Semiannual Patents Review
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KEYWORDS

INTRODUCTION
This review summarizes patents related to paper recycling that were issued during the first 6 months of 1999. The two on-line databases used for this search were Claims/U.S. Patents Abstracts and Derwent World Patents Index. This semiannual feature is intended to inform readers about the latest developments in equipment design, chemicals, and process technology for recycling paper. This review contains only brief summaries of the inventions. For complete information, readers will need to access the full texts of specific patents.

We organized this review into the following broad categories of recycling: Processes/Equipment, Chemicals, Products, Biological Applications, and Efficient Recycling. Some patents overlap several categories by combining a new process with a new chemical or piece of equipment. Others involve additives that enhance the recyclability of the products produced. Inclusive patents are categorized under Efficient Recycling. Note the increase in citations in this patent review that involve agglomeration chemistry and processes designed to deal with the changing composition of the recovered paper stream. We also note the increase in the number of world patents that were issued.

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PROCESSES/EQUIPMENT

Bleaching
A method of oxygen delignification of medium consistency pulp slurry has been developed by Beloit Technologies (1). A slurry of 10-16% consistency, 170-240 °F, adjusted to pH 12 with alkali is thoroughly impregnated with oxygen gas, mixed in a high shear mixer and is held in a pressurized reactor for 5-10 min. The slurry is removed, pH readjusted as necessary, hydrogen peroxide and oxygen is injected, and the mixture is placed in a second pressurized vessel for 30-180 min. It is claimed that the use of hydrogen peroxide in the second, slower bleaching reaction produces a lower kappa number with higher ISO brightness.

Flotation
Research by Deng and Zhu at the Institute of Paper Science and Technology has resulted in a novel modification of conventional flotation deinking (2). Their approach is to introduce the frothing agent as a spray applied only to the upper surface of the pulp slurry in the flotation cell rather than incorporating the surfactant into the pulp suspension during stock preparation. This modification reduces surfactant consumption and facilitates ink removal by maintaining the hydrophobicity of ink particles.

Voith Sulzer Stoffaubereitung GMBH holds the rights to a method for cleaning fiber suspensions (3). This system, based upon successive flotation stages, combines a weak field of gravity with strong centrifugal forces. This design provides efficient separation and removal of solids from a recycled fiber suspension.

The multi-stage flotation column described in one U.S. patent (4) can be used either to deink recycled
paper or treat wastewater. A series of axially arranged draft tubes separated by baffles provides individual mixing stages in the flotation column, creates a loop flow of the feed stock in each flotation stage, and distributes fine bubbles uniformly throughout the column for efficient cleaning.

A novel twist to conventional flotation was devised by Beasley (5). Air is injected into a water-filled tank while waste-containing material is poured on top of the water. Rapidly rising air bubbles provide turbulence and buoyancy to materials that are slightly heavier than water but does not prevent heavier materials from sinking. This apparatus permits simultaneous separation and removal of both floating and sinking contaminants.

Oji Paper Co. (6) holds the Japanese patent for preparing a high whiteness deinked pulp. The process comprises dual coagulation followed by flotation. A cationic coagulant is used in the primary step, and a nonionic hydrophilic surfactant is used in the secondary step. The nonionic surfactant inhibits re-adsorption of ink on the fibers. Small bubble diameter during flotation efficiently removes ink and minimizes fiber loss.

Cleaning/Screening

An alternate system for contaminant removal, screening, and cleaning has also had innovative changes. A patent assigned to Voith Sulzer Paper Technology (7) describes a different approach to conventional screening for separating contaminants from a dilute slurry. Rotation of a pulp slurry concentrates contaminants in the central region of the equipment from which they can be removed. The originality rests in the continuous concentrated contaminant extraction from the central region of the apparatus and “straining” the rejects to reclaim rejected fiber.

Markham and Srivatsa (8) developed an efficient process for recycling mixed paper that includes plastic-coated papers and printed paper. The deinking chemical used agglomerates ink into larger particles that are adsorbed onto the plastic components in the fiberized slurry. The ink/plastic clusters are separated from the fibers. Paper products made from this recycled fiber are also described.

Ikeda and Senbokuya (9) took a novel approach to processing reclaimed fiber. Contaminants are solubilized at elevated temperature within a dilute treating solution and subsequently removed after the addition of another solution, resulting in bright, contaminant-free fiber. The treating solutions contain a citrus (orange) oil, alcohol, limewater, and sodium bicarbonate.

Equipment

A multi-purpose shredder with an adjustable gap between shredding rollers is the focus of Bech’s invention (10). This apparatus can shred either recovered paper or the sludge produced during papermaking and recycling. Shredding and sorting actions are integrated into the same apparatus.

