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INTRODUCTION

This review summarizes patents related to paper recycling that were issued during the last six months of 2000. Two on-line databases, Claims/U.S. Patents Abstracts and Dement 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 comprise this review. For more complete information, readers will need to access the full text of a specific patent.

We organized the patents into broad categories of recycling: equipment and their related processes, chemicals and applications, and products made from reclaimed paper and waste residues. As we have noted in the past, patents reflect the changing needs of the industry. A new category appears in this review: coatings and additives for specialized papers.

EQUIPMENT–PROCESSES

As specific recycling problems are resolved, utilizng a more heterogeneous paper furnish has become possible. Various approaches for separating paper from the abundant supply of unsegregated waste materials are described in the following reviewed patents.

A disc screen machine for classifying recyclable materials from a stream of heterogeneous materials has been invented by Davis. His World patent describes the machine comprised of rows of shafts mounted on the top and bottom layers with removable discs individually mounted on the shafts. Bottles and containers in the incoming stream are segregated and removed into one area allowing paper to be propelled by forced air to a discharge area for recycling (1).

Dry separation of paper and plastic films from the paper fraction of household waste materials has been made possible by another patented process. Capitalizing on differences in density of the materials, Nederlandse Org Toegepast passes the mixed materials through an air stream where separation is accomplished by different "falling" behaviors at elevated temperature (under 50°C). The patent (2) claims to efficiently produce pure paper and plastic film fractions by this method.

Another method for paper–plastic separation is described in a Japanese patent (3). This process dilutes the mixture of waste materials in alkaline water and stirs to fiberize the paper. Fiberized material then passes through a filter to separate the paper from the plastics. The reclaimed paper fibers can then be cleaned and reprocessed. The plastic component can be further separated by differences in specific gravity of the various types for reuse.

A perforated stock preparation drum designed by Voith Sulzer Paper Technology has the benefit of screening foreign matter from dry reclaimed papers. The drum has an open wide end to receive

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mixed paper and an open narrow end to discharge the reclaimed paper. Foils attached to the inside of the rotating drum move the paper furnish from the wide end to the narrow end. Numerous holes permit foreign matter to fall through (4).

GL&V Celleco is the assignee of the device and process for separating contaminants from recovered paper pulp suspensions. Comprised of a rotor inside a cylindrical screen, the equipment's tubular wall deflects the incoming flow of pulp, The cross section of the intake passage is substantially larger than that of the outlet (5).

Thermo Black Clawson has been assigned a patent for streamlining the deinking process through simultaneous high-consistency pulping and dispersing of laser-ink-containing office paper. After high solids processing, the pulp is diluted for flotation, washing, and bleaching. No additional dispersion is required for laser ink removal (6).

A physical separation method for removing wax from OCC and recovered paper is described in US 6053439. In this process, waxed fibers are pulped at an elevated temperature to melt and emulsify the wax with water, The pulp fraction is separated from the emulsion by washing through a finely perforated reverse pressure screen (7).

Mueller has taken a new approach to flotation in his recent patent (8). More efficient ink separation is accomplished by the inclusion of a specialized mixing unit within the flotation cell. A circular flow pattern is generated within the flotation tank by recirculating a portion of dilute pulp already in the tank with incoming pulp, mixing, and exposing the contaminants to air bubbles for ink removal. Pulp flow is limited at the top end of the tank assuring optimal conditions for flotation resulting in clean separation as well as energy savings.

Voith Sulzer Papiertechnik has improved upon traditional flotation for contaminant removal by adding a vertically oriented round sieve with a foam collection zone at the top. Air bubbles are produced when the fiber suspension passes through the sieve, obviating the need for a turbulence generator. Economical, efficient separation of inks and stickies results from this patented assembly (9).

To counter the increased sheet density of paper made from recycled fiber, the Kao Corporation has developed a unique deinking process that increases the sheet bulk while maintaining strength and printability (10). Their solution lies in a carefully controlled flotation process based on adjusting the interfacial potential of ink particles (in the range of −5to −60mV) and of pulp (−5 to + 15mV). They claim that ink is most efficiently stripped and that bulkier sheets result when the difference between the potentials for ink and pulp is 10 mV or greater. The desired potential is obtained by adjusting the pH before or during flotation with acid or inorganic salts in the presence of a nonionic surfactant (10).

