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Chemicals, Deinking, Enzyme, Patent, Recycling, Review, Waste paper.

INTRODUCTION

This review summarizes patents related to paper recycling issued during the last 6 months of 1998. The two online databases used for this search are Claim/US. Patents Abstracts and Derwent World Patents Index. This semiannual feature is intended to inform readers about the latest developments in equipment, chemicals, and technology in the field of paper recycling. This review contains only brief summaries of the inventions. Readers will need to access the full texts of specific patents for complete information.

We have organized this review into the following broad categories of recycling: Processes, Equipment, Products, Chemicals, and Biological Treatments. Some patents overlap several categories because they include not only a new chemical or piece of equipment but also a related process. Others facilitate the collection, segregation, and delivery of recovered paper or are additives that enhance the recyclability of the paper produced. These patents are loosely connected in a category called Efficient Recycling. Patents that are outside of these arbitrary categories are listed under Other.

PROCESSES

Deinking

Many advances in deinking have recently been made to keep up with changing toner formulations and the high volume of computer-generated recovered paper present in today's recycled furnish. Westvaco Corp. (1) is the assignee of a deinking process for laser printed and photocopy printed papers. Magnetite and an agglomerating chemical are added in the pulper. A portion of the agglomerating agent can be replaced with a copolymer of styrene and acrylic monomers to further enhance the ink removal. The pulp slurry is subsequently subjected to a magnetic field to remove the agglomerated ink particles. This process can be used singly or in combination with conventional flotation and washing.

Shell Oil has been granted a pair of related patents (2,3) for deinking chemicals for office recovered paper using flotation and washing. Both surfactants are used at alkaline pH. Blanco's patented surfactant (3) contains an additional component, a detergent range alcohol, and is applicable for office paper mixtures containing xerographic printed material.

Electrostatic ink is targeted in BASF's recently assigned deinking process (4). The deinking agent, a combination of nonionic surfactants, is added to an alkaline slurry of paper fibers. The ratio of the nonionic surfactants is adjusted to provide optimum agglomeration of the electrostatic ink. An optional nonpolar solvent can also be added to the surfactants.

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The Oji Paper Co. holds two patents for a multi-stage deinking process. One patent subjects fiberized paper to extended alkaline soaking followed by acidification (5). Next, the particle size is adjusted by agglomerating dislodged ink particles with an ampholytic electrolyte and mechanical stirring to facilitate removal by flotation. The other patent (6) employs "dipping" the fiberized pulp at neutral pH in a phosphate-containing solution. Flotation completes this deinking process. Both processes claim to maintain pulp yield while increasing brightness.

Removal of water-borne flexographic inks from flexo-printed newspapers has been targeted by Rhodia Inc. (7) in their recent patent. Removal is accomplished by a combination of nonionic surfactants, pH adjustments, and polyelectrolyte addition. Flotation with a cationic polymer completes the sequence. Alternately, cationic polymers and a source of calcium, magnesium, or aluminum ions and a defoaming agent can be used in the flotation cell. Reduced emission of volatile organic compounds (VOCs) during printing is an additional benefit.

KAO Corp. (8) uses the addition of a liquid that is immiscible with water at conventional deinking temperatures to separate fibers and detached ink particles from the pulp slurry. Hydrophilic pulp fibers remain in the aqueous phase and ink particles migrate into the added liquid, resulting in low levels of residual ink in the fiber.

Bleaching

Mitsubishi Paper Mills Ltd. (9) has developed a method to combine reductive bleaching with deinking for removal of direct dye during the repulping of recovered paper. When combined with an oxidative bleach step, the resulting pulp is bright and free of ink and tacky substances.

Excluding air during the reductive bleaching of recycled fiber is described in Voith Sulzer Stoffaufbereitung GmbH's disclosure (10). The patent claims both the process and the assembly with a closed and sealed housing in which fibers are dewatered, compressed to high consistency with a conical screw that excludes air. Bleach chemicals introduced under these conditions are more efficiently used, which results in a higher level of brightness.

Stickie Removal

Voith Sulzer Papiertechnik GMBH (11) discloses a novel method of increasing the flotation and removal of stickies from recovered paper slurries. The method includes a pretreatment step where stickie particles are modified to facilitate removal by flotation.

An alternative for dealing with stickies is to send residual stickies out with the deinked fiber. BASF AG (12) has developed a process for pacifying stickies by adding surfactants and cationic polymers in order to "fix" these dissolved impurities in the finished paper product.

Process Control

Siemens has been issued three patents for sensory equipment and a technique to automate the production of deinked pulp (13, 14, 19). A spectrometer is used to take spectra from at least one point, and discrete mechanical and/or chemical and/or electromagnetic radiation data are derived. The process is then modeled and controlled using variables, such as the ratio of white to colored paper, the ash content, and adhesive contaminants, to optimize the process. This technique has been extended to include both continuous and batch processes.

