

Articles

The effect of evolving ink chemistry on the reclamation of paper fibre

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Keywords

Environmental impact, Inks, Paper industry, Recycling

Abstract

Environmental, economic and market pressures have led to a dramatic increase in the production of recycled paper fibre in recent years and the growing demand for higher quality grades is now focusing attention on the recycling of office wastes. Although the role of chemistry in the recycling process for paper is well established, the introduction of newer inks and adhesives into the recycling chain has added to the existing problems of "getting the chemistry right". This article examines the impact on the deinking of secondary paper fibre resulting from evolving ink technologies, catalysed by developments in the printing processes.

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Introduction

The recycling of cellulose fibre to make paper is far from new. From about AD1250 to 1875 fibre was obtained by recycling old rags made from flax, hemp or cotton. From about 1860 demand began to outstrip supply and the technology was developed to separate virgin fibres from wood pulp by chemical and mechanical means. However, by 1939, the British Board Industry was using 25 per cent recycled paper waste and during the war years, 50 per cent of the paper produced was recycled from waste newsprint. The 1950s saw an increase in recycled wood fibre in paper and board. By the 1990s environmental as well as economic pressures had come to bear resulting in a rapid global increase in the use of recycled fibre of all grades, ranging through newsprint, tissues, printings, writings and top liners.

Today, the growth in paper recycling is driven by economics, customer pressure through increased environmental awareness, and legislation through political response to both public opinion and the high cost of landfill. The global recovery rate for 1996 was 117 million tonnes, representing 42 per cent of total consumption, with a 50 per cent target by the year 2000. Since 1994, the global installation of many new high grade deinking technology plants has taken place. Paper recycling is big business and looks like being here to stay.

These days, if recycled paper is to be acceptable to the printer and his customer, it must fulfil defined printability and runnability criteria which in turn define print quality and economy of print production. For example, newspaper printing is performed at press speeds up to 750 metres per minute and demands minimal web breaks, clean white sheets for duplex process colour printing, and a strong surface to minimise dusting and linting. Graphics papers demand the same colour fidelity and tonal dynamic range as is attainable with virgin chemical pulps. Print sharpness, ink density and tonal range are affected by the surface properties of paper as well as its optical properties of gloss, opacity, and colour. So what has all this to do with pigment and resins chemists?

There are, broadly, two stages to paper recycling; the preparation of the pulp for papermaking and the manufacture of the paper. Whereas the latter is the same as for

conventional papermaking, the pulp preparation entails rather more chemistry and centres on the removal of ink from the waste paper. If ink removal is inefficient, then the required optical properties defined earlier cannot be attained. In fact, newsprint recycling during the war years made no concession to optical quality, the paper simply being repulped and constituted into paper. The result was a grey, bespeckled paper that would be unacceptable today. Not only have paper quality requirements been raised but the number and complexity of ink systems has greatly increased in recent years to meet the requirements of the evolving printing technologies. It is these, together with adhesives, that are creating problems for the paper recycler.

The chemistry involved in deinking follows the stages of pulping, flotation, washing, deposit control and water clarification, the principal chemicals for which are given in Table I. This chemistry was developed for the deinking of newsprint which until recently was the main outlet for printable recycled paper. The main waste resource is a mixture of newsprint and magazine in the proportions of 70 per cent to 30 per cent, printed with relatively simple inks. However, increasingly more advanced ink systems such as for UV coatings and digital printing inks are entering the recycling chain. Moreover, there is now a growing interest in mixed office waste as a source of high quality chemical wood fibre for the manufacture of graphic arts and copier papers, instead of merely downcycling it to tissue grades.

Table I Principal deinking chemicals

Chemical	Application
Sodium hydroxide	Fibre swelling
Sodium silicate	Bleaching and deposit control
Chelating agents	Bleaching protection
Hydrogen peroxide	Bleaching
Surfactants	Flotation, washing
Collector chemicals	Flotation
Agglomeration chemicals	Cleaners
Calcium chloride	Flotation
Dispersants	Washing, stock preparation
Sodium hypochlorite	Bleaching
Sodium hydrosulphite	Bleaching
Formamidine sulphonic acid	Bleaching
Contaminant control	Pulper, storage, stock preparation

There are two main categories of waste paper; pre-consumer and post-consumer. Pre-consumer waste such as over issues, press room waste and mill broke are relatively simple materials containing no contraries (foreign materials). Post-consumer waste is that which has been used by the public and to which a wide range of contraries may have been included. For example, paper clips and wire staples which can be mechanically removed; adhesives which present greater difficulties. It is considered in many circles that adhesives and the "stickies" they produce have created more removal problems than have many inks, and further reference will be made to them later.

