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INTRODUCTION

This review summarizes patents in the area of paper recycling that appeared during the first half of 1998 in either of two on-line data bases: Derwent World Patent Index or Claims/U.S.Patents Abstracts. The information in these data bases is intended to keep readers informed about the latest equipment, chemicals, and technology in this field. The abstracts provide only a brief summary of the inventions. Readers will need to access the full texts of specific patents for complete information.

The patents summarized in this review cover a broad spectrum of recycling processes, equipment, and products made with recycled fiber. Some patents deal with additives to adhesives and papermaking materials that make adhesives easier to remove during recycling. Others address the environmental impact of deinking effluents and solid waste resulting from recycling.

DEINKING PROCESSES

The KAO Corporation has been issued five new patents that focus on various mechanisms to improve flotation efficiency. One method controls the interracial charge potential between ink particles and pulp by adjusting the pH of the slurry or adding an inorganic electrolyte [1]. Another method controls the contact angle between the aqueous solution and the ink particles [2]. This patent claims that flotation is most efficient when the contact angle is at least 70°, which is accomplished by adjusting slurry pH or adding silicon- or fluorine-containing organic compounds and fatty acids. In a third patent, flotation is enhanced through adding cationic, amine, and ampholytic compounds to process white water [3]. Flotation efficiency can also be improved by adding fine particles with a hydrophobic phase boundary [4] or by changing the pH several times during the flotation process [5].

The Sunds Defibrator facilitates flotation through equipment design [6]. The flotation tank inlets are positioned so that the incoming jet of pulp slurry and gas bubbles does not break the suspension surface, ensuring good separation even at increased slurry concentrations and a short. retention time in the flotation cell.

In a patent issued to the Thermo Black Clawson Company, flotation is used following the pulping and beading of mixed recovered papers [7]. After high consistency kneading, the paper stock is diluted and separated by flotation and washing to remove different types of inks. No additional dispersion step is required prior to bleaching or papermaking.

Agglomeration chemistry is used to separate ink particles from fiber in a continuous batch recovery system in a patent assigned to the Pellerin Milnor Corporation [8]. A combined deinking/agglomerating/densifying agent is added during the fiberization stage, which is followed by washing and ink separation.

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Union Camp Corporation targets stickies for agglomeration with one or more long-chain alcohols and then removes them by mechanical filtering [9]. The corporation has found that long-chain alcohols used at pH 7 or above effectively agglomerate stickies. PPG Industries Inc. simultaneously controls flotation froth and reduces stickies by using a nonionic surfactant alone or in combination with other deinking chemicals or other froth-moderating agents [10].

Allied Colloids Ltd. has patented a process to separate cellulosic solids from aqueous suspensions by dispersed air flotation [11]. After coarse fibers are removed by screening, the suspension is subjected to dispersed air flotation in which various additives are used to separate hydrophobic material (fillers) from cellulosic fines.

High Point Chemical Corporation has developed a process that can both enhance brightness and remove ink efficiently [12]. The method uses an alkaline earth metal tallate prior to flotation. The tallate, a dispersion prepared by double displacement, increases pulp brightness by more thoroughly removing ink and other contaminants contained in newsprint, colored printed papers, cardboard, and magazines.

In a process patented by the Valmet Corporation, two pulpers operating at different consistency levels (high and low) are linked in sequence [13]. After the pulp goes through the secondary low-consistency pulper, it is screened and screen rejects are recycled to the primary high-consistency pulper for additional processing before passing through the deinking system.

Voith Sulzer Stoffaufbereitung has patented a process for recovering paper fiber and plastic material from fast food waste [14]. Plastic plate material is disintegrated with hot alkali and later precipitated and reclaimed; food particles and other contaminants are removed by flotation. The separated paper fiber is bleached to remove residual color and residual printing inks.

A process for decolonizing brown fibers in recycled pulp based on fine screening for fiber separation is covered by a patent assigned to International Paper Company [15]. Screened brown fibers are sequentially bleached with oxidative and reductive chemicals at high temperature in a pressurized dispersion unit and recombined with the deinked pulp accepts.

