



Tappi Journal Special Report

Calcium carbonate

and the evolution of alkaline papermaking in North America

By Douglas J. Burke

Most trends and innovations originate in one area and then migrate to other regions, to be accepted, adapted, or rejected. The phenomenon is most obvious in fashion and music, where trends come in vogue and then fade away to the racks of the Goodwill stores or to Muzak and "oldies" radio stations. Technical innovations, on the other hand, are judged more on their value and remain until replaced by the next innovation.

In the case of alkaline papermaking, the trend seen in Europe to move away from acid-based papermaking has been well accepted and the technology has spread to mills in North America.

The alkaline revolution **Wood-free papers**

European producers of wood-free printing and writing papers began switching from acid to alkaline papermaking systems in the 1960s. The driving force for the change was a desire to reduce costs by increasing the mineral content of their wood-free papers, thus

reducing the amount of expensive chemical pulp. Abundant deposits of chalk, limestone, and marble in Western Europe made these forms of calcium carbonate an attractive option as a filler. Calcium carbonate is soluble in acid systems, so the early producers of carbonate-filled papers had to change the chemistry of their wet ends to an alkaline pH.

Fiber and energy savings were the immediate benefits, but it soon became apparent that the alkaline sheets were brighter, stronger, and provided superior printability. The quality benefits set off a boom in alkaline conversions, changing the face of European papermaking.

North American papermakers were aware of the changes taking place in Europe, but they saw no compelling reason to jump on the bandwagon. Abundant supplies of cheap chemical pulp and kaolin fillers removed any immediate incentive to modify the classic acid papermaking system. More important, most customers were happy with the product, so the reasonable approach was to sit tight and avoid rocking the boat.

Sponsored by OMYA Inc.

Vol. 76, No. 4 Tappi Journal 40A

One notable exception was the U.S. Library of Congress, the nation's largest book repository. With an estimated 6 million volumes in an advanced state of deterioration—the result of alum and rosin sizing at acid pH—the agency initiated a massive public-relations effort to educate the public about the impermanence of acid papers. In 1975, they began specifying a 3% calcium carbonate content in all file folders and storage boxes purchased by the agency. Other government agencies and some specialty publishers followed their lead, creating a domestic market for alkaline paper. Still, the alkaline revolution was to remain a largely European phenomenon until pulp prices began to rise in the 1980s.

In the early 1980s, European mills were producing papers with 20–25% CaCO₃, while mills in North America papers typically contained around 8% clay. With pulp prices near US\$ 800/ton, the opportunity to increase filler loads by even a few points provided a powerful incentive to switch to calcium carbonate. Several North American mills began to change the chemistry of their papermaking systems, even though calcium carbonate fillers at that time were more expensive than the readily available kaolin fillers being mined in middle Georgia's clay belt.

The push toward conversion gained momentum as papermakers discovered that carbonate-filled papers drained more readily than clay-filled papers and provided substantial savings in drying energy. For mills with dryer-limited paper machines, the increase in drying capacity translated directly to an increase in daily production. Papermakers also saw a drop in refining-energy requirements, since pulp fibers hydrate and swell more readily in an alkaline furnish. Reduced water demand and improved stability of wet-end pH were additional benefits. There was also a growing awareness that recycling was here to stay and that the quality of the secondary-fiber stream would become an increasingly important issue to producers of all grades. The superior quality of alkaline papers as a source of secondary fiber became one more item on the list of potential benefits.

Today, about 80% of the European production of wood-free printing and writing papers is alkaline, with virtually 100% alkaline production projected for the year 2000. The corresponding figure for North America stands at about 60%, with 85% conversion to alkaline predicted by the turn of the century.

Wood-containing papers

The alkaline revolution ultimately expanded into the wood-containing sector, albeit more slowly, since the economic incentives were not as compelling. The wet-end chemistry also proved to be more challenging than for the wood-free grades. But after a decade of experience running high-solids carbonate coatings on their wood-free grades, the Europeans were ready to transfer that technology to the groundwood-containing lightweight-coated (LWC)

grades. The idea was to produce a coated sheet that printed as well as the competition without using imported clay. Once again, the solubility of calcium carbonate at low pH meant that producers of coated base stock would have to move the wet-end pH toward neutral to accommodate the carbonate entering the papermaking system directly as filler and indirectly in the form of coated broke. LWC producers began switching to neutral or "pseudoneutral" (carbonate-buffered systems containing alum) systems in the early 1980s.