A German patent deals with the recovery of biodegradable surfactant-containing water by separating individual process stages, The system includes at least two wastewater purification units containing a filter, an aerobic bioreactor, a collector for the biologically purified water that can be supplemented with fresh water, and a device to monitor water parameters. The system prevents impurities from building up in the water system (11).

Lion Corp. has been awarded related patents covering both the process and the chemicals required to deink pressure sensitive post-consumer papers. (Their definition of pressure sensitive paper is primarily a "back-carbon" paper). The process involves disaggregation of the paper in an aqueous solution, isolating pulp and desorbing ink using specific mechanical energy (350 kcal/kg). Ink, dyes, and pigments are removed resulting in a high whiteness pulp (12). The deinking agent, an alkylene oxide-based surfactant, permits the recycling of papers previously difficult to deink (13).

CHEMICALS AND APPLICATIONS

Chemicals

Stickies and pitch are removed from fiber slurries by addition of chemicals to agglomerate these problematic compounds. "he chemical additives are comprised of several compounds including an oil-soluble or water-dispersible hydrophobic polymer, a tackifier, and solvent. Agglomerated stickies and pitch can then be separated mechanically from the papermaking fiber (14).

Hard-to-remove flexographic printing is targeted in a novel and sophisticated deinking process that incorporates an emulsion of crosslinked, swellable, ionizable polymer particles in the pulper. The chemicals contained in the emulsion influence the viscosity, hydrophobicity, and hydrophilicity of the pulp slurry to facilitate separation of the ink-containing fraction. The crosslinking additive controls the particle size of the flexo inks so that they can

be more readily removel during flotation (15). These additives also enhance the removal of stickies.

Nalco has recently patented a method to deal with wax in fiber slurries. The disclosed approach involves additives to break down and stabilize wax during the recycling of paper and paperboard. Wax can be separated from the fiber or it can be dispersed and pacified with alum or bentonite and remain with the fiber for inclusion with other products. Plasticizers (esters of adipic acid), dispersants, or polymeric wetting agents are some of the preferred additives for treating wax-containing fibers (16).

Bleaching

Several patents appeared in this search for more efficient bleaching processes. Ahlstrom Machinery's claim (17) is based on the varying bleaching needs of different fiber components in reclaimed paper. Intense mixing is used initially to provide a homogeneous fiber mixture and to assure good distribution of bleach chemicals. Subsequent intermittent mixing redistributes chemicals during retention. Sensing is used to determine bleaching requirements based on initial parameters such as brightness, color, or lignin content and to determine whether a second bleach stage is required (17).

Degussa-Huels has developed a new process for obtaining high-quality bleached pulp based on reductive sulfur-containing agents. Various secondary fibers (containing less than 50?% mechanical fiber) are disintegrated in an aqueous solution containing sodium silicate and sodium hydroxide or carbonate and are then washed and bleached without hydrogen peroxide. The process is effective without the flotation, thickening, or dispersion typically used for deinking. The bleaching process is environmentally compatible (18).

Biochemicals

Enzymes continue to offer an effective, environmentally sound alternative to chemicals for pulp and paper processing in recycling. Novo Nordisk has a new alkaline cellulase to enhance pulp drainage and facilitate deinking of reclaimed fibers. The enzyme preparation is an endoglucanase variant with modified H-bonding potential and hydrophobic interaction relative to the cellulase (19).

Another enzyme-enhanced deinking process uses acid or neutral cellulases, fatty alcohol polyglycol ether and inorganic salts as a collector. The collector combination gives good ink removal during flotation resulting in high brightness pulp. This process requires a low enzyme level compared with prior practice thereby reducing cost (20).

COATINGS AND ADDITIVES FOR SPECIALIZED PAPERS

Release Coatings

A latex undercoat has been developed for release paper for adhesive tapes and labels. The latex contains a predetermined amount (less than 0.3% by weight) of mercapto groups added during emulsion polymerization. This coating has improved solvent barrier properties and can be recycled for reuse (21).