Another process with environmental implications involves deinking solutions containing hydrogen peroxide. A patent assigned to Sued-Chemie minimizes the quantity of sodium silicate required for stabilization and reduces puiping alkahnity to less than pH 9, thereby decreasing the amount of peroxide needed to prevent brightness loss [16]. Ink is separated by flotation using a cationic surfactant.

EQUIPMENT

Two pieces of equipment invented by Lindahl, a dewatering press and a device to measure drain. age, can be used in recycling. The dewatering press extracts liquid from partially dewatered material (such as sludge or pulp) with absorbent felt rollers and several press nips [17]. The drainage device, which is designed to simulate paper machine conditions, has a cylinder for measuring drainage and a hydraulic cylinder for measuring the resilience of partially dewatered material [18]. Drainage properties can be measured quickly, without having to make handsheets. This device could be used to study the effects of different chemicals on drainage, compressibility, shrinkage, or wet bulk.

Thermo Fibertek Inc. has patented an apparatus for washing, thickening, and solids recovery that uses rotating wash sprays to facilitate removal of contaminants and fillers through screens [19]. This apparatus is less bulky than the equipment usually required to handle high-solids furnishes at a high removal rate.

A recovered paper baler equipped with a shredder and high friction rollers designed to compact material into compressed bales without the need for strapping is described in a patent assigned to Star Farm Machinery Manufacturing Company Ltd. [20].

Cellwood Machinery has patented a temperature-controlled reactor screw and related process for bleaching recycled pulp [21]. After dewatered fiber is steam heated and dispersed in a disperser unit, it is compacted in a screw press or plug screw to which oxidative or reductive bleach agents are added. Appropriate bleaching temperatures can be maintained in the unit for each bleaching stage used. No auxiliary devices are required.

ENVIRONMENTAL

Effluents

Several patents aim to improve bleaching of recycled pulps through chelation. Kemira Chem Oy has developed new biodegradable, low nitrogen-content bis or tris dicarboxyethoxyethyl amine derivative chelators [22]. Unlike the commonly used chelators that do not degrade readily in watercourses, these new compounds should be more environmentally acceptable. Sunds Defibrator has taken a different approach by using conventional chelators to bind metal ions [23]. In this process, the chelation liquid is separated and oxidized before being returned to the pulp slurry. Since the bound metal ions are removed from the process water, it can be reused. The environmental advantage is the minimization of water discharged from this process, a plus for the trend toward closing the white water system.

Recycling often adds color, contaminants, ash, and turbidity to process waters. Four patents focus on effluent clarification. General Chemical Corporation has patented a process for using alum-containing process residues, a papermaking by-product, to remove color from effluent [24]. The addition of up to 5 ppm of a polyelectrolyte polymer improves the removal of color and turbidity as well as enhances the settling rate of solids.

Nalco Chemical Company has developed a hydrophilic dispersion flocculent for clarifying ink-laden water from deinking [25]. The flocculent is a copolymer of dimethylaminoethyl methacrylate methyl chloride quat (DMAEA A LMCQ) cationic monomer and acrylamide (AcAm). This dispersion flocculates ink and other suspended impurities, which can then be removed from process water by dissolved air flotation.

ECC International Ltd. describes a process for removing solids, ink particles, and calcium compounds from deinking effluents in their recently, granted patent [26]. The process dilutes and solubilizes calcium solids and separates out undissolved residues. Removal of these solids from process water contributes to brighter, higher grade recycled fiber, which could reduce bleach and additional process requirements. A clarified effluent also reduces environmental impact.

A closed-circuit paper mill effluent treatment process developed by Maier minimizes the discharge of organic residues [27]. To oxidize solids prior to nano-filtration, suspended solids are diluted at acid pH and elevated temperature. This process is especially useful for treating organic substances in effluents from the production of colored paper, tissue, and cartons.