A method for recovering fibers from a reject stream generated during recycling is described in Ahlstrom Machinery’s recent patent (11). Rejects from cleaners in either a deinking system or a papermachine approach system can be fractionated and reprocessed to reclaim good fiber. The coarse fraction, containing most of the fiber and larger solids, is subsequently dispersed and sent back to a cleaner; the fine fraction can be floated to remove ink or other contaminants.

A different approach for making paper from shredded office papers is taken in a Japanese patent assigned to Yokozuka (12). Shredded paper is disintegrated in a series of pulpers and collected into a holding chest where a binder, such as polyvinyl alcohol, is added. The slurried pulp is filled into an injection apparatus, sprayed on to a continuous fibrous sheet where it is remade into paper, dried with a drying roller, and wound into a roll.

An apparatus and method for defibering paper and dry pulp in a substantially dry processing environment has been developed by Dwyer, et al. (13). The method uses a dry processing cell into which cellulose material is supplied. A rotating element introduces turbulent air flow into the cell which causes the cellulose material to circulate and collide with the rotating element, cell walls, and other cellulose matter. These collisions cause defibering of the cellulose material and detachment of fillers, inks and other materials.

CHEMICALS

Surfactants / Agglomeration Chemicals

Several patents cover novel surfactants designed to facilitate deinking or stickie contaminant removal. Henkel KgaA.DE is the assignee of a patent covering chemicals made to control the deposition of stickies from paper stock suspensions during
papermaking (14). These chemicals are alkoxylation products produced by reacting alkylene oxides with carboxylic acids or their derivatives.

IC1 Canada Inc. is the assignee of a deinking process based on repulping without conventional deinking chemicals (15). This method uses a surfactant, a copolymer of ethylene oxide and propylene oxide, to form ink agglomerates that are retained on the pulp rather than removed from the system. The patent claims acceptable brightness and reduced ink sludge.

High Point Chemical Corp. has a new deinking agent comprised of an alkylene oxide adduct of an ester prepared from an unsaturated fatty acid and an alcohol (16). Use of this surfactant for deinking results in a high quality paper sheet with a low ERIC (Effective Residual Ink Concentration) number.

Deinking chemicals continue to be the topic of paper recycling patents. A Japanese patent (17) describes an agent containing a polyether compound and glycerol derivative that is claimed to provide superior coagulation of fine carbon particles. Good yield and foam breakage are two of several advantages mentioned.

A surfactant effective for deinking electrostatic printed ink has been patented by Richmann and Sutton and assigned to Betz Dearborn Inc. (18). The surfactant, a branched alcohol alkoxylate, is used with flotation for efficient ink removal. In another patent assigned to Betz (19), a system in which cationic polyelectrolytes and surfactants are used to remove ink and enhance fiber recovery is described. Especially useful in wash deinking plants, this system combines improved filtrate ink removal and fiber recovery in the dispersed air flotation. When compared with previous processes, the cost of sludge disposal is reduced and filler separation is increased.

An alternative deinking process for reclaimed paper is described in a patent held by Solvay Minerals, Inc. (20). Sodium sulfite, sodium carbonate, and water are added to the pulper, producing fiber slurry with a pH of at least 7.5. A surfactant completes the chemical additives for ink removal in this system.

Srivatsa and Wesolowski (21) developed an agglomeration method effective for removing all types of inks printed by either impact or nonimpact techniques. Their process involves alkaline repulping with one or more nonionic surfactants and/or alkanols. Agglomerated ink particles are then removed conventionally using size and density separation.

Zydex Ind. (22) describes novel functionalized hydroxy fatty acid polymer surfactants and their preparation. These polymeric compounds can be used in various industries including pulp and paper. The patent claims these surfactants have superior surface activity, solubility, dispersibility, and stabilization.

Another agglomeration method for stickie removal is described in a patent assigned to Betz Dearborn, Inc. (23). Slurried fiber is first treated with a surfactant, tackifier, and solvent to agglomerate stickie material and subsequently mechanically separate it from the papermaking fiber. The chemicals used in the surfactant and solvent are either oil-soluble or water-dispersible hydrophobic polymers.

Other novel deinking agents include a compound that demonstrates good cohesion of fine carbon particles, producing high brightness recycled fiber, good yield, and good foam breakage (24). High brightness recycled fiber also results with Kao Corp’s deinking chemicals (25) and process. Ink “peeled” by the use of an alkyleneoxide adduct of a higher alcohol or fatty acid (ester) is removed from the fiber slurry by washing.