Until recent years, ink formulations were relatively simple and little changed. The earliest inks, used for writing, were water based and comprised lamp black mixed with gum Arabic dissolved in water. Since these would not wet Gutenberg's type metal, they were superseded by oil-based inks – surely an early example of developments in the printing process dictating changes in ink formulation. Thereafter, the composition of letterpress, and later, litho inks, seems to have changed little until the 1920s when synthetic resins were introduced.

Today, we have a list of inks and ink components for litho, flexo, gravure, screen and non-impact printing which includes: mineral oils, hydrocarbon resins, phenol-formaldehyde resins, UV-cured inks and coatings, oxidation drying vegetable oils; heat set and cold set vegetable news inks, water-based flexo, water-based gravure, UV water-based flexo, UV water-based gravure, UV litho, UV/water-based screen, UV free radical, UV cationic. Digital inks include liquid and dry toner electrographic and magnetographic; ink jet inks, including water-based dyes, solvent-based dyes, pigmented, solid phase wax, UV cured; and dye sublimation and dye diffusion systems. Any or many of these could turn up in a deinking plant but each may need different removal techniques.

These may be grouped into four categories of ink contaminants:

- (1) News and magazine inks. The problem presented by the deinking of these has been largely resolved and even the introduction of vegetable cold set colour news inks should not create new difficulties.

- (2) Radiation curing inks and coatings have undergone a large growth in use, particularly for varnishing magazine covers and printing of packaging products. Their tough film forming characteristics require special treatment in the recycling process.
- (3) Developments in water-based inks are really riding on the back of environmental concern but paradoxically have created difficulties for the deinking process since by their very nature they are difficult to remove from aqueous fibre slurries.
- (4) The latest category of new inks is that embracing non-impact printing. These include digital offset inks and are predominantly fused toner systems which are difficult to deink; the Indigo electro-ink has a polymerising vehicle. Growing interest in wide format ink jet printing will lead to the development and use of new water- and solvent-based pigmented inks and dyes which may also be potentially difficult. The components of these inks which cause problems in deinking will shortly be discussed and are summarised in Table II. First, however, it is important to understand the stages involved in deinking secondary fibre.

The deinking process

Inks of course comprise two phases, the pigment and the vehicle. The colour strength and opacity of the pigment are influenced by particle size as well as its chemistry. The high colour strength and transparency required for multicolour printing dictate sub-micron particle sizes, as indeed do the thinness of the ink films (1–3 microns) used in offset litho and flexography. In this respect, the size of ink particles should create few removal problems

for the deinking process, if freed from the vehicle, since they are small enough to be washed from the pulp. In practice, the binder in the vehicle retains the pigment and it is the ease of removal and size control of the binder that dictates the ease of deinking. Overall, the process of deinking therefore involves the removal of the pigment bearing binder from the fibre and thence from the slurry.

Traditionally, deinking involves removal of ink from the paper surface by mechanically re-pulping under alkaline conditions (pH 9.5 to 11.0), and in the presence of surfactants. Sodium hydroxide solution swells the cellulose fibres, and the resin-based binders undergo saponification or hydrolysis which assists ink removal. Surfactants and collectors aid removal and collection of the detached particles. The chemical technology of deinking has been fully reviewed elsewhere by the author[1,2]. Under the influence of high consistency mechanical agitation in the pulper, the ink detaches and breaks up into particles of varying sizes. The ease of detachment depends upon the chemical and physical properties of the binder and in some polymerising inks, including those containing oxidation drying vegetable oils, becomes more difficult with progressive binder ageing. The work of adhesion between binder and base paper, and binder and deinking surfactants employed are important factors. The particle size ranges produced are influenced additionally by the printing process and the base paper as indicated in Table III.

Once the ink has been detached, it is essential to remove it from the pulp slurry since it is the presence of residual ink particles that most degrades the optical properties of the finished sheet. Large particles which are visible to the naked eye cause “speckiness”

Table II Some possible ink contaminants in a secondary fibre furnish

Absorption, Evaporation, Auto-oxidation	Laser, Photocopier, Digital	Radiation curing	Water-based
Mineral oils	Styrene-acrylate copolymer	Epoxy acrylates	Dyes
Wax	Styrene-butadiene copolymer	Polyol acrylates	Acrylic acids/esters
Hydrocarbon resins	Vinyl acrylates	Urethane acrylates	Methacrylic acids/esters
Rosin esters	Polyesters	Polyester acrylates	Copolymers with styrene or butadiene
Alkyd resins	Polyvinyl butyral	Hydroxyl polyesters	Acrylic emulsion polymers
Unsaturated fatty acids			
Nitro cellulose resins			
Phenol-formaldehyde resins			

