Making the Most of the New Breed of Fluorochemical Treatments for Paper

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ABSTRACT:

Since the early part of the decade, fluorochemical treatments for food contact applications have changed substantially, such that new products that are free of PFOA, longer-length PFCAs and their precursors (at or above detection limits) have supplanted the traditional grades available in the past. The new fluorochemicals are available in a large range of specific chemistries, and their breadth and depth are often confusing to the paper processor. However, the manufacturing methodologies have not changed that much, with many of these current products exhibiting the same system compatibility issues as in the past.

In this study we provide a short review of the current available technologies, and also examine three different fluorochemicals as representatives of a number of products available in the current paper market. Results of ladder experiments and DOEs to measure performance under various chemical regimes are presented here in graphical form. This permits easy understanding of the underlying challenges faced by papermakers in using the new breed fluorochemicals.

The objective of the study will be to illustrate the role of pH and charge chemistry on the ultimate performance of the new materials, such that paper processors may derive maximum benefits in terms of oil and grease resistance.

INTRODUCTION

Since the early part of the decade, fluorochemical treatments for food contact applications have changed substantially, such that new products that are free of PFOA, longer-length PFCAs and their precursors (at or above detection limits) have supplanted the traditional grades available in the past. These new fluorochemicals are available in a large range of specific chemistries, and their breadth and depth are often confusing to the paper processor. However, the manufacturing methodologies have not changed much, with many of these current products exhibiting the same system compatibility issues as in the past.

In this study we provide a short review of the current available technologies, and also examine two different fluorochemicals as representatives of a number of products available in the current paper market. The objective of the study will be to illustrate the role of pH and charge chemistry on the ultimate performance of the new materials, such that paper processors may derive maximum benefits in terms of oil and grease resistance.

Response to the PFOA Challenge:

The concern over perfluorooctane sulfonic acid (PFOS) in the early 2000s prompted the USEPA to take a closer look at all fluorochemicals similar to it in size and structure. The most prominent of these was PFOA (perfluorooctanoic acid and its salts). PFOA and its related salts have been used for a number of years by the fluorochemical industry, both as a building block for other fluorochemicals and as a processing aid for fluoropolymers. As with PFOS, PFOA has a tendency to accumulate in biological systems, and is extremely persistent in the environment. In response the USEPA asked a number of fluorochemical manufacturers to voluntarily reduce, and then completely phase out the production of, PFOA by 2015. Since PFOA has been a major component of fluorochemicals for paper applications, replacement of this material was not a trivial undertaking.

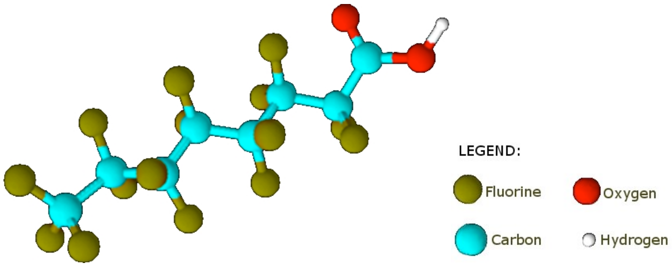


Figure 1: Perfluorooctanoic Acid (PFOA)

The industry responded by developing a number of new, innovative fluorochemical treatments for paper. Though designed to duplicate performance of the old materials, the "new" fluorochemicals tend to be markedly different in chemistry and properties from the legacy materials. Main differences are as follows:

- The new fluorochemicals make use of shorter-chain perfluorinated groups, in which the perfluoronated functional chain is either four or six carbons in length (versus eight carbons for PFOA-inclusive legacy grades). The new shorter-chain perfluoronated groups and their precursors have substantially lower residence times in mammalian biological systems than older (C-8 based) legacy materials, and are also less environmentally-persistent[1,2].

- New fluorochemicals tend to be polymeric, and as such are substantially more resistant to migration than older legacy grades based on monomeric fluorosurfactants. However, the polymeric nature of the new of fluorochemicals means that they are less persistent in their transfer characteristics to cellulose fibers. Subsequently, optimization of processes and formulae is more important than ever.

Some of the old characteristics still apply, however. The new fluorochemicals are still classifiable by charge in solution – Anionic, Amphoteric or Neutral or Cationic. Also, as with legacy treatments, the new fluorochemicals can exhibit sensitivity to pH in paper furnish or external sizing formulations, due to the presence of acid or alkaline buffers required for stability.

Each of the new fluorochemical treatments reflects an individual design philosophy of its parent company, and each has its own strengths and weaknesses dependent upon formulation, manufacturing methodology and / or end use application. Paper manufacturers do well to take the differences into account, for not every fluorochemical is interchangeable in any given system, and often times trying to use a new PFOA-free fluorochemical as a "drop in" replacement where it is not appropriate to do so destroys its performance.

Making the Most of the New Fluorochemicals

In simplest terms, a major factor in making the new fluorochemicals work properly in paper applications is ensuring that there is a sufficient amount of the product being used for the application. Also, the fluorochemicals must go where we wish for them to go – e.g. the cellulose fiber in the treated paper. These two items seem obvious, but they are the main cause of problems with any new-breed fluorochemical system.

In the ensuing examples (**Parts 1 - 3**; below), three different new fluorochemicals are examined for performance under various conditions present during papermaking and external sizing. Each is here given a pseudonym, and all are polymeric materials making use of C6 technology (i.e. six perfluoronated carbon atoms in the active functional group). Fluorochemical #1 (abbreviated as FC #1) is cationic in its chemistry and mildly acidic in pH. Fluorochemicals #2 and #3 (FC #2, #3) are also cationic and acidic in chemistry. (see Table 1 in the **APPENDIX** for details) Together they provide a small sampling of the PFOA-free fluorochemicals* available for paper and packaging applications.

Note - * = PFOA-free at or above current detection limits

EXPERIMENTAL RESULTS:

Part 1: Critical Mass

Whether incorporated through internal or external sizing methods, the new fluorochemicals require "defense in depth" for proper resistance to greases and oils. What this means is that there needs to be a sufficient number of fibers treated on top of the sheet and deep within the sheet to ensure protection, even if the treatment is discontinuous.

For internal sizing of new fluorochemicals into paper there is a practical basis weight limit for each of the different products, such that there is sufficient critical mass of treated fiber to resist oil and water based stains to the degree desired by the end-user[3]. This limit varies from product to product and from formulation to formulation.

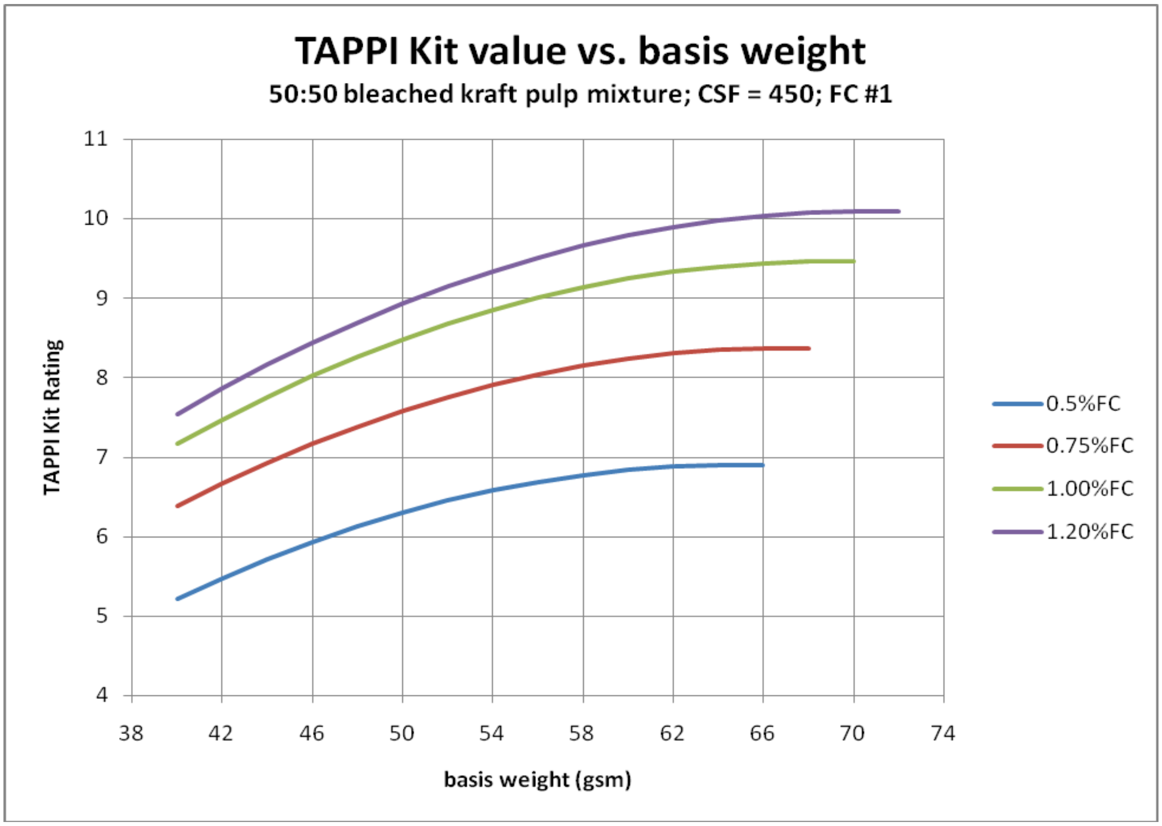


Figure 2: TAPPI Kit value vs. basis weight (taken from Box-Behnken DOE)