Avery Dennison Corp. has been granted a World patent for a release coating composition for adhesive sheets and labels. A free silicone oil additive (molecular weight at least 1000) reduces the tackiness of the adhesive that comes in contact with the release coating. This compound is especially useful for multilayered adhesive tape and label constructions (22).

Coatable ink-receptive compositions and substrates for labels are targeted in the patent awarded to Avery Dennison. The compositions contain pigment dispersed in a binder made of an ethylene vinyl acetate emulsion polymer and at least one water: soluble cationic polymer and copolymers of acrylates. Papers, films, labels, and other printable materials can be produced with this coated substrate (23).

Increased use of pressure sensitive adhesives (PSAs) is causing concern in the recycling community about the recyclability of silicone release lin-, ers used with the adhesives. Moore USA, Inc., holds the patent for a business form with patterned silicone liner that offers one alternative for recyclers. The design of the liner laminate describes a release liner that does not entirely cover the cellulose ply to which it is attached. This strip with no active release material permits the user to strip the liner ply from the form after the adhesive-backed label has been used. This specific patent has a detailed description of the construction of the business form including perforations and positioning of the label segments for easy separation. However, this idea might be expanded to other liner applications such as postal stamps, address labels, etc. (24).

Another approach includes a varnish layer as the novel laminate for the base sheet used as an adhesive release paper. A Japanese company patents this glossy, smooth release sheet. The laminate is recyclable (25).

A recyclable hot melt agent containing wax and a thermoplastic polymer is used to impregnate one surface of a base material for pressure sensitive adhesive tapes. This compound achieves excellent sealing to prevent release agents from penetration into the paper substrate while giving good adhesion to the paper substrate (26).

Other Coatings and Additives

A unique approach to solving the stickies problem has been taken by Ross and Yahiaoui and assigned to Kimberly-Clark. They modified a paper machine substrate to resist contamination by adhesive materials. The substrate has an active agent grafted (by radiation) to the surface that lowers the surface energy of the substrate. The substrate repels isopropyl alcohol but is permeable to water (27).

Both Oji Paper and Mitsubishi have alternative approaches for making specialized paper for ink-jet printing. The material described in Mitsubishi's patent for ink-jet printing has a carrier and a layer containing fine particles of a thermoplastic and organic polymer. The organic polymer particles contain a layer of colloidal silicon dioxide and a barrier layer. After ink-jet printing, the fine particles are dissolved or fused together. The surface is heated by radiation or convection. The paper produced has high gloss and gives a true print reproduction (28). Oji Paper uses a cast coating layer containing a fine silica pigment and an adhesive on the base material. The recording paper has excellent ink drying properties, glossiness, and uniformity (29).

High gloss barrier coatings and coated sheets displaying oil, water, and solvent resistance are described in Overcash and Wallace's patent disclosure. These economical coatings are printable, biodegradable, and recyclable and are especially suited for use with food products. The method for applying these coatings on porous substrates is described as well as printing images on containerboard (30).

A unique coated paper for copiers and printers of electrophotographic systems consists of a chitosan-containing base paper and is coated with pigment and an adhesive. Chitosan is incorporated into a cationic colloid-like solution and an organic acid. The coated paper is excellent for images and printing. The natural polymer adhesive used for manufacture of base paper can be disposed of during waste processing. Fuji Xerox is the assignee of this patent (31).

Minolta has developed a recyclable image recording material for electrophotographic copying machines and printers. The material features a water-swelling resin for rapid toner removal during recycling and fine surface particles for improved paper feed. The material can be reused repeatedly because it maintains excellent printed image quality and rapid toner removal (32). A related patent shared with Minolta Camera KK also describes a recyclable image recording medium for laser printing and copying. The material is water-resistant and strength is maintained after recycling. The sheets also can be folded (33).

A heat fusible, magnetic printing ink composition contains a surface-treated magnetic substance, silane coupling agent, heat fusible resin, and coloring material. The ink is used for printing paper but is removed readily by heat fusing and magnetic force. No organic solvents are required for removal (34).