**Other Chemicals**

Several patents in this review deal with processes for making and incorporating cationic starches with increased retention during papermaking. In the process assigned to Sanwa Cornstarch Co. (26), a cationic starch is prepared by roasting starch in the presence of a cationic polymer. This modified starch provides high retention in paperboard, enhancing paperboard strength and reducing the wastewater load from the paper machine when compared with conventional starch addition. Roquette Freres FR is the assignee of another paper manufacturing process that enhances starch retention and, correspondingly, the physical properties of paper products. A cationic starch exhibiting a high level of fixed nitrogen and a polyaluminum compound is incorporated into pulp slurries. This process enables good starch retention in systems using recycled fibers and/or with significant closure of the process water. This process is especially useful for manufacturing wrapping or packaging papers or in the fluting or liner of corrugated containers (27).
Dahanayake and Yang (28) invented a compound and process for detackifying adhesive contaminants and pitch encountered in recycling recovered paper by the addition of a water-soluble dispersant. The main advantage of this process is reducing the deposition of adhesive contaminants on process equipment.

PRODUCTS

Paper and Containers

A lightweight <49g/m²) coated printing paper is described in a recent U.S. patent assigned to Haindl Papier GmbH (29). Recycled newsprint is blended with other wood-containing fibers and coated with conventional pigments, sodium bentonite, and starch. Light calendering makes the paper suitable for offset or rotogravure printing.

A unique use for recycled fiber, blending it with processed straw for papermaking, is proposed by Fuller in a world patent assigned to Weyerhaeuser (30). Chopped straw from rye grass, wheat, or other cereals is steam exploded and pressed to separate out lignin and hemicellulose components from the straw fibers. After fiberization, the straw pulp is blended with recycled fiber for papermaking.

Fuji Xerox Office Supply KK (31) is the assignee of a patent for paper containing a high level of recycled mechanical fiber that can be used for either photocopiers or ink-jet applications. Recycling the mechanical pulp introduces a sizing effect that produces a bleed-proof paper surface without requiring a sizing agent.

Several approaches for producing superior paperboard are described in recent Japanese patents assigned to Oji Paper Co. One patent covers a process for producing paperboard from recovered paper (32). This approach subjects alkaline-treated pulp to elevated temperature. The resulting board, containing the treated wastepaper pulp in the middle layer, achieves improved stiffness without increasing basis weight or requiring additional chemicals. The other patented approach uses beating or kneading followed by fractionation (33). After filler ash and fines are removed from the slurry, the recovered fiber is used in the bottom layer of a cardboard product.

Composites

A Japanese patent describes molded composites made from waste materials (34). A heterogeneous mixture, composed of recovered paper, construction waste, earthenware waste, and waste plastics or glass, is the raw material for various useful products.

Wrapping material made with screen rejects from recovered paper is the product Oji Paper Co. targeted (35). Recovered paper is disintegrated and screened to remove foreign materials. Screen rejects are combined with an inexpensive additive to produce a durable cast pulp wrapping.

A Japanese patent uses recovered paper pulp as the primary constituent of a polyolefin composition useful for preventing rust on mould die (36). Pulp and hydrotalcite are the plastic modifiers used with crystalline polyolefin.

Recovered paper, gelatin, lime, casein, and bark from eucalyptus, cedar, or cypress can be combined to form a mulch material. The novel approach of this patent by Obayashi (35) is for environmentally sound weed management: weed suppression without the use of agricultural chemicals.

A process for forming a packing material from recycled paper and the equipment necessary to accomplish this are described in a Japanese patent (38). This energy-efficient process includes grinding of the recovered paper, kneading with adhesive and water, and injection molding the mixture to obtain a compact product.

Building Materials

Recovered paper-containing composites used for alternative building materials are featured in several new patents. The approach described by Alves (39) involves a cement-paper composite that includes a calcium compound. This product exhibits enhanced strength, improved acoustic and thermal insulating properties, and can be used for external facing panels for buildings. Herbst (40) invented a light, granular building material containing recovered paper, corrugated containers, and clay. This material can be molded into blocks, boards, or slabs and pressed and dried at a temperature less than the ignition point of the fibers. It can also be used as a filling or coating material and insulation against sound or extreme temperatures.
Biological Applications

Novo Nordisk is the assignee for three recent patents applicable to recycling recovered paper and in improving papermaking. The first deals with alkaline cellulases derived from the strain *Myceliophthora thermophilapis* (41). These cellulases are effective for deinking recovered paper and enhancing pulp drainage as well as being suitable for textile applications. Starch-coated printing papers can be deinked using another enzymatic approach. This method, invented by Sakaguchi, Sharyo, and Shimoto (42) uses a starch-degrading enzyme, such as an amylase or pullulanase, to disrupt the printing substrate and facilitate ink release. Ink is subsequently removed by conventional flotation or washing. These enzymes can be applied singly or paired with a cellulase, hemicellulase or lipase to further improve deinking efficiency and increase pulp brightness. The third Novo patent (43) represents the joint efforts of a team of researchers. This broad patent covers enzyme modification both by genetic engineering and chemical alteration and offers exciting possibilities for numerous applications in the pulp and paper industry. Enzymes selected for modification to enhance ink and stickie removal include amylases, lipases, pectinases, and hemicellulases. These modifications focus on improved surface activity and performance under alkaline conditions. Derivitized enzymes were found to penetrate fiber walls readily, which will enable more efficient processing and recycling of high yield pulps.