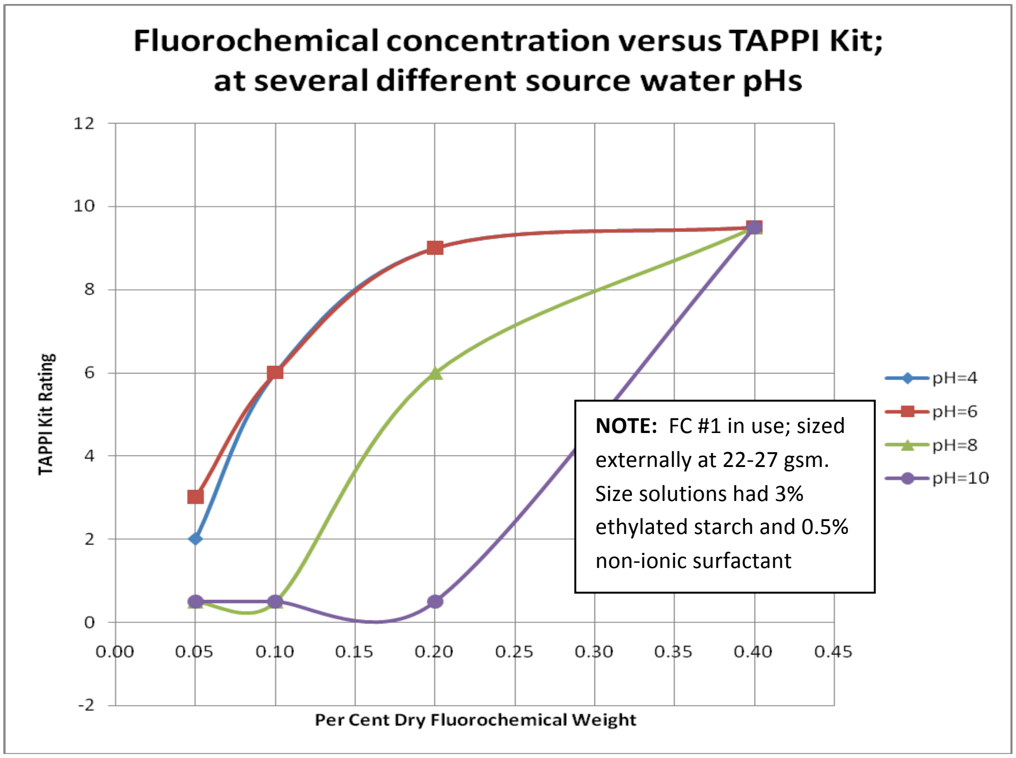
In the example above (Figure 2) a cationic C6 fluorochemical (FC #1) was evaluated in a 50:50 mixture of bleached hardwood and softwood kraft pulps (CSF = 450) to determine the relationship between basis weight and TAPPI kit rating, given different levels of the fluorochemical (percentage on-dry fiber) and paper refinement (Canadian Standard Freeness). As is evident from the 3D renderings there is a near-linear relationship between basis weight and performance until the basis weight reaches about 62-65 gsm. At the 62-65 gsm level the performance reaches a plateau (which may be considered the “critical mass” for that system), and at that level further increases in basis weight have a much less dramatic effect on performance.

External sizing with new fluorochemicals relies on uptake of the size into the paper sheet, as well as on the concentration of the fluorochemical additive in the size. When uptake or fluorochemical concentration is insufficient, the defense-in-depth provided by the treated fibers deep within the sheet is not available, and the paper fails to protect against food-based stains. As before, laboratory experimentation is required to determine the appropriate loading of the fluorochemical in conjunction with the proper uptake rate into the sheet.

Part 2: pH buffering

As was often the case with legacy fluorochemicals the “new” fluorochemicals can be adversely affected by the pH of their host furnish or size solutions. In order to make the “new” fluorochemicals water-soluble, manufacturers will produce them as water-based emulsions or convert them into acid or alkaline salts. The process makes use of pH buffering of the fluorochemical to either mildly acidic or mildly alkaline conditions, which, if reversed, often will result in instability of the fluorochemical to the extent where performance is compromised.

Sometimes the pH of the papermaker's process water varies for different reasons, such as a change in the supply water quality, the presence of dissolved pigments or fillers (such as precipitated calcium carbonate), poor water circulation, use of chelating agents, and / or sulfuric acid and alum dosage. Use of an alkaline-buffered fluorochemical is not a problem in this case, but acid-buffered fluorochemicals can be severely impacted, especially at low concentrations in solution. The lower the concentration, the more severe the impact is on water-based and oil-based stain resistance of the resultant paper. Paper manufacturers may avoid this problem by readjusting pH levels to more neutral conditions just prior to the introduction of the pH-sensitive fluorochemical. An example is provided in Figures 3 and 4 on the next page, in which Fluorochemical #1 is introduced into external sizing formulas made up with water at different pH levels. (Note – host water pH was adjusted, using sulfuric acid and sodium hydroxide buffers.)



NOTE: FC #1 in use; sized externally at 22-27 gsm. Size solutions had 3% ethylated starch and 0.5% non-ionic surfactant

Figure 3: FC #1 TAPPI Kit ratings at different pH ratings

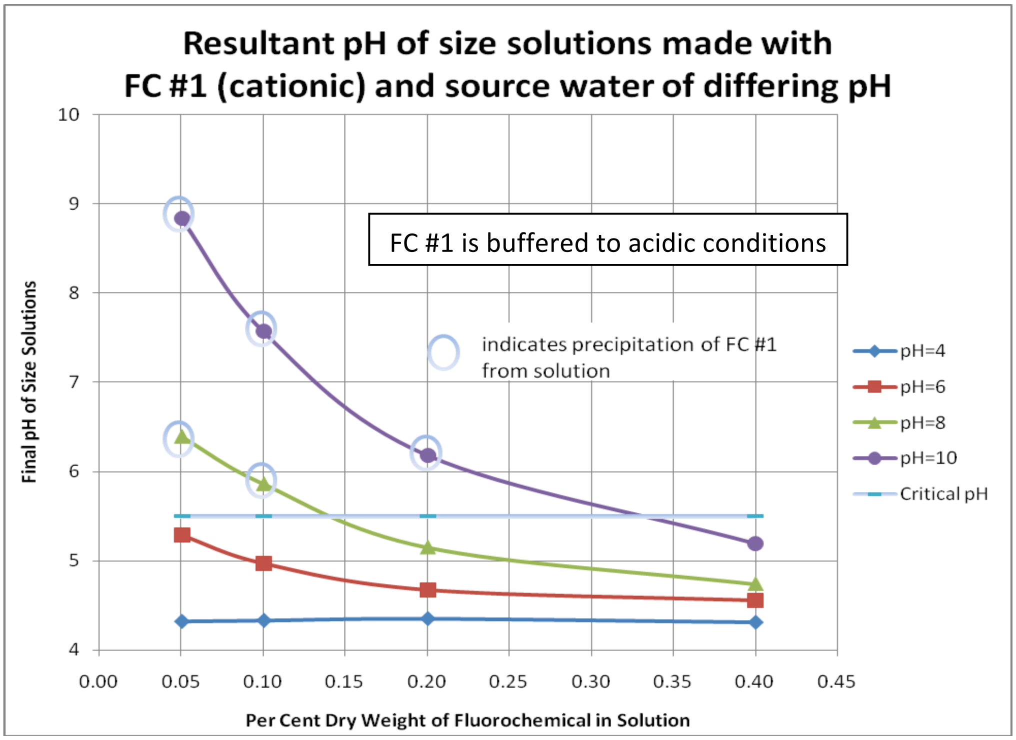


Figure 4: FC #1 initial and final pH in external size solution

The two figures above show the consequences of insufficient attention given to solution buffering. In this case Fluorochemical #1 (cationic and acid-buffered) exhibits substantially-degraded TAPPI kit performance as solution pH rises. Although the fluorochemical is acid-buffered, the buffering is insufficient to protect the product as it is exposed to increasingly alkaline conditions, and the end result is precipitation of the free-base fluorochemical in solution. This is reflected in the increasingly poor performance of the resultant paper in resistance to oil-based stains (as measured by the TAPPI Kit test)[4].