Sludge Treatment

A patent issued to Minerals Technologies Inc. describes a process for recycling mineral fillers from deinking sludge [28]. Filler residues are oxidized at high temperature, releasing carbon dioxide, heat, and water. These products can be captured and reused in the process. Ashed particles are subsequently reacted with an aqueous slurry of calcium hydroxide into which carbon dioxide is bubbled to precipitate calcium carbonate (PCC). The recycled PCC, using mineral ash as the crystal "core", has properties similar to those of virgin PCC.

BIOLOGICAL APPLICATIONS

Biotechnology continues to make inroads into the pulp and paper industry. Four new patents for enhancing freeness, increasing brightness, and improving deinking appeared in the data bases searched.

The International Paper Company holds a patent for treating recovered fiber with an enzyme mixture to enhance pulp freeness while maintaining brightness and strength [29]. Deinked pulp is treated at low consistency with celulase, xylanase, and pectinase for several hours. These enzymes eliminate the need for polymer drainage aids and addition of softwood pulp in papermaking.

Novo-Nordisk describes a new endo-gluconase from *Cellvibrio* species and related DNA that can be used for deinking and improving the drainage of recovered paper [30]. The presence of other enzymes such as xylanase and lipase could also provide other benefits for recycled pulp. The unique advantage of the endo-gluconase preparation is its broad cellulolytic activity over acid, neutral and alkaline pH.

A different biological approach is taken by BK Ladenburg in their patent for maintaining pulp brightness during flotation deinking [31]. A bacterial (Bacillaceae or Pseudomonadaceae) suspension is added to recovered paper after repulping with alkaline peroxide. After incubation, the bacteria-containing pulp slurry is floated with fatty acid agents.

A new *Chysosporium lucknowense* strain, and the neutral or alkaline cellulases produced by it, comprise another claim [32]. Enzymes isolated from this wild-type or mutant *Chrysospotium* can be used for deinking and bleaching recovered paper at neutral or alkaline pH.

A patent issued to BASF AG describes the use of a different type of chelating agent based on disuccinic or diglutaric acids [33]. These amino-acid chelators have been used in washing agents, but they can be applied to the deinking and bleaching of recycled fiber. Their use eliminates the need for silicate in these processes.

CHEMICALS

Several new chemicals for deinking and papermaking with recycled fiber also appear in the patents reviewed. These patents address the continuing problems caused by stickies and inks, especially in regard to pulp brightness.

A deinking agent consisting of maleic anhydride and a copolymer has been developed by Nippon Oils and Fats Company Ltd. [34]. When this agent is used to deink newsprint and office paper, frothing is minimized during flotation and the resulting pulp is bright.

Zuckerforschung Tulln GMBH has developed a modified starch that is effective when used in combination with cationized amylopectin starch and either ASA or AKD for paper sizing [35]. The polyelectrolyte properties reduce the formation of stickies and eliminate the need to add alum to systems with high calcium content. This modifed starch is effective on furnishes with a relatively high fraction of recovered paper.

PRODUCTS

New recyclable products predominate in this category. Three repulpable pressure-sensitive adhesives (PSAs) and one thermoplastic adhesive head the list of new products. Avery Dennison has patented a multi-layered PSA made with two types of laminates: a tacky polymer layer that is not dispersible in water and a tacky water-dispersible polymer layer [36]. The dispersible layer is positioned closer to the facestock than the nondispersible layer, thereby improving both adhesive performance and recyclability. Another PSA, used for labels or tape, has a silicone-free release coat made of polyacrylonitrile-polybutadiene copolymer [37]. Finally, Saiden Kagaku has patented a water-dispersible PSA consisting of a mixture of an acrylic acid alkyl ester, vinyl acetate, acrylic acid, and caprolactone adduct of acrylic acid [38]. Since this PSA can be repulped readily with pulp, the usual stickie problems can be avoided.

A thermoplastic, biodegradable, starch-based adhesive has been designed for use on paper, glass, or polyethylene recyclable or biodegradable packaging and labeling [39]. The precursor for making this adhesive can be sold as a solid material (granules, strands, or sheets) and is converted to a low viscosity, degradable adhesive only during use.