Table III Ink particle sizes (in microns) in the repulper

	Uncoated paper	Coated paper
Letterpress	2-30	10-100
Offset litho	2-30	5-100
Flexo	0.3-1	0.7-2
Gravure	2-30	5-30
Laser/photocopier	40-400	40-400
UV	Large continuous sheets	

Source: Ferguson LD Introduction to Printing Technology and Ink Chemistry, TAPPI, De-inking seminar notes, TAPPI Press, Atlanta, GA, 1992

whereas those smaller than 40 microns across cannot be visually resolved but instead contribute a greyness to the appearance of the paper. This in turn reduces the dynamic range attainable on the printed sheet as well as its optical brightness. Indeed, the success of the deinking process is usually judged by the ISO brightness of the final pulp. Factors not dependent on the deinking process but which influence the final brightness of the pulp are those variations which arise from different fibre types present in the furnish. These can vary from the high brightness exhibited by the bleached kraft fibres used in printing and writing papers to the low brightness of thermomechanical pulps used in many magazines and newspapers.

The sizes of ink particles that occur in a deinked pulp are important because of the significant effect they have on its optical properties and because size influences their ease of removal. Leighton and Miranda[3] have shown that reducing the particle size at the same mass concentration of ink decreases the optical reflectance of the pulp. For example, small particles such as those produced by flexographic inks and less than 1 micron in size absorb light uniformly over their entire surface area, thus reducing the overall reflectance. Conversely, the large platelets of 200 microns or more released by laser and UV-cured inks produce a non-uniformity of absorption. This is probably because more light is absorbed by the top side of a particle than by its under side, and the effect is pronounced by large flat particles[4]. The combined affect of reflectance due to fibre type and ink particle size distribution is such that high reflectance pulps experience greater reflectance loss than low reflectance pulps for a given amount of residual ink[5].

The problem now becomes one of removing the detached ink particles from the

recycled fibre slurry. However, since particle size influences not only the optical properties of the pulp but also ease of removal, the importance of rendering detached ink particles into collectible size ranges cannot be overstated. The difficulty is that different particle size ranges require different methods for their removal; a typical pulp will contain a wide range of sizes. The papermaking technologies suitable for the removal of ink particles and other contraries are represented in Figure 1.

Screening

Pressurised slotted screens remove particles from 200 microns in size upwards, such as very large bulky ink particles as well as paper clips and other large contraries.

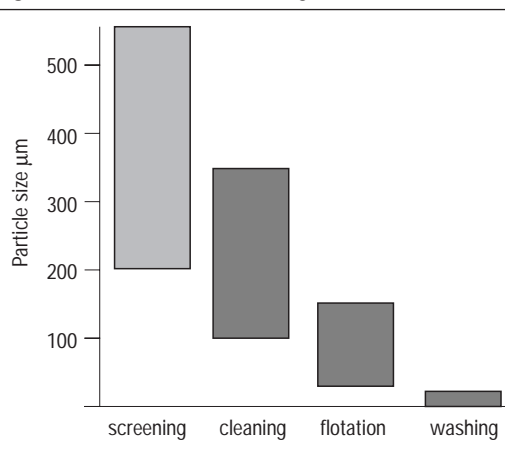
Centrifugal cleaners

Vortex cleaners employ a centrifugal action which separates fibre from non-fibre according to relative density differences; the differences must be large for cleaning to succeed. Cleaners will then remove particles in the size range 100 to 350 microns.

Flotation

The most important ink removal process and one by which the majority of particles are separated is flotation which removes particles in the size range 20 to 150 microns. In flotation deinking, air bubbles are introduced into the pulp slurry containing collector chemicals (surfactants) which increase the hydrophobic interface at the ink particle boundaries and hence their reluctance to associate with water. The ink particle must penetrate the hydrophobic air-water boundary of the bubble in order to attach itself. Hydrophilic

Figure 1 Particle size removal ranges



particles such as those formed by water-based inks will remain with the water environment. Hence flotation deinking will not work for many conventional water-based inks. This is an important consideration for the deinking of water-based systems.

Ink particles which do attach themselves to bubbles may acquire sufficient buoyancy to float them to the surface whence they are removed. Particles which are less than 20 microns across generally have insufficient inertia to penetrate to the hydrophobic air-water interface of the bubble and remain unattached. Particles which are larger than about 150 microns are too heavy to gain sufficient buoyancy from bubbles and do not float. The particle size range collectible by flotation must therefore lie approximately within 20 to 150 microns for efficient removal to occur. Ink particles detached in the pulper must therefore lie in this range; this is a key requirement for flotation deinking.