Part 3: Charge Potential Considerations[5]

As was the case for legacy products the new fluorochemicals are defined by their electrical charge potential in solution –cationic (electropositive), neutral/amphoteric or anionic (electronegative). Charge potential of the fluorochemicals is an important consideration to paper makers as it determines where within the forming paper sheet the chemicals will reside, and, ultimately, how the fluorochemical treatment performs in resisting food-based stains.

Ideally, fluorochemicals should be attracted to and bind with the cellulose fibers (which are slightly anionic). This is particularly true for cationic fluorochemicals, which are attracted to the mild anionic areas in the cellulose fibers (due to opposites attracting). Figure #5 provides an example:

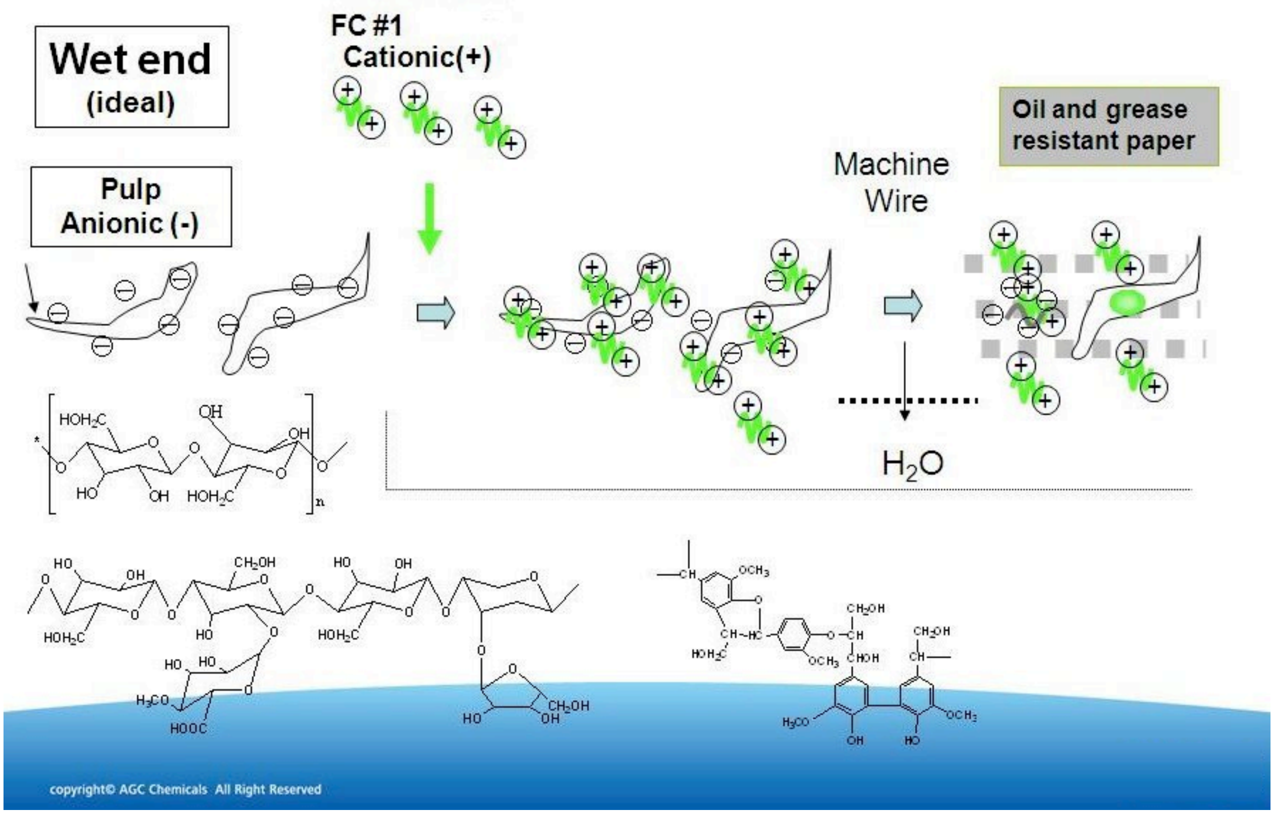


Figure 5: Ideal incorporation of cationic fluorochemicals - wet end

Such is not always the case, however, for other sources of anionic and / or cationic charge can be present in the paper furnish or size solution. These other sources compete (often destructively) with cellulose as host for the fluorochemical. Examples include (but are not limited to) anionic trash, mineral fillers (PCC; titanium dioxide; kaolin and other clays; silicas) and anionic retention aids.

As an example, the aforementioned cationic fluorochemical treatment can bind to strongly-charged anionic trash in recycled white water, instead of to the less-strongly charged cellulose fibers in the paper sheet. This results in the waste of fluorochemicals and in poor resistance to food-based stains. A depiction is provided in Figure 6, below:

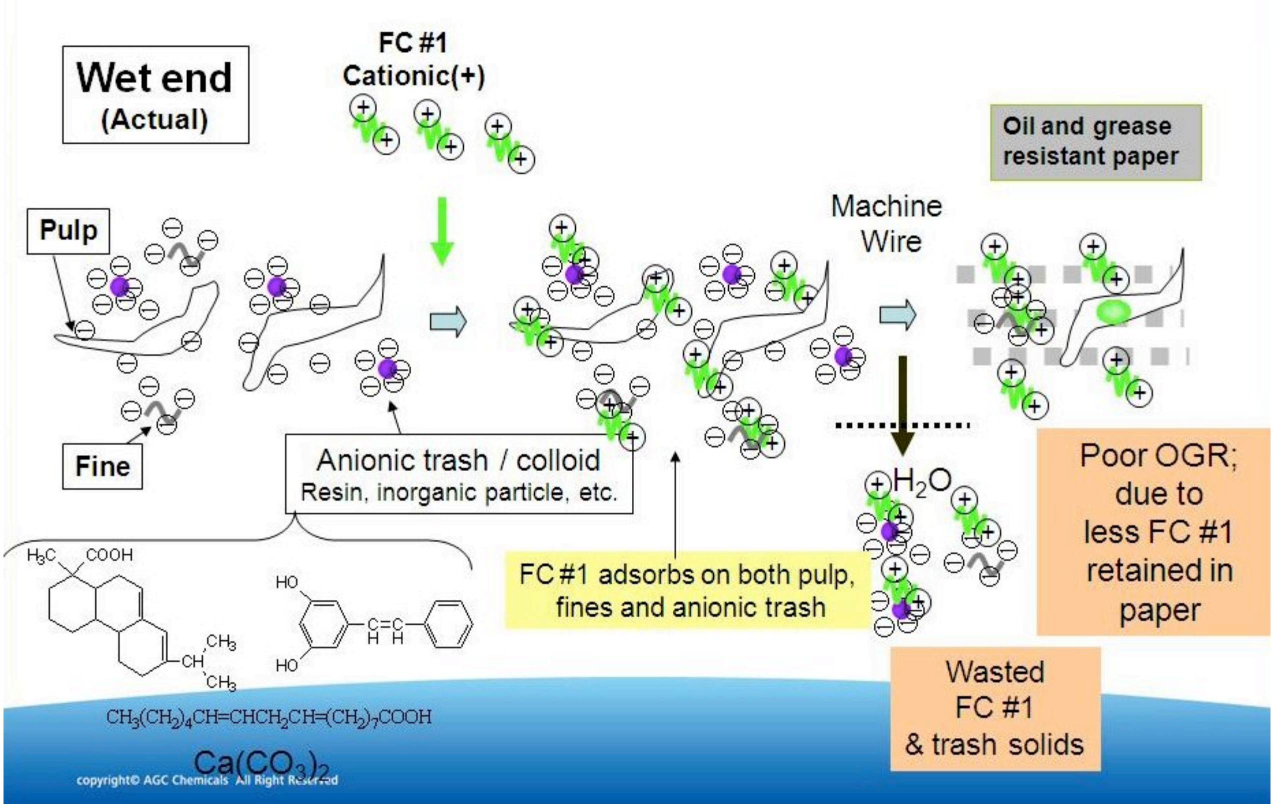


Figure 6: Sequestration of Cationic FC by Anionic Trash

One solution to the problem is to pre-treat the paper furnish with an appropriate cationic coagulant chemical, such that the coagulant binds up the anionic trash, leaving the cationic fluorochemical free to bind to the cellulose. A depiction of this is found in Figure 7 on the following page, in which a commercially-available coagulant chemical (Nalco 7607) is used for purposes of pre-sequestration of anionic trash (from the recycle stream) prior to addition of a cationic fluorochemical.