PRODUCTS

A process for treating rejects from recovered paper deinking is described in a recent U.S. patent (35). Inorganic paper additives and fibers contained in the rejects are chemically treated with an aqueous suspension of carbonate and alkaline metal ions. The resulting insoluble carbonate precipitate entrains ink particles, fibers, and inorganic particles into the floc. The precipitated reject material can be reused as a pigment for filling or coating pulp during papermaking (35).

Deinking sludge, which often creates a disposal problem, can be converted into useful products. A Japanese patent suggests heating the sludge with an aqueous suspension of calcium hydroxide and injecting carbon dioxide to precipitate calcium carbonate. After aging at elevated temperature, the resulting $CaCO_3$ formed from the sludge slurry has high whiteness and opacity and low abrasion, which are properties that make it suitable for incorporation as a filler during papermaking (36).

A process using steam explosion to liberate fiber from recycling sludge has been patented by Kimberly-Clark (37). Sludge is fed into a vessel and

steam heated to an elevated pressure and temperature. The sludge is then discharged into a vented vessel to create an explosive decompression of the sludge thereby separating fiber. An independent claim is included for producing modified cellulose fiber fines that have an improved curl index and separation efficiency.

Lower quality reclaimed paper can be used for making low-density packing and cushioning materials. Bulky sheets formed from a mixture of ground fiber and synthetic fibers (2–10 mm) have moderate cushioning and air permeability suitable for packaging (38).

Discarded waste paper is used for a building material for surface and underground construction. Molded bricks are made inexpensively from an aqueous slurry of crushed water-repellent resin binder and waste newspaper and packaging material. The molded material is lightweight, heat insulating, compatible with paints or other damp-proofing material, and recyclable (39).

A novel application of low-quality recycled pulp fiber is described in a Dutch patent (40) for a method to improve sludge dewatering. Pulp and a flocking agent are added to low-consistency sewage or industrial wastes to facilitate drainage in subsequent dewatering.

Rather than binding waste paper bundles with plastic or string that have to be removed before pulping, a Japanese patent suggests the obvious: use a paper-based material for binding. Reclaimed fiber is processed into "string" by twisting strips of recycled pulp beaten to achieve target strength properties. Strips of recycled paper are cut, twisted, and used to tie bundles of paper weighing at least 5 kg for recycling (41).

Fiberboard can be produced from recycled food packaging containers. Cellulose fibers recovered from boxes are mixed with a bonding agent and pressed into boards using heat and pressure. High-quality boards result from this low-cost, environmentally benign process patented by Nystroem and Otto (42).

Recyclable shipping and storage pallets made from OCC and corrugated plastic boards are covered in a recent patent (43). The pallets are die cut into patterns that can be interfitted to form a main pallet support. They can be customized to accommodate specific size and strength applications and are designed to be easily movable by forklift or pallet jacks.

PATENTS CITED

1. Davis, R.M. Disc machine for separating or classifying recyclable material. Assigned to CP Mfg. WO 0045966 (August 10,2000) and AU 200028600 (August 25,2000).

2. Verschut, C. Paper and plastic film dry separation for waste processing. Assigned to Nederlandse Org Toegepast. WO 0023236 (April 27, 2000) and NL 1010338 (April 20,2000).

3. NKK Corp (NIKN). Waste plastic separation method involves stirring paper and plastic refuse with water. JP 2000127170 (May 9,2000).

4. Doelle, K. Perforated drum in a stock preparation system for screening foreign matter from recycled paper. Assigned to Voith Sulzer Paper Technology North America. US 6095442 (August 1, 2000).

5. Selin, R. Device for separating contaminants from fibre pulp suspensions. GL&V Celleco, assignee. US 6131742 (October 17,2000).

6. Fondow, W.; Grantz, D.; and others. Apparatus for pulping and deinking. Assigned to Thermo Black Clawson. US 6120648 (September 19,2000).

7. Locke, R.; Prentice, G.; Vitori, C. Reducing wax content and enhancing quality of recycled pulp from OCC and waste paper. Inland Paperboard and Packaging Inc and Thermo Black Clawson, assignees. US 6053439 (April 25,2000).