On this basis, then, reference to Table III shows that flotation is suited to letterpress, litho and solvent-based gravure inks but not to water-based flexo. Moreover, only a small proportion of laser, photocopier and UV ink particles can be removed without further size reduction.

Washing

Finally, the removal of ink particles by wash deinking is only effective for particles less than about 10 microns in size. Larger particles and especially those which are still attached to fibre clumps may become trapped in the fibre slurry and are difficult to wash out. Wash deinking chemicals are necessary to prevent redeposition of ink particles in much the same way that household detergents perform the same task. Extensive washing, however, is uneconomical because it demands very large volumes of water which subsequently requires environmentally demanding clarification procedures. Wash deinking is therefore used only to remove the smallest particles, and then only in moderation, using efficient technology[2].

Overall then, flotation is the preferred removal option but the importance of particle size distribution has now been explained. The deinking strategy then becomes the dual operation of detaching ink from the fibre and in the process producing the best particle size distribution for ease of collection. Inks which are difficult to deink are those which

not only may be difficult to remove from the fibre but which also do not produce easily collectible particles.

Inks for sheet and web-fed litho

Current deinking technology copes well with these long-established inks. A typical formulation for sheet fed paper and board, for example, could be: 20 per cent pigment, 65 per cent varnish, 5 per cent wax paste, 3 per cent antiset-off paste, 2 per cent cobalt and manganese driers and 5 per cent additional petroleum distillate. The varnish is usually a resin dissolved in a mixture of vegetable (oxidation drying) oil and petroleum distillates. The partial replacement of petroleum distillates with soya bean oil now offers the opportunity for "greener" coldset vegetable newsprint inks for web offset and quickset inks with reduced distillates. These resins and oils should present no problems to recycling in modern plants where they are easily broken down under the alkaline conditions in the pulper and subsequent disperger treatment.

Inks which cause difficulties in deinking

Water-based flexographic and gravure inks

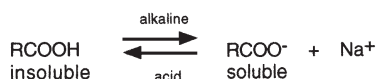
Water-based inks are attractive options for both flexography and gravure printing because they offer the prospect of replacing harmful VOCs. In fact, they have been used for many years on paper and board and some low specification polythene printing. However, water-soluble resins that give high gloss to the inks are scarce and the subject of current R&D. Solvent soluble resins give the best gloss and adhesion characteristics, both of which are important for printing high specification films and foils.

Water-based inks are difficult to separate by flotation for two reasons. First, the resins used must be hydrophilic to be dispersible in water, and this makes it difficult to separate them from the aqueous environment of the pulp slurry. Second, although new emulsion and graft polymer resins are being developed, the particle sizes produced after pulping may be too small to float (Table III).

Although cellulosic packaging waste is recycled, the biggest threat from water-based inks is currently felt in the recycling of some newsprints. Water-based flexographic newspaper printing now offers greatly improved

quality and is already well established and set to increase in volume with the installation of further flexo presses. The future will probably also see a growth in the use of water-based gravure inks for magazine printing.

The problem with water-based newsprint inks lies in their composition and application. They are usually formulated using acrylic resins which are soluble under alkaline conditions where they exist in the water soluble ionic form but become insoluble when converted to the carboxylic acid form:



The ink is therefore printed in slightly alkaline solution and subsequently saponified back to the insoluble carboxylic acid form. This reversal occurs either on making contact with the acidic newsprint or, if alkaline ammonium salt is used, by heating; the ink then “sets”. Because the reaction is reversible these inks show notoriously poor alkali resistance. Although this causes problems for packaging printing where alkaline consumer contents may be experienced, it is not relevant for newspaper printing. However, in the recycling process the resin resolubilises in the alkaline environment of the deinking repulper and the ink can then only be removed by prohibitively extensive washing but not at all by flotation. The nature of the problem is such that recycling plants prefer not to accept “returns” and “overs” from flexo newsprint printers. Nevertheless, small quantities inevitably enter the waste system from consumer sources.

An ingenious technique devised to overcome the problem is that of Gallan *et al.* [6]. They experimented with the addition of a primary acidic flotation stage in which acidified resin is precipitated and coalesced into flotatable size ranges. These are removed in a primary flotation cell. This sequence is then followed by the usual alkaline treatment to detach conventional resin-based inks, followed by a secondary flotation stage to remove them.

More stable water-based inks have recently been devised, particularly for packaging printing, and we may now expect these to find their way into the paper recycling chain. In this category, emulsion polymer vehicles comprise emulsions or dispersions in water of resin containing pigments. Dispersions of this type enable higher solids to be used and therefore higher gloss to be achieved. They “set” by

coalescence of resin particles as the water is removed; setting is irreversible. This irreversibility gives stability towards alkalinity and acidity encountered in many packaging applications.