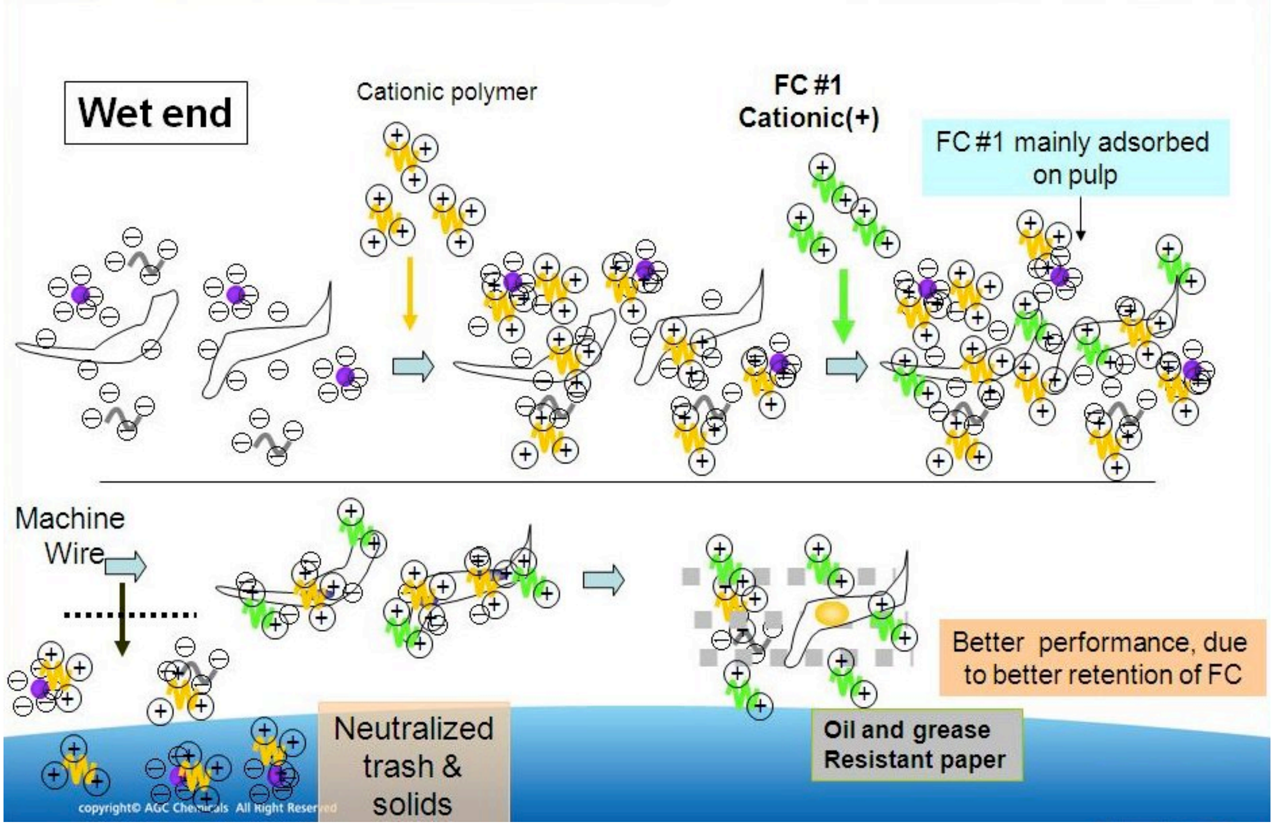


Figure 7: Sequestration of anionic trash, using a cationic coagulant

A cationic starch may also be employed in the paper-furnish, both for mitigation of anionic trash and for its contribution to the internal strength of the paper.

Interestingly, the use of cationic coagulant chemicals to mitigate anionic trash is not limited to the wet end. Cationic coagulants can also be used to pre-treat water used for make-up of external sizing solutions. This fact can be particularly useful to those papermakers who wish to make use of a cationic fluorochemical and still utilize process white-water (with associated anionic trash) for economic reasons, or for those that must include anionic components into their external sizing formulations.

Figure 8 (see following page) provides an example of the use of Nalco 7607, a commercially-available coagulant, for pre-treatment of an anionic hydrophobic starch sizing formula$_6$ prior to addition of a cationic fluorochemical (in this case, FC #1).

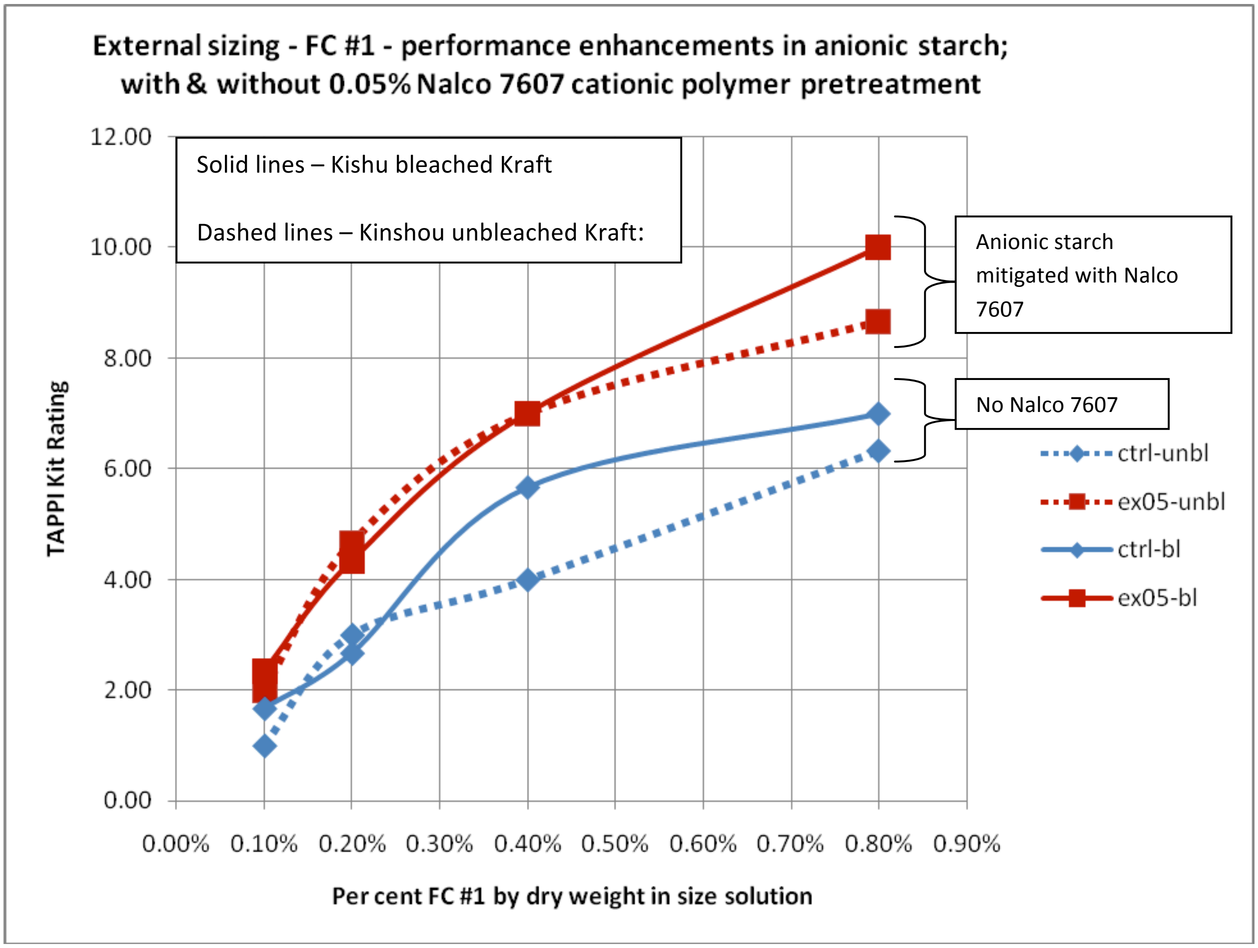


Figure 8: Use of a cationic coagulant for mitigation of anionic behavior of hydrophobic starch

Mineral fillers can have high anionic charge density along with high pH, and as a result can be problematic for cationic fluorochemicals. This is particularly true for calcium carbonate, which possesses a strong carbonate anion in water solutions.