The effort to reduce coating costs without sacrificing printability and optical properties yielded dividends in the form of improved coating rheology. The clay coatings used on acid papers tended to dewater under the blade at high machine speeds, limiting the speed at which coatings could be applied. Carbonate coatings eliminated this problem, allowing producers to increase machine speeds and achieve greater productivity. Carbonate coatings also required less binder, which meant that mills could reduce their consumption of costly binders. Customers were happy because the carbonate coatings provided superior brightness, runnability, and printability.

There were also some problems. The warm, neutral waters of the papermaking system promoted microbial growth and slime formation, forcing mills to add additional biocides to the system. Retention and pitch formation were common afflictions requiring individual solutions. While additives were available to manage these conditions, the unique wet-end chemistry at each mill usually meant a period of trial and error to determine the proper balance of additives, dosage rates, and points of addition.

Despite these concerns, total European production of coated groundwood had grown to about 5.0 million tons by 1989. Ap-

I. Relative advantages of alkaline and acid papermaking

	Alkaline	Acid
Sheet		
Mechanical properties	x	...
Optical properties	x	...
Recyclability	x	...
Permanence	x	...
Mill		
Filler options	x	...
Energy requirements	x	...
Makeup water	x	...
Effluent treatment	x	...
Corrosion	x	...
pH stability	x	...
Retention	...	x
Pitch	...	x
Microbial contamination	...	x
Printing		
Opacity	x	...
Brightness	x	...
Stiffness	x	...
Ink holdout	x	...

Table I lists the relative advantages of alkaline and acid papermaking in several key categories.

proximately 1.3 million tons was being produced under neutral conditions on eight paper machines, with another 0.6 million tons produced under pseudoneutral conditions on eight smaller machines, for a total 38% neutral or pseudoneutral production. Today, almost 50% of European LWC production is produced under neutral or pseudoneutral conditions.

In the meantime, North American mills were producing acid LWC using traditional coating formulations—all clay, lots of starch, with calcined clay or titanium dioxide thrown in for opacity. From the standpoint of pigment cost—the major incentive for European papermakers—there was no reason to switch to calcium carbonate. So the second wave of the alkaline revolution remained a curious European phenomenon. Curiosity turned into concern when North American printers began importing large quantities of carbonate-loaded LWC paper from Europe during the 1980s.

The first North American LWC mill to go neutral made the move in 1988. Changing the pH of the wet end was not a principal goal. The mill simply wanted to improve coating rheology so it could run the machine faster and produce more paper. Pilot coating trials demonstrated that speeds could be improved significantly by adding as little as 10–15 parts calcium carbonate to their traditional clay-based coating formulation. The mill modified its coating formulation and increased speed by more than 10%. With coated broke entering the papermaking system, the mill allowed the wet end to gradually shift to a neutral pH and then started adding 1–2% carbonate filler at the wet end to buffer the system, reduce fiber content, and increase sheet brightness.

Since then, eight other North American LWC machines have converted to pseudoneutral conditions. (Most of the North American mills are still using alum.) Lured by the prospect of higher coating speeds, these mills have also lowered their costs of production while increasing sheet strength, brightness, and printability. Several mills have increased sheet brightness by 3–4 points at equal opacity, forcing competitors to boost the quality of their sheets by adding more titanium dioxide or chemical fiber.

Still, these benefits were not obtained without a price. Mills have had to tinker with retention aids and biocides while coping with pitch formation. However, the European experience with these problems has helped make the conversions somewhat less trouble-

some. North American experience from the nine neutral conversions since 1988 should, in turn, make it easier for the other mills that are planning to go neutral.

Carbonate coatings for LWC

The driving force for conversion

The outcome of the alkaline revolution in the wood-free grades is no longer in question. By the end of the century, virtually all of the coated wood-free grades in Europe and North America will be alkaline, and coatings for these grades will contain high levels of carbonates. The action has moved on to the coated groundwood-containing grades, especially in North America, where the push for neutral papermaking has been driven entirely by the coating end of the production process.

Machines speeds finally reached the point where the rheology of the North American clay-based coatings became a limiting factor in machine productivity. When mills learned that they could increase speeds considerably by substituting as little as 10 parts calcium carbonate for clay in the coating formulation, they began converting their wet ends from acid to neutral.

