully controlled to prevent the contamination of the accept material. The rejects are passed to secondary stages to recover additional material. The final stages of air classification by cyclones are used to remove the dust. The accepts are uniform and of high quality for subsequent deinking.

The second process (9) is similar to the patent just described. The main exception is that an improved air classifier device is used to further process the accept stream. The improved classifier uses a counter-current airflow relative to the accept fraction flow and has variable cross-sectional areas to alter the airflow velocity. The resulting accepts from this process contain minimal dust and have increased whiteness.

**MECHANICAL PULP CLEANING**

An improved, lower cost method for multistage hydrocycloning of recycled pulp is suggested in this recently awarded patent (10). The premise of the process modification is the use of a jet pump for the rejects fraction from the first stage of hydrocycloning. The jet pump uses injected water to provide both dilution and motive force to carry the rejects to subsequent stages of the process. Also, a settling vessel is placed between the jet pump effluent and the second stage of hydrocycloning to provide additional separation of contaminants.

A second patent (11) shows techniques for the removal of microstickies and other impurities in the size range of 150 µm or less, while still recovering fiber. The technique includes the additional step of fine fractionation of precleaned pulp by use of a pressure screen with 0.15-mm slots. The slot size allows small contaminants and fibers to pass while the long, previously cleaned fibers are rejected as the coarse fraction and fed forward. The fine fraction is passed to a flotation cell where the contaminants are floated off, and the fine fiber accepts can be fed forward to mix with the coarse fraction or back to the pulper.

**ENZYMES/ CHEMICALS FOR BLEACHING AND DEINKING**

Enzyme preparations continue to prove effective for deinking and bleaching recycled pulps. Recently issued patents affirm the growing acceptance of replacing chemicals with enzymes for processing recycled fiber.

Use of enzymes for deinking is not a new application. However, this patent (12) targets the point of addition of the enzyme during the recycling process. Application of a cellulase preparation at the kneader or disperser, rather than in the pulper, is claimed to be a more efficient application point for the enzymes. Improved removal of toner inks can be achieved at this point of recycling because toner is continuously released during kneading and can be removed in subsequent washing.

Another application of enzymes in the deinking process is presented in this Chinese patent (13). The methodology involves soaking a crude cellulase preparation in water and applying the resulting cellulase liquor to the fiberized recovered papers in the kneader section during recycling. The pulp is then processed by screening and flotation to complete the fiber–ink separation.
A world patent covering 94 countries has been awarded for a novel process for bleaching colored fiber (14). The process involves adding an oxidizing agent and a water-soluble metallic complex, such as a phthalocyanine, to recycled pulp after ink has been removed. The patent claims to effectively bleach colored fibers in the pulp slurry.

A newly developed polypeptide having alpha-amylase activity could prove useful for recycling starch-reinforced papers when repulped at a pH above 7 (15). The enzyme displays its highest activity at pH 8.5 and at temperatures between 30°C to 75°C but could be used at pH 7 to 11 or higher. The wide pH and temperature ranges are superior to those required by other α-amylases. The enzyme promotes the breakdown of the starch components and subsequent release of inks.

Novel xylanases derived from filamentous fungus or bacterium could enhance the bleaching and brightening of mechanical and unbleached kraft fibers contained in recycled pulps (16). Useful for altering the properties of xylan-containing substrates, these xylanases could promote bleaching of these fibers prior to papermaking.

Applications of both enzymatic deinking and decolorizing paper are addressed in a recently issued U.S. patent (17). Enzymes added into the pulper with fiberized office paper effectively dislodge inks from the pulp fibers. Dyes in the pulp slurry subsequently can be decolorized with laccase in the presence of oxygen and one or more chemical mediators. Previously issued patents focused on either deinking or bleaching recycled fiber with enzyme preparations. This patent combines enzymatic treatments in both stages of processing.

Several newly issued patents offer more traditional deinking and bleaching methods. Deinked pulp of high brightness can be obtained inexpensively according to one recent patent (18). This process applies bleach chemicals in the kneader, followed by tower storage, and then by a second stage of kneading with a shear force and pressure significantly higher than those applied during tower storage.

Another patent covers a novel deinking agent, an alkoxylated nonionic surfactant, as the chemical of choice (19). Use of this surfactant during flotation results in superior ink and contaminant removal to produce a cleaner, brighter recycled pulp.

A method for controlling wax and other contaminants in recycled paper and paperboard is offered in a continuation of US 6273993 granted for a dispersant (20). This chemical contaminant dispersant comprises a plasticizer, an anionic surfactant, an acid or lecithin, and a preneutralized component.