An example of this situation is represented in Figure 9 (following page), in which cationic fluorochemical FC #1 is tested with and without 2% of precipitated calcium carbonate (See Table 2 of the **APPENDIX**) when used for 90 gsm hand-sheets. As is evident from the graph, the high pH and strong anionic nature of the precipitated calcium carbonate reduces the resultant grease and oil resistance of the paper (as measured by TAPPI Kit) by a factor of approximately forty per cent$_7$.

If paper processors cannot use a cationic coagulant polymer for mitigation of anionic behavior of the filler, switching to an anionic-type fluorochemical often solves the problem. Though transfer efficiency is not as good as for cationic fluorochemicals, the anionic grades are a good choice for use in anionic paper furnishes with high minerals content where the papermaker is willing to trade some performance for the ability to use low-cost raw materials in substitution for cellulose.

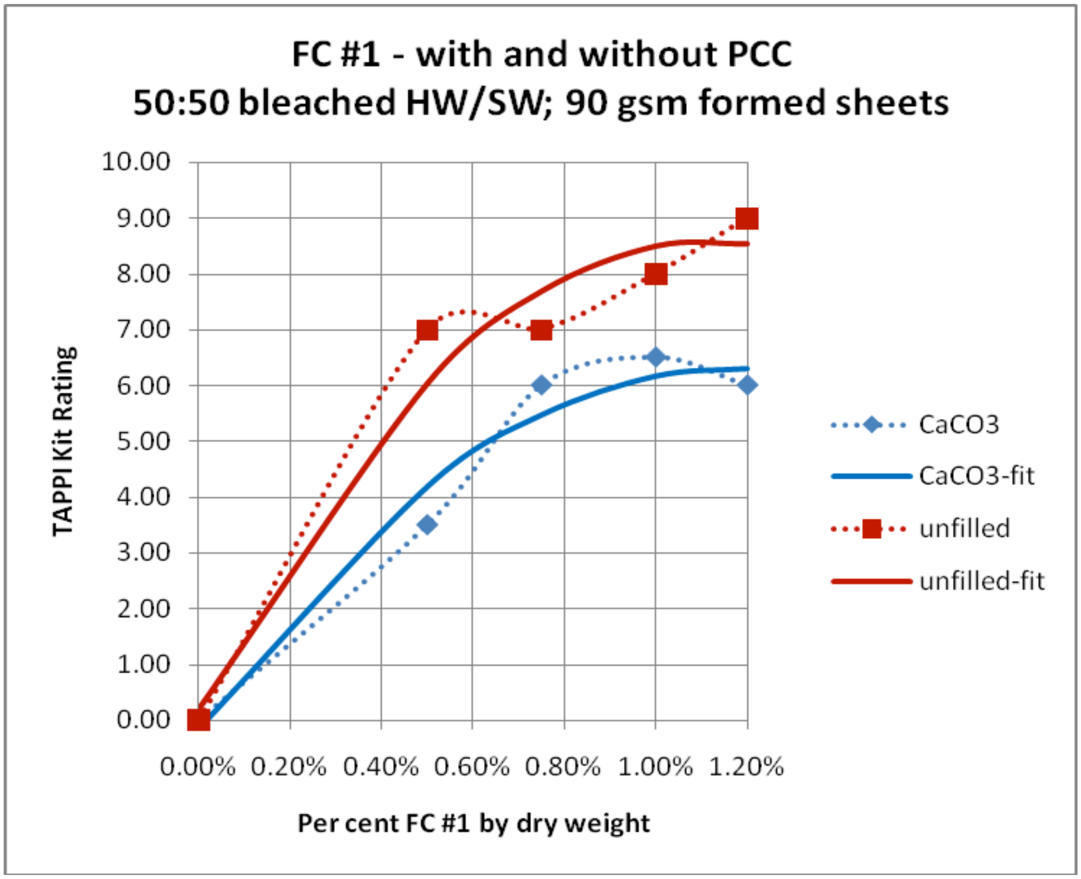


Figure 9: Effect of precipitated calcium carbonate on (cationic) fluorochemical #1

Optimal use of the fluorochemical treatment depends on understanding the nature of the charge differences between the fluorochemical itself and other system components. Once this understanding is achieved the papermaker is then able to optimize the electrical charge balance to favor incorporation of the fluorochemical into the cellulose. In short, the papermaker can adjust properties of the paper furnish so that the fluorochemical goes where it is needed, and so that it does not go anywhere else.

Part 3: Examples – New Breed fluorochemicals$_8$

Example #1 (internal): Fluorochemicals FC #1, FC #2 and FC #3 (all cationic) were used to induce oil and grease resistance in a simple paper furnish of 60% bleached hardwood Kraft (CSF = 400) and 40% bleached softwood Kraft (CSF = 550). This particular paper furnish was mildly anionic in nature, due mainly to the nature of the cellulose fiber itself. The paper furnish incorporated 1% of an ethylated starch for sizing purposes. Fluorochemicals were added to the paper furnish at 1.2% consistency, just prior to sheet formation. Sheets were then created in accordance with the standard TAPPI procedure (T205 sp-02), then dried / cured against an Adirondack contact dryer for one minute at 110 deg. C. TAPPI Kit test results were taken for formed sheets at 60 gsm and 160 gsm basis weights. Results are shown in Figures 10 and 11 on the following page.