Like the wood-free papermakers, they found that calcium carbonate provided several other significant benefits.

- ▶ Superior brightness of calcium carbonate reduced the demand for costly calcined clay
- ▶ Stronger coated surface reduced the demand for binder adhesive in the coating
- ▶ Improved drainage reduced the demand for steam in the dryer

- ▶ Higher sheet strength reduced the demand for chemical fiber and allowed the use of more broke in the furnish
- ▶ Alkaline wet end reduced refining-energy requirements.

The mills were also well aware that these benefits came at a price in the form of higher costs for biocide, retention aids, and talc. Pigment costs were not considered to be a significant factor. Suppliers of ground calcium carbonate had stepped up their efforts to provide a steady supply of pigment, and with seven GCC plants operating in North America, the cost of ground calcium carbonate and kaolin are now comparable.

II. Relative advantages of GCC, PCC, and kaolin pigments

	GCC	PCC Filler	Calcined kaolin
Cost	x	x	x
Strength/filler loading	x	...	...
Brightness	x	x	...
Opacity	...	x	x
Gloss	...	...	x
Smoothness	...	...	x
Drainage/drying	x	...	...
Abrasion	x	x	...
Coating			
Cost	x	x	x
Strength/binder demand	x	...	...
Brightness	x	x	...
Opacity	...	x	x
Gloss	...	...	x
Smoothness	...	...	x
Drainage/drying	x	...	...
Rheology	x	...	...
Solids content	x	...	...

Table II summarizes the relative advantages of GCC, PCC, and calcined kaolin pigments in coating and filler applications.

For filler applications, many mills were attracted to the idea of producing synthetic calcium carbonate in on-site satellite plants. The technology was appealing from a cost perspective, and the ability to produce calcium carbonate in house guaranteed a stable supply of the high-brightness pigment. One mill made the leap, and then another, creating a bandwagon effect as mill after mill set up on-site carbonate plants in the late 1980s. The boom tapered off as mills began to understand the hidden costs associated with the new technology.

The hidden cost of alkaline paper

Calcium carbonate (CaCO_3)—one of the most common, stable, and widely dispersed materials in the world—occurs naturally in oyster shells, limestone, chalk, and marble. Natural carbonate is mined from surface deposits; synthetic carbonate can be formed by any of several chemical reactions. While both materials share the same chemical formula, their shapes are quite different. Natural ground calcium carbonate (GCC) is rhombohedral, sort of a slanted cube. Precipitated calcium carbonate (PCC) is scalenohedral, a shape that brings cauliflower to mind.

The wide availability of natural calcium carbonate in Europe made this the pigment of choice in European papers and coatings. The situation was different in North America, where the wide availability of kaolins made them the traditional papermaking pigment. When the alkaline revolution swept through Europe and across the Atlantic, there was some concern about the availability of GCC. Consequently, many North American mills opted to set up satellite plants, where they generated precipitated calcium carbonate (PCC) from boiler flue gases and lime.

The PCC plants were competitive with GCC on a pound-for-pound basis. As an added bonus, the irregularly shaped PCC particles were touted for their opacifying power—a function of the light-scattering efficiency of the chunky PCC particles. The downside was that the irregularly shaped PCC particles could not be packed together as efficiently as the blocky GCC particles, resulting in a weaker sheet. This imposed limits on the amount of PCC filler that could be added to the sheet.

At first, this was not a problem. After all, papermakers were concerned primarily with the rheology of the coatings and the associated increase in the speed and quality of the coating process. There was also widespread apprehension about trying to accomplish too much in a short period of time. The changes to the coating formulations and the wet-end chemistry were scary enough. In the minds of machine managers and mill superintendents, high filler contents spelled potential trouble. They liked PCC because its high opacifying power made it possible to produce an alkaline sheet with

very little filler. But once their neutral systems were operating smoothly, attention began to shift to the impressive economic benefits to be gained by increasing sheet filler levels. The problem was that sheet strength suffered when PCC was used as a filler. Mills with sizable investments in on-site plants now find themselves underutilizing their PCC production capacity and purchasing supplemental GCC to maximize filler loading, reduce sizing costs, and increase speeds.