8. Mueller, J. Flotation process and mixing device. Assigned to Voith Sulzer Stoffaufbereitung GmbH. US 6129212 (October 10,2000).

9. Veh, G. Assembly for cleaning a paper fiber suspension. Assigned to Voith Sulzer Papiertechnik GMBH. DE 19856207 (June 8,2000).

10. Irinatsu, Y.; Miyauchi, Y.; Takahashi, H. Method for controlling deinking flotation using interfacial potential of ink particles and pulp. Assigned to Kao Corp. JP. US 610356 (August 15,2000).

11. Calandri, D.; Hesselman, D.; Schneider, T. Recovery of biodegradable surfactant-containing wa-

ters. Assigned to Buck Werke GMBH & Co. IK. DE199005301 (August 10,2000).

12. Lion Corp. and Mishima Seishi KK. Deinking pressure sensitive used paper for use as reclaimed paper. JP 2000119981 (April 25,2000).

13. Lion Corp. Deinking agent for used pressure-sensitive paper, permitting efficient removal of inks. JP 2000119699 (April 25,2000).

14. Ling, T-F.; Scholz, W. Methods and compositions for treating stickies. Assigned to Betz Dearborn Inc. US 6150452 (November 21,2000).

15. Bingham, T.; Dungworth, H.; Stockwell, J. Deinking processes polymers-in-water emulsion for use in deinking processes for flexographic or other printed paper. Assigned to Ciba Specialty Chemicals Water Treatments Ltd. US 6111009 (August 29,2000).

16. Coffey, M.; Severtson, S. Use of additives to breakdown and stabilize wax during fiber recycle; adding plasticizer; dispersing to obtain treated fiber; separating fiber from slurry containing wax; recovering fiber. Assigned to Nalco Chemical Co. US 6113738 (September 5,2000).

17. Phillips, J.; Sharpe, P.; Stromberg, C.; Torregrossa, L. Bleaching cellulose pulp having cleanliness which varies significantly over time using at least two different bleaching stages and bleaching chemicals. Assigned to Ahlstrom Machinery Inc. US 6153300 (November 28,2000).

18. Cronis, J.; Taylor, R. Formation of bleached pulp from secondary fiber sources - involves bleaching washed pulp slurry using sulfur containing bleaching agents without usage of hydrogen peroxide. Assigned to Degussa-Huels AG. EP 1031657 (August 30,2000).

19. Von der Osten, C.; Hansen, S.; Schulein, M.; Rosholm, P.; Nielsen, J. Alkaline cellulases; endoglucanase variant with adjusted hydrogen bonding; for efficient drainage of paper pulp; for deinking. Assigned to Novo Nordisk A/S DK. US 6117664 (September 12,2000).

20. Pinilla, J.; Pi Subriana, R. Deinking of waste paper comprises flotation of an aqueous slurry of printed paper in the presence of an assistant comprising a mixture of acid and neutral cellulases, fatty alcohol polyglycol ether and (in)organic salts. Assigned to Cognis Deut GMBH. WO 0032867 (June 8,2000)

21. Asahi Kasei Kogyo KK. Latex for releasing paper undercoats for adhesive tapes, adhesive labels, packaged goods or containers. JP 200000178897 (June 27,2000).

22. Keustermans, J.; Willekens, J. Release coating composition for adhesive sheets and label constructions comprises free silicone oil additive having specific molecular weight and viscosity in release coating matrix. Assigned to Avery Dennison Corp. WO 0039231 (July 6,2000) and AU 200030439 (July 31,2000).

23. Lin, K.; Shih, F.Y-J. Ink-receptive compositions and coated products; contain pigment dispersed in binder composed of ethylene vinyl acetate polymer and water soluble, cationic polymer, such as polydiallyldimethylammonium chloride and copolymers of a quaternary amino acrylate and hydroxyalkyl acrylate. Assigned to Avery Dennison Corp. US 6153288 (November 28,2000).

24. Chess, S. Construction of a business form with patterned silicone liner. Assigned to Moore U.S.A., Inc. US 6036234 (March 14,2000).