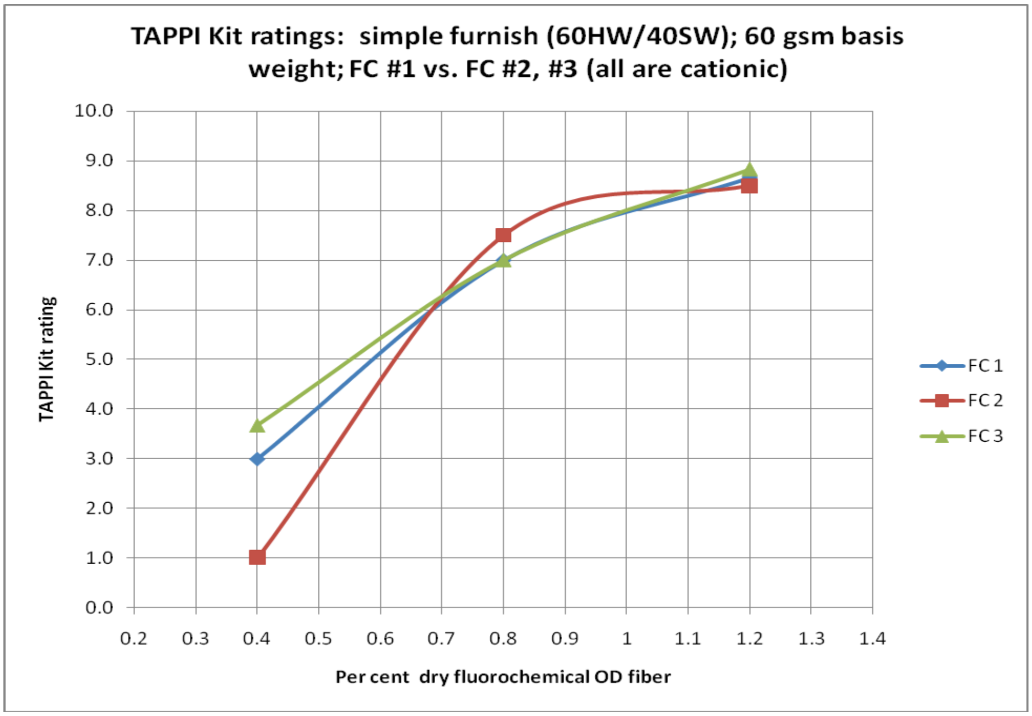


Figure 10: TAPPI Kit results - simple furnish; 60 gsm basis weight

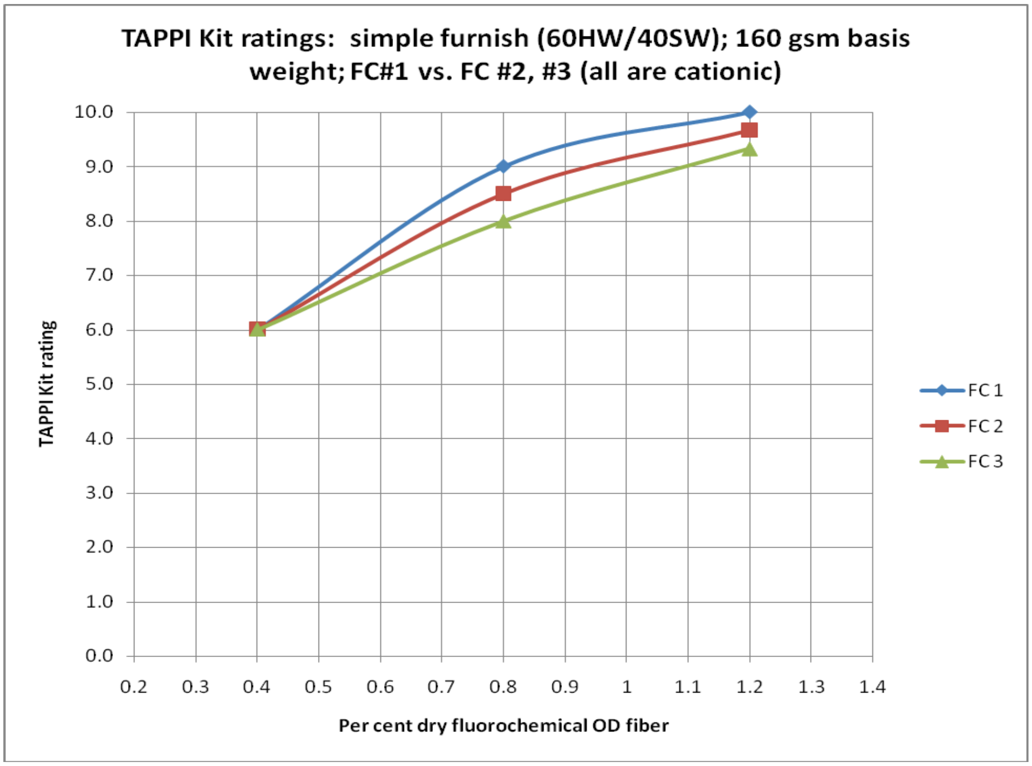


Figure 11: TAPPI Kit Results - Simple Furnish; 160 gsm basis weight

(Note the difference in TAPPI Kit values due to basis weight. This is caused by the “critical mass” issue discussed in Part 1 of this study.)

In a simple furnish, with little interference from other chemicals or anionic trash, the three fluorochemicals were observed to perform similarly. Fluorochemical FC #1 shows a slight advantage over the anionic FCs (#2, #3) at 160 gsm basis weight, due to its cationic nature (which favors incorporation into anionic cellulose).

Example #2 (internal): This paper furnish was designed to be similar to those used in paper mills for production of high-quality packaging paper. The basic pulp mixture was again a mixture of 60% bleached hardwood Kraft (CSF = 400) and 40% bleached softwood Kraft (CSF = 550). However, prior to addition of the fluorochemicals, a cationic coagulant (Nalco 7607) was added to the paper furnish to mitigate any anionic trash that might have been present. 1% of a cationic starch was next added for sizing and strength purposes. Lastly, an anionic PAM and a drainage aid were added to the paper furnish. As before, the fluorochemicals were added to the paper furnish at 1.2% consistency, just prior to sheet formation. Sheet formation and drying were conducted as in example #1. TAPPI Kit test results were taken for formed sheets at 64 gsm and 167 gsm basis weights. Results are shown in Figures 12 and 13, below:

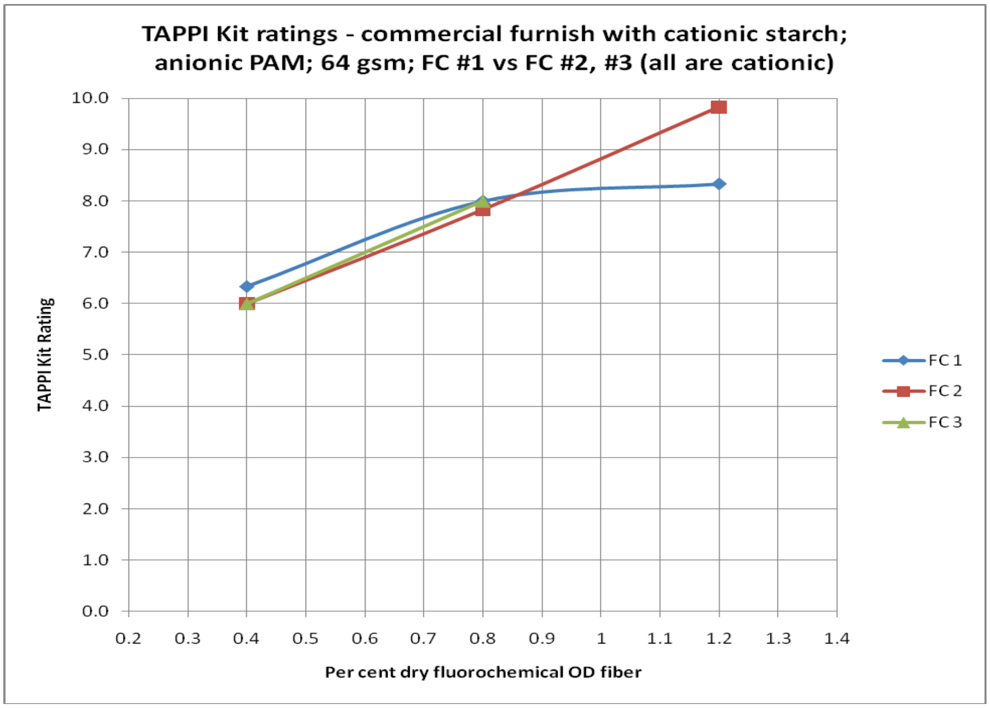


Figure 12: TAPPI Kit results - commercial furnish; 64 gsm basis weight

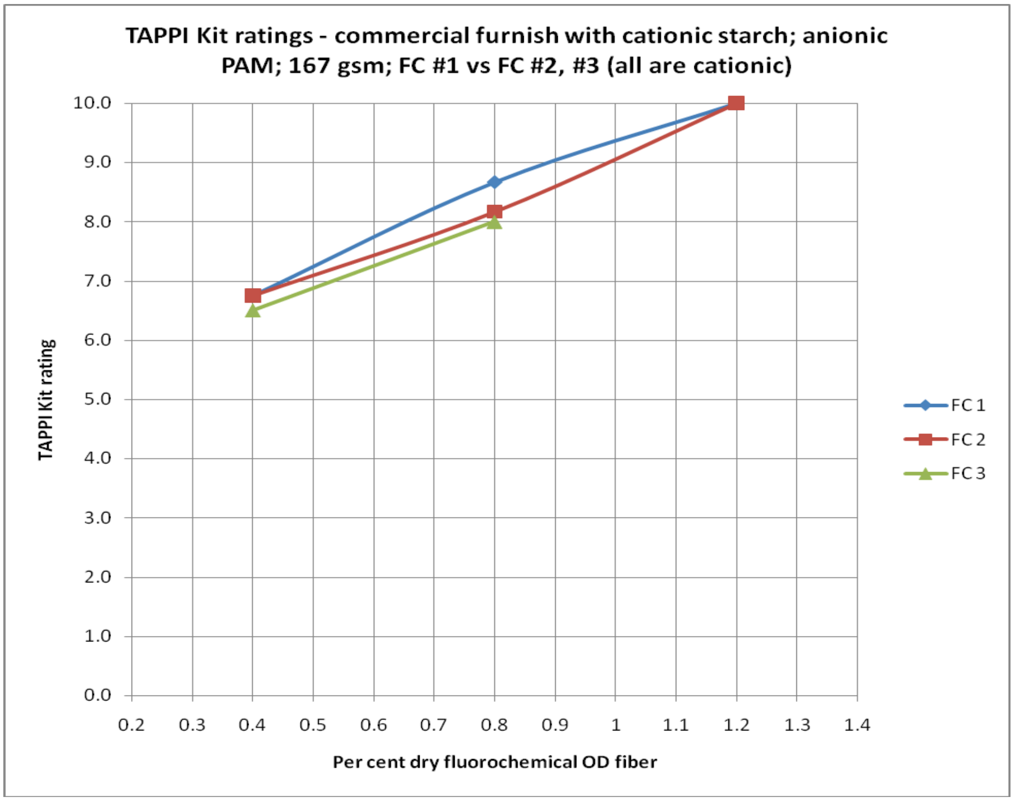


Figure 13: TAPPI Kit results - commercial furnish; 167 gsm basis weight

When used in the commercial paper furnish the three fluorochemicals showed better performance at the lighter basis weight than they did in the simple paper furnish. This may have been due to the improved retention provided by the anionic PAM in comparison to the simple paper furnish. Surprisingly, the anionic PAM did not appear to adversely affect the performance of any of the three cationic fluorochemicals. (FC #1, #2, #3). Overall performance of the three fluorochemicals was again quite similar.