The vehicles comprise glycol ethers built into the backbone of insoluble styrene-acrylate resins. The hydroxyl groups in the ethers condense with the carboxyl groups in the resin, conferring a hydrophilicity which enables it to be dispersed in water. The downside is that because the “set” resin is insoluble and cannot be reversed, clogging of the anilox roller cells, plate surface and gravure cells is commonplace. These lead to the successive paling of the ink colours necessitating ultrasonic cleaning with its consequent downtime.

In the context of deinking, even if they do not revert to their original colloidal sizes during repulping, the thin films printed seem to produce very small particles which, combined with the hydrophilic properties imparted by the glycol ethers, makes them difficult to remove by flotation.

The latest developments in water-based resins involve the use of graft copolymers which also contain hydrophilic polymer segments. These have been chemically grafted onto the resins to make them hydrophilic and, although they have yet to be evaluated for deinkability, they are likely to be as difficult to remove as other emulsion types.

Generally speaking, water-based ink formulations tend to have delicately balanced chemistries which are difficult to modify in order to provide a solution of the deinking problem. A tactic that has been adopted instead is that of developing flotation deinking additives such as agglomerants and collector surfactants rather than in making modifications to the ink formulations which tend to be delicately balanced. Indeed, considerable research has been conducted to make flotation deinking feasible by changing the flotation cell chemistry in order to render the ink particles hydrophobic so that they may be coagulated into collectible sizes. However, this does require that paper recyclers modify their flotation cells and chemical systems.

UV curing inks and coatings

UV curing inks and coatings have been used with litho for many years and have found many applications where instantaneous drying is required for high speed printing,

plastic and metal decorating. They have been extensively developed for packaging applications for printing impervious substrates on the reel by flexo and gravure; low taint and good adhesion are important.

Today UV curing inks are available for all printing processes including ink-jet. The advantages for print quality are that instantaneous curing not only enables faster printing speeds but also controls ink spread and hence reduction of dot gain.

The environmental advantage is that no solvents are present in UV ink formulations.

The main source of UV-cured inks and coatings in recycled furnishes is magazine covers. Magazines provide a source of chemical wood fibre necessary to raise the quality of recycled newsprint furnishes (typically 70 per cent newsprint to 30 per cent magazine). Conventional UV curing systems are based on epoxypolyacrylate binders reacting by free radical polymerisation induced by a UV activated initiator. However, free radical curing vehicles only react chemically as they pass under the UV light source and the reaction does not proceed thereafter. The result is an incomplete reaction of monomer, especially in thick films, which gives a residual and characteristic "acrylate" odour. Although this may disappear with time, both the odour and the probable toxicity of these monomers restrict their use in certain food packaging applications.

The recent introduction of cationic UV curing inks and coating has overcome this problem in that these inks continue curing after UV initiation, leaving no residual monomer; they cure throughout the film. In the cationic curing mechanism the covalent bond in the photoinitiator dissociates to give charged ions instead of the shorter lived free radicals. Once triggered by UV light, the reaction is autocatalytic. These inks are therefore also finding application in thick films such as those used in "flash cured" water-based screen printing with film weights up to 60 microns. Cationic inks are now also in use as low odour water-based flexo and gravure inks. They have yet to be fully evaluated for deinkability.

The problem for deinking is that UV curing inks and coatings form tough, cross-linked continuous films which bond very firmly to the cellulose fibres. These films form an impermeable layer which also resists the alkaline recycling environment and consequent break-

down in the pulper. UV-cured films therefore tend to separate in large pieces, sometimes even in single continuous sheets where solid areas of ink have been printed. The largest of these pieces may be removed by screening but because they are flat and plate-like, many are able to deform and escape through the slotted screens along with the fibre.