Slurry solids were another issue. The rheology of PCC coatings limited the solids content to about the same level as clay formulations, while GCC solids could go several points higher. PCC coatings also required much more binder than GCC coatings. All of these factors have contributed to the growing popularity of GCC in North America, a trend accelerated by the routine availability of ultrafine grades of GCC, allowing even higher filler loadings and better drainage.

The future

Papermaking is a capital-intensive industry, which is another way of saying that the cost of the machinery far outweighs the cost of labor. Large investments in physical plants have made it possible to produce vast quantities of paper at reasonable cost. The tradeoff is that the sheer magnitude of such investments is an impediment to rapid change. Still, market forces compel incremental change, even in the most stolid of industries. The alkaline revolution now under way in North America is proof that the irresistible force has the power to move the apparently immovable object.

In recent years, U.S. printers have imported 700,000 tons of European paper. The reason: North American papermakers are producing sheets that are stiffer and more opaque than they need to be from the standpoint of printability. European papermakers operate at lower opacity and stiffness specifications—and at a lower cost—with improved print quality.

If North American papers are to compete in a global marketplace, papermakers will have to emulate their European competitors and learn to produce a better sheet with less fiber. European papers now contain twice as much filler as American papers, but the gap is closing. Clearly, filler levels in paper will continue to rise, with papermakers becoming increasingly reliant on GCC to maximize filler loads. The only uncertainty is the rate of change, which will be determined by the magnitude of irresistible economic forces operating on a massive but movable object.

Burke is a freelance writer specializing in the pulp and paper industry, 1011 Larch Ave., Takoma Park, MD 20912.

Survey finds varying uses and views on paper fillers

A survey conducted early this year on behalf of TAPPI was sent to 741 North American mills, of which 195 responded (26.3%); of those, 143 of the mills (19.3%) use filler. The responses from the 143 mills were tabulated and grouped by whether the mill runs an acid-, neutral-, or alkaline-based system. Roughly 43% of the respondents are running acid, nearly 17% are neutral, and 40% are alkaline.

As a whole, the 143 mills account for 193 paper machines. Most (42.5%) of the machines are used to produce uncoated freesheet, 22.8% are used to make coated freesheet, 15% are used for uncoated groundwood, 13.5% for coated groundwood, and the rest are assigned to various other grades.

Daily production was reported for 169 of the 193 machines. Of those 169 machines, 29.6% (50) produce no more than 200 tpd of paper. Another 27.8% (47) produce 201–500 tpd of paper; 22.5% (38) produce 501–900 tpd; 12.4% (21) produce 901–1300 tpd; and 7.1% (12) produce 1401–2500 tpd. One mill (0.6%) produces between 4901–5000 tpd.

Acid

As might be expected, with few exceptions, mills running acid limited their choice of filler to clay or calcined clay, primarily for opacity or surface properties. A few also added TiO_2 . Several identified low cost for opacity as an advantage of clay. Others, however, considered the cost for opacity high. Abrasiveness was also a concern. One mill using #2 clay, for example, noted that it is hard to retain in the sheet, reduces sheet strength, and hurts machine runnability (in LWC).

Another response came from a mill that produces coated and uncoated freesheet, using a blend of clay and calcined clay primarily for opacity and secondarily for fiber replacement (8%). The fillers tend to decrease drying time and steam use at that mill. The respondent noted that “manufacturing costs are high due to

customer demands for optical properties.” In addition, “our filler clay is cost effective for fiber replacement (but) bulk is a problem.”

Grades – Total

Grades produced at all mills responding,
by number of machines (%)

Grades – Acid

Grades produced at responding acid mills

Grades – Neutral

Grades produced at responding neutral mills

Another mill commented that its clay fillers improve opacity and brightness for coated groundwood and they provide more-uniform sheet properties. Weaknesses included reduction in sheet strength and buildup on the paper machine and dryers.

Neutral

Just over 9% of the surveys returned came from mills operating neutral systems. Those 18 responses account for 23 machines used primarily to produce coated free sheet (43.5%). Most of the 18 use filler for opacity, followed by brightness.

The mills running neutral were least predictable in their choice of filler: some preferred clay, others preferred calcium carbonate, others used a blend, and several added TiO_2 . A common complaint was the cost of TiO_2 .