Example #3 (external): In this example, hydrophobic (anionic) starch-based solutions with the three fluorochemicals (FC #1, #2, #3) were puddle-sized into two different pre-sized Kraft papers (Kinshou 75 gsm unbleached; Kishu 50 gsm bleached), such that wet-uptake was approximately 25 gsm for each of the paper types. After sizing the sheets were contact-dried at 110 deg. C for one minute each. TAPPI Kit testing was then performed, with results illustrated in Figures 14 and 15 (following page).

As is evident from the Kit results, there was a sizable difference in oil and grease resistance attained by each of the fluorochemicals, with fluorochemicals #2 and #3 yielding substantially better performance than the FC #1 fluorochemical. The poor results shown by FC #1 may have been due to the anionic nature of the starch used for the sizing, which could have acted to sequester some of the FC #1 fluorochemical in a destructive manner. The #2 and #3 fluorochemicals appeared to be more resistant to this effect, as evidenced by the higher TAPPI Kit ratings.

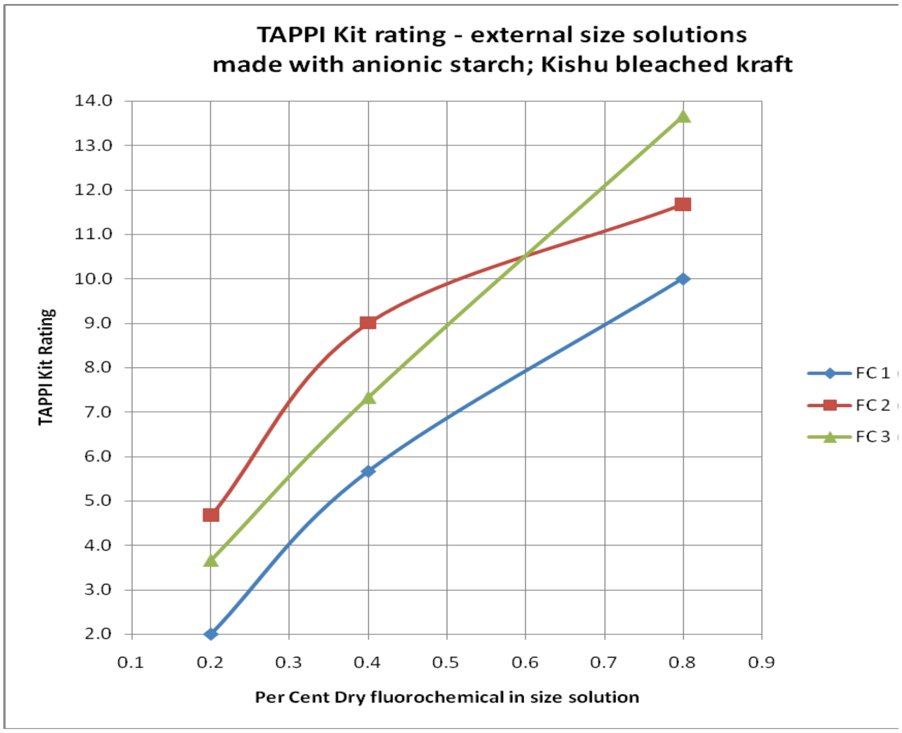


Figure 14: TAPPI Kit ratings - Kishu bleached kraft; hydrophobic / anionic starch size

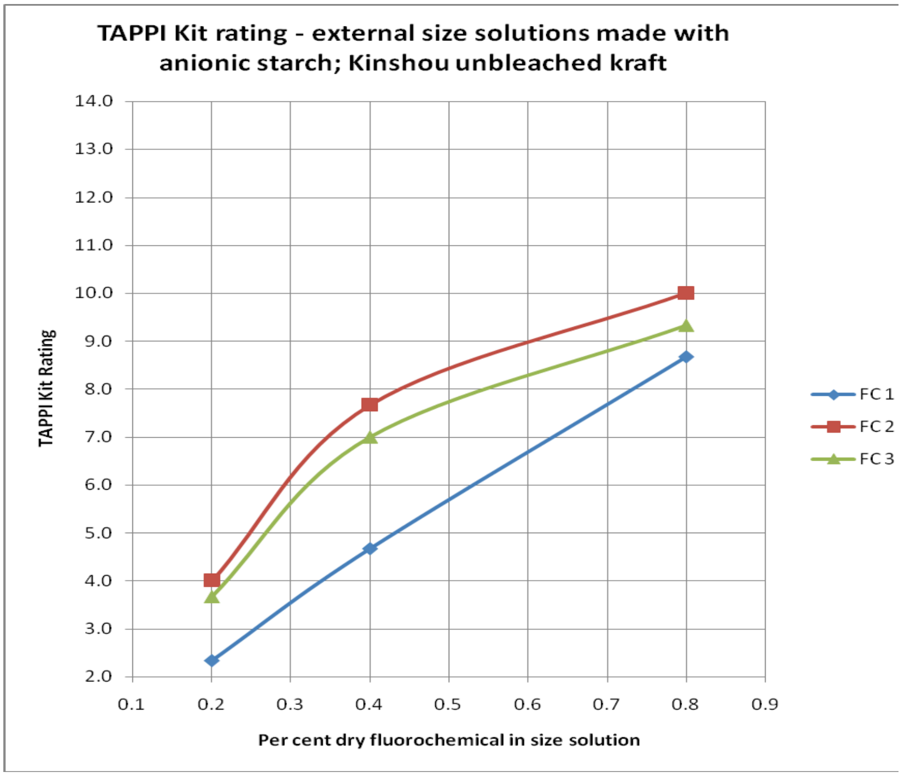


Figure 15: TAPPI Kit ratings - Kinshou unbleached kraft; hydrophobic / anionic size

Example #4 (external): For the final example cationic starch-based solutions with the three fluorochemicals (FC #1, #2, #3) were puddle-sized into two different pre-sized Kraft papers (Kinshou 75 gsm unbleached; Kishu 50 gsm bleached). Wet-uptake was again approximately 25 gsm for each of the paper types. Contact drying and TAPPI Kit testing were performed as before, with results illustrated in Figures 16 and 17, below.

There was again a sizable difference in oil and grease resistance attained by each of the fluorochemical types. However, in this case fluorochemical FC #1 had better performance than the other cationic flurochemicals (#2, #3). The cationic starch used for the size solutions may have had a synergistic effect on oil and grease resistance of the FC #1 fluorochemical, and this effect may not have been present with the other fluorochemicals (#2, #3) evaluated during the test protocol.