25. Shinomura Kagaku Kogyo KK. Releasing paper for adhesive sheet has removing layer and varnish layer sequentially laminated on a paper base material. JP 2000144066 (May 26,2000).

26. Nichiban KK. Hot melt type impregnating agent composition that contains wax and thermoplastic polymer and base material for pressure sensitive adhesive tapes. JP 2000144093 (May 26,2000).

27. Ross, R.; Yahiaoui, A. Paper machine substrate which is resistant to contamination by adhesive materials has paper machine substrate and active agent. Assigned to Kimberly-Clark Worldwide Inc. WO 0036213 (June 22,2000).

28. Ashida, T.; and others. Paper for ink-jet printing has carrier layer and layer of fine thermoplastic organic polymer particles to be dissolved or fused to form layer. Assigned to Mitsubishi Paper Mills LTD. DE 19956999 (May 31, 2000) and JP 2000158803 (June 13,2000).

29. Oji Paper Co. Inkjet recording paper for inkjet printer contains silica particles and adhesive on a base material. JP 2000085242 (March 28,2000).

30. Overcash, D.; Wallace, R. High gloss barrier coatings and coated sheets - printable, biodegradable, recyclable, repulpable, suitable for use with food products. Assigned to A*ware Tech L C. US 6132822 (October 17, 2000).

31. Fuji Xerox Co. LTD. Coated paper for copiers, printers of electrophotographic system has base paper containing chitosan coated with a composition containing pigment and an adhesive: JP 2000147823 (May 26,2000).

32. Fujiwara, T.; Yamaoka, C.; Yoshie, N. Recyclable image-recording medium useful for laser printing with toners comprises base pulp fibers treated to have water resistance and water-swelling surface layer. Assigned to Minolta Co. LTD. EP 1024409 (August 2, 2000) and JP 2000214621 (August 4, 2000).

33. Fujiwara, T.; Yamaoka, C.; Yoshie, N. Recyclable image recording material for electro-photographic copying comprises water-swelling resin for rapid toner removal during recycling and surface fine particles for improved paper feeding. Assigned to Minolta Co. LTD and Minolta Camera KK. EP 102077200 (July 19,2000) and JP 2000202934 (July 25,2000).

34. Minolta Camera KK. Heat fusible magnetic ink composition for removing printed matter. JP 2000136338 (May 16,2000).

35. Bleakley, I.; Toivonen, H. Waste paper treatment process. US'6159381 (December 12,2000).

36. Okutama Kogyo KK. Manufacture of PCC useful as filler for paper manufacture, involves heating used paper sludge and mixing with calcium hydroxide solution followed by carbonization. JP 2000178024 (June 27,2000).

37. Hsu, J.C.; Hu, S. Recovery of fibers from fiber processing waste sludges using steam explosion treatment. CN 2292469 (June 18,2000).

38. Kanai, H. Paper sheet for packing and cushioning materials, comprises wet ground synthetic fiber and pulp. JP 2000192393 (July ll, 2000).

39. Richter, R. Building material, especially molded brick for surface and underground construction, consists of bonded cellulosic material, especially waste paper. DE 19951908 (June 15,2000).

40. Schmidt, J. Sludge dewatering method, comprises adding paper pulp and flocking agent to the sludge prior to dewatering. NL 1010823 (June 19, 2000).

41. Morioto KK. Used paper recycling paper string manufacture involves carrying out beating and twisting used paper pulp. JP 2000129547 (May 9, 2000).

42. Nystroem, T.; Otto, T. Fiberboard, comprises cellulose fibers separated from recycled foodstuff packaging cardboard and bonding agent. Assigned to Tetra Laval Holdings & Finance SA. DE 19947856 (April 20,2000) and SE 9803538 (April 15,2000).

43. Chilcutt, G. Shipping pallets and accessories made of corrugated cardboard and corrugated plastic board. US 6155181 (December 5,2000). m

Key to Abbreviations

CN = Canadian patent
DE = German patent
EP = European patent
FR = French patent
JP = Japanese patent
NL = Netherland patent
US = United States patent
WO = World patent