One respondent who has three machines running neutral uses PCC on one of the machines to supplement TiO_2 . (The respondent longed for a friendlier precipitated calcium carbonate supplier, however, one more willing to help with the switch to alkaline and easier to deal with on cost.) Another said, “we have to use coated broke to keep the mill in balance. TiO_2 is added for opacity and PCC for chemistry.”

Yet another mill, which produces coated free sheet and coated groundwood, uses about 85% filler for fiber replacement. The mill blends PCC and ground calcium carbonate. It described the strengths and weaknesses of each as follows:

- ① Precipitated—debonding, harder drying, higher steam usage, better opacity
- ② Ground—better running with respect to easier drying, lower steam usage; not as good an opacifier; better with respect to higher loading with less debonding.

A mill that uses clay as filler in uncoated groundwood to between 20–25% described it as a consistent product that performs well. However, the dispersants in the clay hurt formation, foaming and handling in winter can be a problem, breaks can occur, and overall machine cleanliness is affected.

Alkaline

A little more than 24% of surveys returned came from mills running alkaline systems. Those 47 mills run a total of 58 machines, of which 62.1% are used to produce uncoated free sheet and 27.6% are used to make coated free sheet.

Most of the alkaline mills used some form of calcium carbonate as filler. One mill that blends fillers uses PCC to increase opacity and brightness but notes that PCC lowers physical strength. The mill favors GCC for fiber replacement and its ability to decrease drying time.

In contrasting ground and precipitated calcium carbonate, a respondent said GCC is cheap but doesn't give opacifying properties while PCC, though more expensive, gives excellent opacity. The drawback of PCC is that it decreases the internal strength of the sheet.

Finally, one respondent whose mill produces uncoated free sheet regretted the switch to alkaline and was particularly critical of PCC. "PCC is awful for paper quality and machine runnability...causes high porosity...causes dusting on printing presses...is very difficult to retain...and very expensive," the person wrote.

Grades – Neutral

One respondent who uses clay and PCC listed brightness and opacity as the strengths of fillers in acid, poor adhesion and dusting as weaknesses. That person listed fiber replacement and brightness as strengths of fillers in alkaline; low porosity, weaker bonding, and increased drying time were listed as weaknesses.

The switch to alkaline has apparently been successful enough for one mill that the respondent would like to change two of the machines still running acid. That mill uses PCC for its coated free sheet, describing the filler as a good opacifier for the money.

Another mill using PCC for uncoated free sheets has found the alkaline system to be more complicated. It also requires longer boil-outs and machine cleanups. However, it allows the mill to use more filler for fiber, without strength loss.

A respondent who uses clay and PCC would like a filler with "more brightness without loss of bulk and stiffness." That person would also like to see a filler developed that could be more universally applied to various paper grades.

Results of the survey also indicate a keen interest within the paper industry to reduce production costs, a driving force in the conversion to alkaline papermaking. It then allows papermakers to take advantage of the higher strength properties of alkaline fibers and use less of them—substituting filler for fiber. That, in turn, allows for notable savings and improvements in paper properties. Survey results and literature indicate that papermakers can increase filler use after converting from acid and that fillers such as ground calcium carbonate could be used at even greater levels than reported by most respondents.

Combinations

About 5.5% of the responding mills that use filler run split systems. Most often, one machine runs acid, another alkaline. Some mills even run acid, neutral, and alkaline. Percent filler for fiber replacement was a maximum of 20% among mills running split systems. With few exceptions, the main grade produced by those mills was uncoated free sheet. Coated groundwood accounted for most of the production at three or four of the mills.

Strengths and weaknesses of fillers (Based on survey responses)

Strengths				
<u>Clay</u>	<u>Calc. Clay</u>	<u>PCC</u>	<u>GCC</u>	<u>TiO₂</u>
Low cost	Opacity	Opacity	Low cost	Opacity
Performance	(Brightness)	Good bulk	Better drying	
Consistency		Brightness	Higher loading	
Low abrasion		On-site prod.	Less debonding	
Weaknesses				
<u>Clay</u>	<u>Calc. Clay</u>	<u>PCC</u>	<u>GCC</u>	<u>TiO₂</u>
Poor brightness	Cost	Cost	Opacity	Cost
Felt filling	Felt filling	Strength weakened	Wear	Strength
Dirty machinery	Crumbling	Poor retention		weakened
		Hard to size		