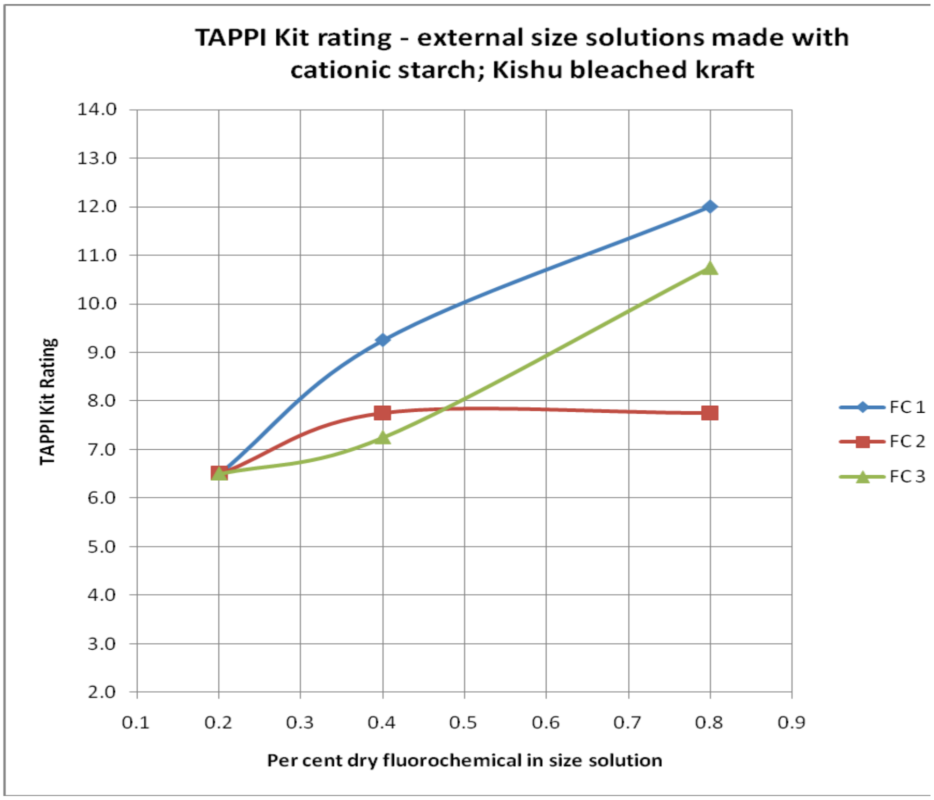


Figure 16: TAPPI Kit ratings - Kishu bleached kraft; cationic size

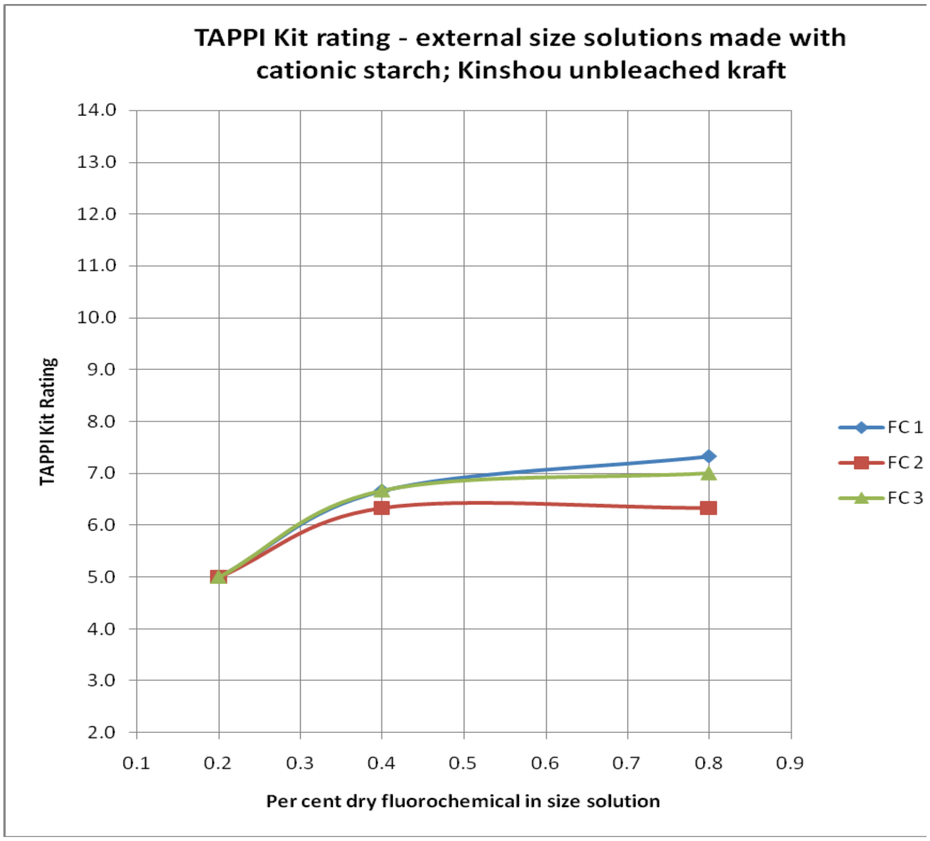


Figure 17: TAPPI Kit ratings - Kinshou unbleached kraft; cationic size

Examples - Summary:

- For internal sizing applications - when anionic trash is not present and pH levels are near neutral the cationic fluorochemicals may be expected to have similar overall performance, with a slight advantage in performance for fluorochemical #1.
- For external sizing applications – performance of the fluorochemcals may be significantly affected by choice of the starch used in the size formulation, with cationic fluorochemical #1 being more sensitive to starch selection than the other cationic fluorochemicals (#2, #3).

CONCLUSIONS

The new fluorochemicals permit papermakers to make use of proven technology, with all of its inherent benefits (chemical release, consistent stain resistance and barrier properties, reduction in bulk, breathability, single (vs. multiple) processes during manufacture, etc.) and without any of the regulatory compliance issues of the old (PFOA-inclusive) versions. The new fluorochemicals achieve favorable results despite possessing (sometimes) substantially different chemical and physical properties.

Achieving these favorable results is as complicated a process as it has ever been, and the replacement of the old by the new must never be considered a simple "quick-change", "one-size-fits-all" process. This is especially true when the papermaker changes from cationic to anionic fluorochemicals, or the reverse. Experimentation in laboratory is a useful first-step, as it can significantly aid papermakers in discerning where the performance window is located for these new chemicals in old paper furnishes or size solutions. Pilot-scale laboratories are available at a number of universities, and these can be extremely useful in allowing papermakers to simulate their production lines. Lastly, the companies that developed the new fluorochemicals have always been willing partners to the papermaker and can offer considerable insight on performance enhancement and compatibility.

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1. Christopher P. Chengelis[a], Jeannie B. Kirkpatrick[a,] , Nichole R. Myers[a], Motoki Shinohara[b], Philip L. Stetson[a] and Daniel W. Sved[a], ***"Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane-1-sulfonic acid (PFBS) in cynomolgus monkeys and rats"*****;** **Reproductive Toxicology**, Volume 27, Issues 3-4, June 2009, Pages 400-406, Recent Advances in Perfluoroalkyl Acid Research

   Note – Authors Chengelis, Kirkpatrick, Myers, Stetson and Syed are of WIL Research Laboratories, LLC, 1407 George Road, Ashland, OH 44805-9281, United States. Author Shinohara is of AGC Chemicals, Asahi Glass Company, Ltd., Japan. Please also see **Appendix** for more details.

2. Naomi Kudo, Erika Suzuki-Nakajima, Atsushi Mitsumoto and Yoichi Kawashima, ***"Responses of the Liver to Perfluorinated Fatty Acids with Different Carbon Chain Length in Male and Female Mice:In Relation to Induction of Hepatomegaly, Peroxisomal β-Oxidation and Microsomal 1-Acylglycerophosphocholine Acyltransferase",*** **Biol. Pharm. Bull.,** Vol. **29**, 1952-1957 (2006) - see **http://www.jstage.jst.go.jp/article/bpb/29/9/1952/_pdf**

3. AGC-Exton internal study; June-July 2009.

4. AGC-Exton internal study; June 2008.

5. Mechanistic charts provided by AGC-Japan

6. AGC-Exton internal study; September 2009.

7. AGC-Exton internal study; June 2009.

8. AGC-Exton internal study; November 2009.

APPENDIX

Fluorochemicals Experiment - Streaming current and solution pH values:			
FC #:	**low gain**	**high gain**	**pH**
FC #1 - 0.02% dry wt. sol'n	off-scale	off-scale	4.67
FC #2 - 0.02% dry wt. sol'n	4.59	off-scale	3.82
FC #3 - 0.02% dry wt. sol'n	2.80	6.80	4.10

Table 1: Characteristics of the fluorochemicals evaluated in this paper

Fluorochemicals Experiment - Streaming current and solution pH values:			
Chemical:	**low gain**	**high gain**	**pH**
PCC Slurry; 0.012% by dry wt. / sol'n	-4.27	off-scale	9.25
Anionic PAM; 0.0006% by dry wt. / sol'n	off-scale	off-scale	N/A

Table 2: Characteristics of chemicals evaluated during this experiment

Table 3: Comparative Toxicology Data

Fluorochemical Technology		**PFHxA**	**PFBS**	**PFOA**	**PFOS**
Functionality		carboxylic acid	sulfonic acid	carboxylic acid	sulfonic acid
Number of Carbons:		6	4	8	8
Pharmokinetic half-life: (lower is better)	blood of male rat	1 - 1.3 hours	2.1 hours	138 - 202 hours	180 hours
	blood of male monkey	5.2 hours	15 hours	20.9 days	200 days
Bioconcentration Factor (BCF) (lower is better)		< 1	< 1	1.8 - 9.4	3000

Notes:

1) Internal AGC data

2) PFHxA (C6) and PFBS (C4) form the basis for the "new breed" of non-PFOA fluorochemicals.