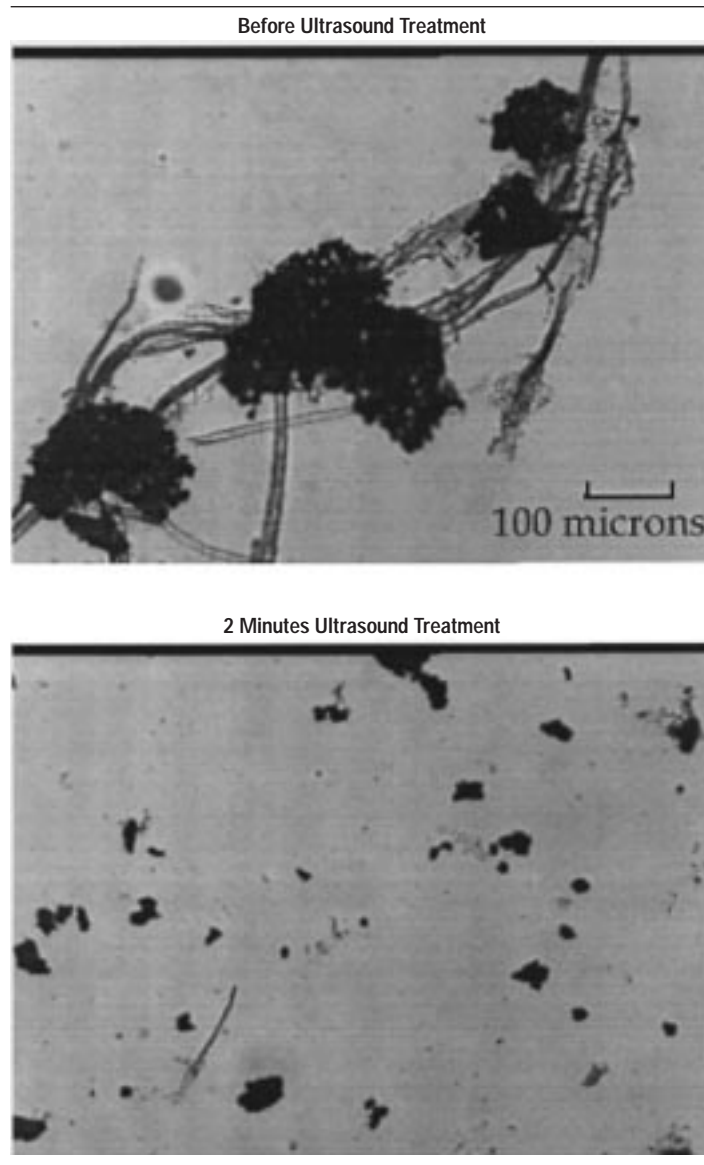
Furthermore, centrifugal cleaning may not be very efficient since the relative densities of the cured films are often fairly close to that of water (1.25 to 1.35). Finally, their cross-linked surfaces also resist attachment to the collector chemicals necessary for successful flotation, resulting in a lowered flotation efficiency.

To reduce the detached UV-cured ink flakes down to particles of flotatable size, new plant has been introduced into the recycling process. Dispersers or dispergers mechanically break the particles by a rubbing or kneading action. To reduce fibre damage, high slurry consistencies (30 to 35 per cent) are employed and particle size reductions from the range 150 to 400 microns down to the 40 to 150 micron are achieved. Nevertheless, the union between cured film and fibre is tenacious and it is likely that inks and coatings do not detach and that fibre is inevitably lost along with removed ink.

Research at the London College of Printing on thick UV-cured screen process films has shown that these can be broken down to flotatable sizes in a controlled way by applying intense ultrasound fields (Figure 2). The collapsing cavitation bubbles produced by the 20kHz ultrasound fields generate localised temperatures of 5,500K and micro jet streams travelling at up to 170ms⁻¹. These impact onto surfaces at pressures of the order of 1,000Nm⁻², breaking down and dispersing particles without the use of chemicals.

Dispersion occurs because the localised forces in the ultrasound field are much greater than those supplied by mechanical action in the pulper. The large platelets of cured ink can be tailored down from sizes greatly in excess of 400 microns to those within the flotatable range. Furthermore, it has been found that fibre cutting is substantially less with ultrasound fields than with mechanical repulping, an important consideration for sustained recycling. Work on 30 micron films of cationic UV-cured water-based screen process inks suggests that although broken down into flotatable sizes, the ink particles are

Figure 2 Micrographs demonstrating fibre detachment and particle size reduction



difficult to detach from the fibre. Work elsewhere using conventional repulping has found similar detachment problems for cationic UV-cured water-based flexographic inks. The thin films printed by flexo, however, yield particles which are too small for flotation, but the presence of attached fibres makes them difficult to separate by washing. Failure to remove the particles results in an effective “dyeing” of the stock.

Non-impact inks

The vast quantities of paper generated by office printers and photocopiers, christened mixed office waste (MOW), offer a source of good quality recyclable chemical wood fibre. MOW contains a high proportion of non-impact printed material, much of which is

difficult to deink. As well as the predominant electrostatic waste, ink-jet printed papers containing water/solvent-based, dye or pigmented, as well as solid phase wax inks are also to be found in mixed office waste. In addition to non-impact printed MOW, material from the new larger format digital presses such as Indigo, Xeicon, Chromapress and Docutec will also find its way into the recycling chain. New inks for the non-impact processes include high density laser and photocopier toners, digital offset inks, and increasingly, coloured laser and photocopier toners.