Another common venue for new products included in this patent review is recyclable containers. Dainippon Printing Company, Ltd. has patented a recyclable paper carton for storing fluids [40]. The container includes an alkali-soluble resin between the paper and gas barrier layers. This construction allows the paper layer to be peeled away for separate processing.

Bloch and Finestone patented a high-strength sealing tape for cartons that is designed to be stripped entirely from the carton for reuse or recycling [41]. The surfaces of the plastic film base layer are treated with dual corona discharge, which enables one side of the paper to be bonded with water-based adhesive and the other side with water-remoistenable adhesive [41].

A novel use for recycled paper is as an oil-absorbing material [42]. Fiber is mixed with an aqueous solution of a lipophilic resin made by polymerizing fatty acid with an emulsifier, surfactant, and water. The resulting mixture is dewatered and hot pressed at a cross-linking temperature to produce a felt-like sheet.

Finally, sludge from papermaking seines as a replacement for fiber in multilayer paperboard [43]. Paper sludge is mixed with an adhesive and fiber suspension in acidic or neutral medium. A flocculent is added to promote retention of filler on a paperboard machine. The board has multiple layers and weighs between 450 and 5,000 g/m^2. The advantage of this patented product is that it uses waste materials.

PATENTS CITED

1. Irinatsu, J.; Miyauchi, Y.; Takahashi, H. Process for deinking waste paper that controls the interfacial potential between ink particles and pulp. Assigned to Kao Corp. WO 9746753 (Dec. 11, 1997).

2. Irinatsu, J.; Miyauchi, Y.; Takahashi, H. Process for deinking waste paper in which the contact angle of the pulp is adjusted before flotation. Assigned to Kao Corp. WO 9746754 (Dec. 11, 1997).

3. Irinatsu, J.; Miyauchi, Y.; Takahashi, H. A deinking process that uses white water in the presence of cationic compounds. Assigned to Kao Corp. EP 834614 (April 8, 1998).

4. Kao Corp. Method for deinking by flotation in the presence of fine particles with a hydrophobic phase boundary. JP 10088489 (April 7, 1998).

5. Kao Corp. Method for deinking newspapers and other waste paper by flotation. JP 10053988 (Feb. 24, 1997).

6. Eriksson, T.; Fredriksson, B.; Wikstrom, T.; Wikstroem, T. Purification of fiber suspensions by flotation using a tank where the inlet jet does not break the suspension surface. Assigned to Sunds Defibrator Ind. WO 9808610 (March 5, 1998).

7. Fondow, W.; Grantz, D.; Kelly, A. Methods and apparatus for pulping and deinking. Assigned to Black Clawson Co. US 5762756 (June 9, 1998).

8. Kulakowski, C.; Mulligan, D.; Poy, R. Method for recovering fiber from waste paper by continuous batch recovery system using agglomerating/densifying composition to separate ink particles. Assigned to Pellerin Milnor Corp. US 5714040 (Feb 3, 1998).

9. Thurman, R. Process for agglomerating stickies in waste paper slurries by adding long-chain alcohol agglomerating agents. Assigned to Union Camp Corp. WO 9809017 (March 5, 1998).

10. Chin, L.; Longhini, D.; Vijayendran, B. Method for controlling froth and reducing stickies in flotation process using nonionic surfactants. Assigned to PPG Industries, Inc. US 5718801 (Feb. 17, 1998).

11. Cutts, P.; Drehmer, B.; Eriksson, I.; Green, M.; Johansson, H. Separation of cellulosic solids from aqueous suspensions by dispersed air flotation after screening to remove cellulose fines. Assigned to Allied Colloids Ltd. WO 9815686 (April 16, 1998).

12. Brooks, R.; Robinson, P.; Singleton, T. Deinking of printed waste paper by flotation using an alkaline earth metal tallate dispersion prepared by a double-displacement method. Assigned to High Point Chemical Corp. WO 9748850 (Dec. 24, 1997).