**DEPOSIT INHIBITORS**

It is well known that deposits of resinous materials on pulp and papermaking equipment can be costly to papermakers. Two recently issued patents provide liquid agents for the minimization of these deposits. The first (21) utilizes a solution of condensates of dicyandiamide and polyalkylene polyamine, cationic surfactant, and a nonionic surfactant that is sprayed onto the papermaking equipment. The second formulation (22) uses alcohol ethoxylate and a blend of cleaning solvents. The patent claims that this formulation is an environmentally friendly way to prevent pitch deposition in the felts and pressing equipment.

**RECYCLE COMPATIBLE ADHESIVES**

A pulping agent to improve the removal of hot melt adhesive resins from recovered papers is suggested in this Japanese patent (23). The formulations can include cationic surfactants, water-soluble cationic organic polymers and amphoteric organic polymers. The formulation can also include water-soluble anionic and nonionic organic polymers.

Several patents deal with adhesives modified to make them recyclable. The first describes a removable adhesive applied to a base sheet with a polyvinyl alcohol coating at the interface (24). The recyclable adhesive paper has excellent water resistance, good printability, and is inexpensive to produce. Another invention is for a recyclable envelope sealing method based on a biodegradable resin film on one side and a biodegradable adhesive coating on another side (25). The sealing can be peeled off without damaging the envelope.

Papers coated with hot melt wax are difficult to repulp because these papers were designed to prevent water penetration. An alternative is proposed in which one chemical compound used in the coating serves as a latent dispersant or is capable of being modified to act as a dispersant in an aqueous environment (26). Presence of a dispersing agent facilitates the repulping of these coated papers.

Various approaches can be taken to remediate sticky contaminants contained in recycled paper. This recently patented method (27) also can be used for reducing tackiness associated with coated broke when repulped. The process uses polyvinyl alcohols and bentonite to pacify sticky materials.

**SPECIALTY PAPERS**
A drawback to using water-resistant paperboard for containers is the issue of subsequent recycling. A Japanese patent (28) addresses this issue by describing a method to form a multilayer board that has water resistance yet can be fairly easily disintegrated for recycling. The board is coated on both sides with a synthetic resin that prevents water permeation, and a small amount of wet-strength enhancer is added internally into the stock. The board can be recycled using preset pulper conditions. A potential application of this process is for recyclable containers for frozen foodstuffs.

Ink jet papers could be produced by methods disclosed in two current patents. The first details the process and composition of coatings applied to a base sheet of paper to provide an ink-absorbing layer (29). The top coating consists of colloidal silica, a plastic pigment, and acrylic latex. The bottom side is coated with polyvinyl alcohol or starch. High smoothness, low polish, and recyclability are the benefits of this process. The second patented method utilizes a coating on lightweight recycled paper (30). The coating consists mainly of light calcium carbonate and a binder. The dust-free paper has excellent whiteness, high opacity, and good ink fixing properties.

Recyclable paper suitable for documents, newspapers, and, if laminated, shipping containers (heavier grades) can be made by a process described in a Japanese patent (31). The addition of a polyether amine coating increases both the sizing and strength of the paper. The advantage of this process is a product that provides good wet and dry strength, high permeability resistance, and competitive cost without compromising its recyclability.

A unique use for shellfish shells is presented in a patent for making odor-adsorbing papers (32). The ground shells provide calcium carbonate in the calcite crystal form. When fixed to the paper, the calcite crystals contribute a porous grain property that helps to improve air quality by adsorbing odors and fine particulates in the air.

Rustproof liners can be manufactured from recycled papers by the addition of an emulsion sizing compound and a hydrophobic cationic copolymer, according to this patent (33). The resulting paper has excellent size performance while being easily and inexpensively manufactured.

**PROCESS AND WASTE WATER TREATMENT**

Numerous recently issued patents address the need to treat the process or wastewater from the pulp and papermaking systems. The first is a wastewater treatment process (34) for pulp and paper effluents containing high levels of organics and dissolved electrolytes. The first step of the process entails treatment in an anaerobic reactor where select bacteria convert the organics to methane and carbon dioxide and sulfate ions to H₂S. A portion of the effluent is discharged to an aerobic stripping tank with the addition of NaOH while another portion is recycled back to the inlet. The water in the aerobic tank is stripped with CO₂, eventually converting the calcium ions to calcium carbonate. The water along with the precipitated calcium carbonate is discharged to a settling tank where the water and CaCO₃ are separated. In the case of OCC recycling, the reuse of this water shows improved paper strength properties compared with using white water.