Toners are usually produced by each machine manufacturer and vary in composition but generally consist of pigment, base binder resin, modifier resin and charge control agent. Carbon black pigments, coloured pigments or copolymer dyes which may be of the azo (yellow), quinacridone/xanthene (magenta) and phthalocyanine (cyan) types are the likely colourants. The base binder resin is heat fusible and is selected according to the press fuser characteristics of the printer. These resins may be blends of styrene-acrylate, polyester or epoxy type materials. The modifier resin may be natural rosin which is added to modify the paper surface and thereby improve toner transfer from heated drum to paper. The charge control agents may be iron oxide, Cr(III) or Co(III) complexes of azo dyes, salicylates, nigrosines, or cetylpyridinium chloride, depending on whether the toners are negative or positive working, coloured or plain black. Other additives include slip agents such as polypropylene wax or silicones.

Surface energy studies indicate that ink composition influences deinking efficiency and that different compositions present different degrees of difficulty. Moreover, the chemical characteristics of both the paper surface and the toner play a major role in toner removal by flotation[7,8]. Overall, deinking efficiency is influenced by the surface energy relationships between toner, deinking surfactant and base paper and more than one surfactant is needed to deal with all types of toner; uncoated papers are more difficult to deink than coated.

Although still based on electrostatic transfer technology, new inks have been developed for the digital offset printing processes. The electro-inks developed for the Indigo digital offset presses are different from heat fusible

toners in that during transfer they start to “set” from a liquid toner state by a polymerisation process; this may progress to full setting over a period of days. These polymers are thought to soften at the temperatures used in the recycling plant and may cause “stickie” as well as deinking problems. The Xeicon digital offset press uses a heat fusible thermoplastic polymer loaded with “microtoner” capable of producing high resolution images. The 7 to 8 micron diameter microtoner particles are triboelectrically attached to ferric carrier particles to reduce the tendency to smoke and to assist transport in the press.

Laser and electrostatic inks generally are applied to the paper surface by a combination of heat and pressure. During fusion the glass transition temperature of the toner binder is exceeded, allowing the particles to flow together and stick onto the cellulose fibres in the paper surface; it produces a very stable copy.

Toner may be removed from the fibre surface by repulping under alkaline conditions but in common with UV-cured films, the detached particles are large, flat and plate-like, ranging in size from 40 to several hundred microns. The larger of these particles cannot be floated. Moreover, the conventional deinking process is not very efficient at detaching toner from the paper fibres which cluster together to form ink-fibre aggregates.

Removal of toner that does detach from fibre is difficult for three reasons:

- (1) the flat particles can flex through the screens along with paper fibre;
- (2) the relative density of the separated material is close to that of water, making centrifugal separation difficult; and
- (3) many of the particles produced are too small to be removed by cleaners and screens but too large to be removed by flotation.

Attempts to solve the problem have taken two approaches. One has been to reduce the size of detached particles down to ranges that can be collected by flotation. The other has been to increase the particle size range to facilitate separation by screening. In the latter, the surfaces of the platelets are chemically modified to encourage them to agglomerate into clusters large enough to be removed by slotted pressure screens and centrifugal cleaners. This is achieved using a two-component chemical system. The first component lowers

the glass transition temperature of the toner to below 60°C so that it softens and becomes tacky under normal recycling conditions. The second acts as a collector which promotes coagulation into spherical particles[9].

Reducing particle sizes in the range 40 to 300 microns down to 40 microns has been achieved by installing dispergers in the recycling plant. Steam explosion technology has also been developed whereby the thickened pulp is heated at 200°C, under pressure, and discharged through a blow valve[10,11]. Rapid expansion through the valve breaks up the softened particles and disperses them. Particle sizes tend to be in the washable size range.

The Materials Research Group at The London College of Printing has successfully applied high intensity ultrasound fields to both the removal and size reduction of fused toners from mixed office waste[12,13]. The micrographs shown in Figure 2 demonstrate that fibre detachment and particle size reduction is achieved. Particles can be tailored down to floatable sizes by controlling the ultrasound dose. Moreover, it has been found that ultrasonic reduction produces two particle size categories; 25 microns and 90 microns[13]. It appears that the toner in question is prepared from two sets of pigment doped resin beads of size 25 and 90 microns and that these revert to their primary sizes under the influence of the strong ultrasound field. This is very convenient for the deinking process as both sizes lie in the floatable size range and may indicate a way forward for producing more recycler friendly toner systems.