13. Hautala, J. Method and apparatus for defibering and screening recycled waste fiber material using two linked vertical pulpers operating at high and low consistencies. Assigned to Valmet Corp. EP 812950 (Dec. 17, 1997).

14. Matzke, W.; Messmer, P.; Selder, H. Recovery of valuable materials from fast food packages using hot chemical treatments to form plastic emulsion for precipitation and separating food residues by flotation. Assigned to Voith Sulzer Stoffaufbereitung. DE 19641911 (April 9, 1998).

15. Beltz, L.; Markham, L. Decolorizing brown fibers in recycled pulp. Assigned to International Paper Co. US 5733412 (March 31, 1998).

16. Ruf, F.; Schiessling, H. Deinking with cationic surfactant as collector at specified pH and minimum water glass concentration; useful for deinking paper without discoloration. Assigned to Sued–Chemie. DE 19631150 (Feb. 5, 1998).

17. Lindahl, A. Dewatering press for sludge or pulp that includes several press nips. SE 506724 (Feb.2, 1998).

18. Lindahl, A. Device for measuring drainage and resilience properties of pulp to simulate paper machine conditions. SE 9601306 (Oct. 5, 1997).

19. Bolton, J. Apparatus for washing, thickening, and solids recovery from aqueous slurries by which rotating sprays direct slurry onto inner face of inverted conical screen; facilitates contaminant removal and exiting of recovered stock from screen base. Assigned to Thermo Fibertek Inc. WO 9801616 (Jan. 15, 1998).

20. Takada, M.; Tamamori, Y. Waste paper baler with shredder and rollers for compacting material; coating on rollers provides highly frictional that rotates to form compressed bales. Assigned to Star Farm Machinery Mfg. Co. Ltd. and Star Noki. DE 19712793 (Dec.11, 1997).

21. Kurtz, R. Method and apparatus for bleaching wood pulp containing recycled waste paper; uses temperature-controlled reactor screw bleaching process. Assigned to Cellwood Machinery. WO 9804774 (Feb. 5, 1998).

22. Aksela, R.; Jakara, J.;Parenm, A.; Renvall, I.; Jaekaerae, J. Bleaching high-yield or recycled paper pulp by treating with bleaching chemical and a chelating agent specified bis or tris dicarboxyethoxyethyl amine derivative. Assigned to Kemira Chem Oy. WO 9745585 (Dec. 4, 1997).

23. Germgard, U. Treatment of metal ions in peroxide pulp bleaching by treating (pulp) with chelating agent; liquid is separated, oxidized to inactivate chelated metal ions, and returned to pulp. Assigned to Sunds Defibrator Ind. WO 9814657 (Apr. 9, 1998).

24. Kennedy, D.; Lind. C. Color removal from effluent waters. Assigned to General Chemical Corp. US 5766485 (June 16, 1998).

25. Tubergen, K.; Wong, S. Hydrophilic dispersion polymers for clarification of deinking process waters. Assigned to Nalco Chemical Co. US 5750034 (May 12, 1998).

26. Phipps, J. Process for removing solids-containing material from paper deinking plant effluent by diluting, dissolving solids, removing undissolved solids, and precipitation. Assigned to ECC Int. Ltd. GB 2315743 (Feb. 11, 1998).

27. Maier, J. Closed-circuit water effluent treatment process; regulates suspended solids, pH, temperature, oxidation, and filtration. WO 9749639 (Dec.31, 1997).

28. Sohara, J.; Young, T. Recycling of mineral fillers from residue of paper deinking plant. Assigned to Minerals Technologies Inc. US 5759258 (June 2, 1998).

29. Hubbe, M.; Olsen, W.; Zhu, H. Enhancing freeness of pulp from secondary fiber by treatment with enzyme mixture consisting of cellulase and pectinase. Assigned to International Paper Co. WO 9806892 (Feb.19, 1998).

30. Bjornvad, M.; Nielsen, P. Use of new endoglucanase from Cellvibrio species to degrade plant material or treat fabric or paper pulp. Assigned to Novo–Nordisk. WO 9808940 (March 5, 1998).