Hans-Peter Call (44) developed a bleaching system with enzymatically produced oxidation agents for the production of highly selective oxidants. This system is composed of a hydrolase, a fatty acid, a precursor-oxidizing agent for reaction with the enzymes, and a ketone. Useful for deinking and bleaching reclaimed fibers and mechanical pulp, this patent claims to be effective in reducing COD of waste liquors. A related patent issued to Call (45) is based upon an enzyme, oxidant, mediator, and co-mediator for deinking and bleaching recovered paper. This patent emphasizes the application to wastewater treatment. The system has a strong, selective oxidizing and bleaching power without the environmental problems of purely chemical systems or the economic limitations of a purely enzymatic system.

The Consortium. Fur Elektrochemische Industrie GMBH holds the patent rights to a new DNA encoding of *Trametes versicolor* laccase protein that offers new possibilities to the pulp and paper industry for deinking recovered paper, polymerizing aromatic compounds in wastewater, and depolymerizing high molecular weight aggregates (46).

Efficient Recycling

Some recent patents deal with products designed to be more easily recycled. One example is a multiply label that has collectible components (47). It was designed to minimize the amount of adhesive applied to a label by positioning the adhesive in “rails” rather than covering the entire label. The construction of the label, two layers of paper secured with a release liner, permits the consumer to remove the “label” and secure it to another substrate.

Avery Dennison Corp. has recently issued three patents for pressure-sensitive adhesives (PSAs) and processes for efficient removal during recycling. Scholz invented a PSA that promotes removal of contaminants from printed paper (48). This adhesive, which is used for labels or tapes, serves as a collector of inks, other adhesives, and plastic fragments and can subsequently be removed by screening and cleaning. The adhesive maintains its integrity under high shear, even under high temperature and pressure. Another patent covers a repulpable PSA for labels and tapes (49). The adhesive composition, a blend of repulpable and non-repulpable acrylic copolymers, is made from inexpensive monomers. The adhesive performs well on a wide range of substrates and has good shelf life, humidity, and age performance, without exhibiting bleed often experienced with water-soluble adhesives. Dennison’s (50) third PSA patent deals with an acrylic-based adhesive formed from sequential polymerization of alkyl acrylates, vinyl esters, and saturated carboxylic acids. This inherently tacky adhesive, made by incremental additions of the component polymers, displays improved properties.

Release liners, such as those on which the PSAs are attached, are frequently silicone coated to facilitate clean removal of labels from the release substrate. One such liner made from a thermoplastic elastomeric olefin has been patented by 3M (51). Because increased use of PSAs will also impact the volume of release liners entering the reclaimed office paper stream, we anticipate new formulations for release liners in the coming year to address the potential problem of silicone build-up.

Progress in Paper Recycling/Northern 1999
Another approach for facilitating recyclability is taken by a patent assigned to Corn Products Int. Inc. (52). A dry blend composition of starch and ground plant germ is used as a complete or partial replacement for corrugating adhesive. The procedure for making the “adhesive” is detailed. Equally unique is Tian’s patent for a screw extrusion-formed packing paper made from soybean dregs, starch, salt, water, plant fiber, and adhesive (53). The paper can be used for disposable paper products that, in turn, can be recycled as either animal feed or fertilizer.

Papermaking with deinked fiber could be facilitated by Albany Int. Corp’s patent for epoxy-silicone coating for paper-machine clothing (54). This durable coating introduces resistance to inks, adhesives, and other polymers present in recycled paper fiber without substantially limiting fabric permeability.

Dainippon Printing Co. has developed a multi-layered paper container for beverage storage that includes a water-soluble resin layer to facilitate separation during recycling (55). A water-soluble resin layer, made by extruding a thermoplastic resin, is positioned between the paper layer and the barrier layer.

A peelable label system is the topic of a world patent assigned to Northstar Print Group (56). The label system comprises a primary label having a release layer on one side and a secondary label temporarily adhered to the primary label by a PSA. It is especially useful as a coupon label in which the coupon is “releasably” attached to a label adhered to a product. The advantage of this label design is that the peelable label or coupon can be removed intact without damaging the primary label or printing on either label, even after aging.

PATENTS CITED


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