Flotation sensors are used in a flotation process created at Beloit Technologies Inc. (16). A multiframe pressurized deinking module that has been fitted with flotation sensors allows the foam head to be maintained at stock level. Air injection ports are used to control the amount of foam generated and the amount of ink removed.

EQUIPMENT

Separating ink particles from valuable fibers contained in flotation rejects is an approach Voith Sulzer Stoffaufbereitung GmbH (17) exploits to improve pulp yield. The foam fraction from the flotation cell is filtered through a wet sieve unit that separates a fiber-containing coarse fraction from the ink-containing fine fraction. The coarse fraction is further clarified to reclaim fibers that are essentially ink free.

Bolton (18) has designed a washer, thickener, and classifier for recovering fibers from slurries. A conical screen retains fibers cleaned by sprayers situated within the cone and rejects unwanted

solids and contaminants through the screen. The cleaned stock exits at the apex of the screen for subsequent processing.

Several patents deal with equipment designed for fiber segregation and classification. Bulk Handling System is the assignee for an apparatus (19) that does bulk separation with a series of disc screens positioned in several sequential stages. Debris is agitated and moved along a shaft; ultimately, large particles of debris are discharged from the unit.

Ishikawajima K K JP (20) is the assignee for the separation of contaminants and defibration of unfiberized paper in a single unit. Stock that does not pass through the main screen plate is passed through a defibering section and is further separated. Only the stock ultimately remaining on the screen plate is rejected from the system, thereby optimizing fiber yield.

Another apparatus for treating slurried recovered paper composed of fibers of various lengths and types of impurities has been patented by Alfa-Laval Celleco (21). The fiber slurry is sprayed through a gaseous medium on to a screen that separates long fibers and large impurities from small fibers and fine impurities.

Modification of the pulper rotor design to enhance pulp flow rate is the focus of Cellwood Machinery's patent (22). Tapered helical blades are joined to winged edges that generate pressure pulses to force pulp through the adjacent screens preventing clogging. This design facilitates the flow rate of high recycled content furnishes.

BIOLOGICAL TREATMENTS

A biological deinking method developed by Ow and Eom (23) that replaces conventional deinking chemicals with an enzyme preparation is described in their patent recently assigned to KRICT Rep. of Korea. The preferred enzymes are acid resistant carbohydrases. The enzyme preparation is added into the pulper at a pH <7 and a temperature at which the enzyme is active, <60 °C. Flotation or washing removes the dislodged ink from the fiber slurry. This method is effective for deinking newsprint as well as laser or xerographic printed office papers.

Neutral enzymatic deinking of recovered office paper is accomplished with the addition of a proprietary nonionic surfactant described in Asbrand and Jobbins recently issued patents

(24,25). The surfactant is added into the pulper along with an enzyme preparation active in neutral pH range on fiberized recovered paper. Ink is then removed by flotation and washing.

An unidentified enzyme preparation is combined with a surfactant in Lion Corp.'s (26) recent patent for the deinking and regeneration of recovered paper. Nova Nordisk DK (27) holds the patent rights to the method of bleaching of either a lignin-containing pulp for papermaking or decolorizing wastewater from pulp manufacture. Laccase, or an enzyme related to laccase, is used with a mediator for dye removal or the enzymatic polymerization or modification of lignin, facilitating color removal.

Lipase enzymes are used for the enzymatic degradation of biodegradable polymers used in recycling paper containing adhesives used for coatings and laminates in Bayer AG's patent (28). Often one or more lipases are used in combination with other enzymes to degrade adhesives or binders used in papermaking.

Filamentous fungi are used to clarify wastewater in a biological method described by Ishikawajima Harima Heavy Ind. (29). The fungi, introduced via an aerator, promote oxidative decomposition of organic matter contained in the water from various processes including papermaking. These fungi are recovered on a mesh-like screen and recirculated back to the aerator.

A novel biological approach by Canada Min Agriculture (30) links soybean seed coat peroxidases to recovered paper deinking. Soybean coat peroxidases are useful industrially because of their high thermal stability, even at extreme pH levels. The seed coat peroxidase isozyme has been purified, and it is possible to express this gene in transformed cells using recombinant DNA. These peroxidases can replace chlorine bleach in the paper industry as well as serving as an effective deinking agent for printed recovered paper.

CHEMICALS

Various new surfactants for facilitating flotation deinking continue to appear in the patent databases. Lion Corp. recently had two patents for deinking chemicals issued. One such polymer designed for improved ink removal and brightness contains ethylene oxide, alkylene oxide, and propylene oxide units (31). Another deinking agent that is used at ambient temperatures eliminates the need for a heating facility, or saponification facility

(32). It contains a polyphosphoroso carboxylic acid, its salt or amide compound, alkali earth metal, ammonium, amine, or hydrogen.