31. Hoeoetmann, U.; Hoffmann–Elsaesser, C.; Salzburger, W. Improving pulp whiteness in alkali deinking process by adding bacterial suspension to pulp before flotation. Assigned to BK Ladenburg GMBH. DE 19620952 (Nov.27, 1997).

32. Ben–Bassat, A.; Burlingame, R.; Chernoglazov, V.; Emalfarb, M.; Okounev, O.; Olson, P.; Sinitsyn, A.; Solovjeva, I. New *Chrysosporium lucknowense* strain VKM F-3500D and neutral or alkaline cellulases produced by it and related species; useful in deinking paper. Assigned to Emalfarb M.A. WO 9815633 (April 16, 1998).

33. Lorencak, P.; Potthoff, K. Use of amino-acids as chelating agents in bleaching pulp and deinking wastepaper using ethylene–diamine–disuccinic or diglutaric acid and/or hydroxy–proplyene–diamine–disuccinic acid. Assigned to BASF AG. WO 9804775 (Feb. 5, 1998).

34. Nippon Oils and Fats Co. Ltd. Deinking agent for recycling waste paper; consists of oxyalkylene compound and maleic anhydride; addition of another monomer is optional. JP 9279494 (Oct. 28, 1997).

35. Gruell, D.; Kubadinow, N.; Wastyn, M. Modified starch for use with hydrophobic paper sizing; cationic and hydroxy-alkylated and amphoteric amlyo-pectin starch. Assigned to Zuckerforschung Tulln GMBH. EP 824161 (Feb. 2, 1998).

36. Luigi, S.; Scholz, W. Repulpable pressure-sensitive adhesives with multiple layers; lamination of nondispersible tacky polymer and tacky water-dispersible polymer. Assigned to Avery Dennison Corp. US 5718958 (Feb. 17, 1998).

37. Dehler, K.; Gunia, P.; Heininger, H. Adhesive article (self-adhesive label, sticky tape) consisting of surface material, contact adhesive layer, and substrate (base layer) and silicone-free release coat made of polyacrylonitrile–polybutadiene copolymer. Assigned to Steinbeis Gessner GMBH. EP 835916 (April 4, 1998).

38. Saiden Kagaku, K.K. Pressure-sensitive water-dispersible adhesives consisting of mixture of (meth)acrylic acid alkyl ester, vinyl acetate, and caprolactone adduct of (meth)acrylic acid. JP 9328666 (Dec.2, 1997).

39. Feil, H.; Hulleman, S.; Jongboom, R. Thermoplastic, biodegradable, starch-based adhesive is heated to above the hydrolysis temperature before use, but kept below this temperature when making a catalyst-containing precursor. Assigned to ATO–DLO Inst. Agrotechnologisch Onderzoek. WO 9802496 (Jan. 22, 1998).

40. Dainippon Printing Co. Ltd. Reusable paper carton for storing juice, alcoholic beverage, mineral water, wine; includes alkali-soluble resin interposed between paper and gas barrier layers. JP 10071662 (March 17, 1998).

41. Bloch, G.; Finestone, A. Sealing tape for cartons that can be stripped entirely so that carton can be reused or recycled. EP 823466 (Feb.11, 1998).

42. Kaneko, T.; Miyazaki, Y. Production of oil-absorbing waste from recycled waste paper using aqueous solution consisting of resin lipophilic agent; obtained by polymerizing higher fatty acid with emulsifier, surfactant, and water. JP 8060589 (March 5, 1996).

43. Fejes, F.; Hernadi, S.; Krakker, K.; Laszlo, C.; Lele, I.; Toth, J. Paper sludge used for manufacture of multi-layer paperboard by replacing primary and/or secondary fiber by paper sludge, adding adhesive and flocculant for retention. Assigned to Papiripari KFT. HU 75845 (May 28, 1997).

Key to Abbreviations

DE = German patent
EP = European patent
GB = British patent
HU = Hungarian patent
JP = Japanese patent
SE = Swedish patent
US = United States patent
WO = World patent