A Chinese patent (35) addresses the issue of lignin in the process water and an electric oxidation method for bleaching these lignin components. The technique uses an electric field generated in the process water that oxidizes and degrades the lignin. The process is nonpolluting and has a high electric current efficiency.

A third water treatment method (36) for process or wastewaters is an improvement to a previously patented process (WO9749639). It is especially useful in partially or fully closed papermaking processes. The treatment system includes pretreatment by filtration, followed by multistage membrane filtration. The resulting purified water can be reused while the residual material is concentrated and combusted without drying. The benefits include reduced fresh water, reduction in biocide dosage, and reduced quantities of waste compared with previous processes.

A Chinese patent for treating wastewater from recycling to reduce its toxicity to the environment features an evaporator to concentrate the water for recovery (37). The “black liquor” generated in the middle stage (perhaps from flotation) is recycled several times before recovery and subsequent use for preparing adhesives or chemical products.

Another disclosure deals with wastewater from the tact of preventing the buildup of undesirable contaminants in the water. The process uses recycled fibers to produce paper or cartons for moist conditions (38). The method uses a formulation of clay, binder, and retention aid to decrease the chemical oxygen demand (COD) of the effluent of the process. The formulation, typically containing cured starch and retention aids, is added to the fiber slurry before formation of the product. The water effluent is low in soluble or colloidal starch.

White water is used for a deinking process using amine compounds (39). This method includes a flotation step in which cationic compounds, amines, acid salts of amine compounds, and amphlytic compounds are added into the white water. A high whiteness pulp results while good fiber yield is maintained.
PRODUCTS FROM PAPER SLUDGE

Several newly awarded patents suggest uses for the rejected solids from the pulp and papermaking process. The first patented process (40) describes how improved zeolite materials can be produced from paper sludge and incinerated ash containing a high level of unburned carbon. Sludge and ash are heated or pressed in the presence of silicic acid or aluminum-enriched materials to improve the ion exchange ability and surface absorption capacity. The process not only transforms discarded materials into a useful zeolite product but also reduces the COD of sludge-containing water.

The second patent (41) suggests an alternative production method for granular absorbent materials from recovered papers containing kaolin clay. The reject stream from the screening process is sent to a flotation unit where the solids are separated from the water. The solids are subsequently dewatered to 35% to 55% consistency, the resulting pad broken into granules and dried. The granules have high absorbency and are free flowing, dust free, and resistant to attrition.

MISCELLANEOUS

Bales of paper destined for recycling are bound with wire or heavy plastic tape. A safer and more recyclable alternative is offered in a patent assigned to Western Paper Wire, Inc. (42). A cord formed by twisting strips of wet lap paper can be used to bind recovered paper bales that weigh about 1,200 lb (544.3 kg). Entire bales, paper cord included, can be dropped into the pulper and subsequently converted into pulp for papermaking.

The last reviewed patent (43) suggests means for injection molding both virgin and recycled paper fibers. Conventional injection molding equipment is utilized with the exception of a molding cavity made of porous material. The porous material allows a path for the water and moisture to exit the compressed fibers.

PATENTS CITED


6. Cherbit, M. Pulp machine for defibrating raw material such as paper, cardboard or cellulose. Assigned to Exportation Matériel Ind. SARL. WO 200138631 (May 31, 2001).


9. Hueskens, J.; Straetmans, K. Method and device for adjusting the whiteness degree of a bulk material consisting of comminuted paper fractions. Assigned to Bueckmann GMBH Tech Gewebe & Masch; Trienekens Sortier & Aufbereitungsanlage; Trienekens AG. WO 200166852 (September 13, 2001).


13. Duan, Y.; Gao, P. Enzyme process of eliminating ink from waste paper. Assigned to Y. Duan. CN 1299902 (June 20, 2001).


36. Maier, J. Waste water treatment, especially for use in the paper industry comprises pretreatment, eg by filtration or complex-former addition, prior to multistage membrane filtration and combustion of residues. Assigned to Maier. DE 10004590 (May 31, 2001).


38. Davey, N. Additive composition for the paper industry, and process for using the same. Assigned to MPC; Resources Chim; MPC SARL. EP 1138824 (October 4, 2001).


43. Bosse, M.; Frommann, L.; Ziegmann, G. Three-dimensional pressure injection molding of paper, for molding paper to complex shapes from fibrous cellulosics suspensions comprises supplying filled suspensions to porous mold. DE 1005793 (June 28, 2001).