Nippon Oils & Fats Co. Ltd. has patented a deinking chemical that comprises a copolymer of an alkenyl polyoxyalkylene compound, maleic anhydride, and an oxyalkylene compound (33). It is capable of producing a deinked pulp that has a high level of brightness with very little residual ink. Henkel KGAA (34) has been assigned the patent rights for a deinking agent composed of alkyl polyglycoside(s). The alkyl polyglycosides are effective for use on a wide range of recovered paper.

A resin designed to enhance the strength of recycled fiber containing furnishes has been assigned to the Weyerhaeuser Co. (35). The additive is a cationic wet-strength resin that especially improves dry strength without adversely affecting subsequent repulpability. Up to 30% of the furnish is treated with the resin and allowed to bond to the fiber before mixing with the untreated balance of the furnish at a point prior to the paper machine.

New methods of preparing silicon dioxide compounds and silicon peroxo-acids have been discovered by Koenigstein (36). These compounds are obtained by reacting silanes with hydrogen peroxide and are used as oxidants for a variety of bleaching applications including bleaching pulp, recovered paper, and in treating waste liquor. The advantage of these compounds is the versatility, cost-effectiveness of manufacturing, and the ecologically harmless degradation product (silica).

Recycled Products

In the past 6 months, several products have been developed that incorporate recovered paper and papermill waste. The Fort James Corp. has acquired a patent (37) for a one-ply paper tissue product and method of making this product that combines high strength and softness as well as low sidedness. Another paper product, a coated glossy paper, has been patented by Nippon Seishi KK (38). It is produced by coating a wood-free base paper with a mixture of pigment and adhesive. This method produces a product that has superior brightness, glossiness, and surface strength. Recycled paper is also used in a food-grade container patented by Tenma Seishi KK (39). Fujimasu Sogo Kagaku Kenkyusho KK has patented a method of making a fireproof board that is made by IR irradiating a board made of recovered paper, wood or plastic, and a tie-resistant additive (40).

Several novel products using paper waste have also been developed, ranging from soil improvement to bowling pins. Ube Nitto Dasei Co. has found a way to recycle a fiber reinforced thermoplastic heat-molded product into a resin product using melt extrusion (41). A molding that utilizes recovered paper has been assigned to Tamai Kankyo System KK (42). Bondarenko et al. (43) have found a way to incorporate ground paper, paper manufacturing waste, and thermoplastics into a composite building material. Paper waste and fly ash are used to make a pelletized soil improvement material in a process patented by Hedstroem and Henningson (44). Tsumoto Presentation KK (45) has incorporated waste materials such as thermoplastics, old paper, and wood into an outer covering for a bowling pin. Finally, Linhares (46) has patented a briquette and method of producing a briquette made of paper, cardboard, charcoal waste, old tires, and other waste materials.

EFFICIENT RECYCLING

Several products have been designed with ease of recyclability in mind. Two new chemical adhesives and an adhesive tape top the list. BASF AG has designed a self-adhesive coating that is easier to recycle than present coating compounds (47). Similarly, Saiden Kagaku KK has developed a water-redispersing tackifier composition for use in tack paper and pressure sensitive adhesive tapes (48). A patent by Beiersdorf AG describes a repulpable adhesive tape for reversible bonding that is useful for flying splice and manual splicing in the paper and printing industry (49). The adhesive is a polyacrylate dispersion that can be applied and removed without damaging the paper.

In a patent assigned to Sato (50), a product for collecting recovered paper is described. It is an extendible paper pack container that saves time and storage space of recovered paper as well as improving the efficiency of recycling. Britton, Warsing, and Woodward (51) have developed a self-contained transportable unit that sorts recyclable materials into segregated bins and compacts them. This unit could be useful for collecting recyclable waste on passenger trains, aircraft, or ships and moving it to respective recycling sites.

MISCELLANEOUS

Two patents have been issued to aid in recycling specialty papers. A collaboration of efforts between Inland Paperboard & Packaging Inc. and Thermo Black Clawson (52) has produced a method for recycling wax-coated paper and cartons using high

temperature and a series of reverse pressure screens. Andreoli et al. (53) have patented a process for recycling paper containing formal-melamine-based chemical additives that are used to impart water resistance to paper. The process comprises treatment with alkali at 60°C to 150°C.

A process involving the separation and separate treatment of short and long fibers has been patented by Lindahl (54). At least one of the fractions is treated with an enzyme followed by an alkali. Other suitable treatments include phosphates, surfactants, and chelating agents. This process can be carried out using existing equipment and has the advantages of maintaining the long fiber length and reducing electrical consumption for the pulping process.

Kurita Water Ind. Ltd. has devised a wastewater treatment that uses sodium nitrate at ambient temperature and a primary flocculent to separate it into a solid and a liquid phase (55).

Finally, a method for dewatering deinking sludge using a water soluble block polymer has been issued to BetzDearborn Inc. (56).

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