The control and removal of “stickies”

Before concluding this discussion of the difficulties presented by inks for the recycling process, it is worth placing into context the difficulties created by adhesives. “Stickies” arise from various sources such as adhesives, pitch, ink resins and plastic films that have found their way into the recycling waste. Adhesives provide the biggest problem and include materials from bindings such as those used for telephone directories, self-adhesive labels, peel and seal envelopes and tapes. The best and possibly the only satisfactory way of dealing with stickies is not to allow them into the waste mix in the first place but this is impossible. A major problem lies with the

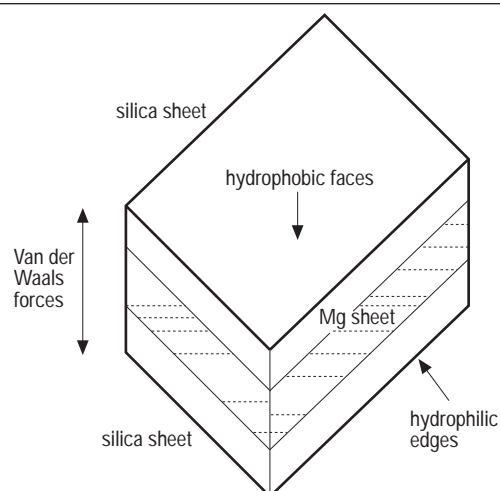
ingenuity of adhesive manufacturers in developing an increasing range of different adhesive types so that what may be a reasonable recycling solution for one stickie may be ineffective with another; their formulations are both complex and varied. To give some idea of the range, we must consider pressure sensitive polyacrylates from peel and seal envelopes, polyisoprenes from self-seal envelopes, polybutadienes and natural rubbers. Hot melts include polyethenes, waxes and tackifying resins used in bindings. In the recycling process they stick to felts, foils, and press rolls. In the final sheet they degrade the printability and runnability of the paper they contaminate. There is no single effective way to remove or control stickies. Moreover, their “stickiness” is aggravated by the recycling environment, increasing above room temperature, at high pH and high rates of shear, by the adsorption of ionic charges, and in the presence of other additives.

The stickies themselves vary widely in size, ranging from the fully dissolved, through colloidal sized particles one micron and under, up to the large primary stickies formed by the break-up of adhesives directly from the substrate. Much work has been done to remove them by mechanical and chemical means. Dispersers are used to break up large stickies such as hot melts, and pressure screens with 0.23mm slots show promise for removal of pressure sensitive adhesives, styro-foam and waxes. It is difficult to remove them using centrifugal cleaners because they often have the same density as or a similar density to water. Moreover, being flexible they can deform and flex their way through mechanical screens.

Chemical approaches have focused on three main areas, the use of inorganic talcs, dispersants and synthetic fibres:

- (1) Talc is added to the pulp to immobilise the stickies. It has an interesting structure in that planes or sheets of magnesium atoms are sandwiched between planes of silica molecules, the assembly being held together by Van der Waals forces (Figure 3). The edges of these structures exposing magnesium are hydrophilic, allowing the talc to be dispersed in water. The silica faces, on the other hand, are hydrophobic enabling them to adhere to stickies. Small stickies coat the talc faces, whereas talc particles themselves coat the surfaces of large stickies. Moreover, talc acts as a

Figure 3 Sandwich structure of talc, held together by Van der Waals forces



white filler, improving the brightness and printability of the final paper.

- (2) Dispersants comprise anionic polymers which adsorb onto the stickie, thus imparting negative charges which in turn repel like charged stickies and prevent them from agglomerating into large particles.
- (3) Synthetic fibres having a fibril structure and large surface areas which wrap up stickies and reduce their ability to foul wires and felts.

All in all, however, there is no one single method for controlling all types of stickies and it is generally considered that there is no sure cure by conventional means. An alternative strategy that is gaining momentum is for papermakers and research organisations to work alongside adhesives manufacturers towards developing “recycle friendly” adhesives which, although inevitably entering the recycling chain, will not interfere with it [14].

Conclusion

Developments in the printing processes have fostered a diverse range of inks of increased complexity. Many of the binders of these new inks and coatings have created problems in the deinking of waste paper, that did not exist in the early days of paper recycling. Combating these problems has fostered the development of chemical and mechanical solutions. In addition to development costs there are added capital and running expenses and many solutions are far from complete. At first sight the interests of the ink manufacture and paper recycler are divergent. For the first the goal is

to provide durable films which stick tenaciously to paper; for the second, it is to remove them. Perhaps a convergence of objectives is needed.

Reduction of the problems caused by stickies is being tackled by cooperative research initiatives between adhesives chemists and paper recycling technologists. New generations of inks for non-impact printing are on the very near horizon. Ink jet may well dominate the digital scene during the next decade. Is it not possible to consider now the development of, for example, stable yet bleachable colourants for ink jet or toner systems which easily break down to flotatable sizes? The question is that, given an understanding of the nature of the problem, can the ink chemist build recyclability into new products without substantially increasing costs, and before customer pressure demands it?

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