# Telioform System A New Multi Component Organic/Inorganic System From Ciba Specialty Chemicals

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# **Abstract**

Microparticle and micropolymer retention and drainage aid systems are powerful tools for paper and board making on a variety of machines. Drawbacks attributed to the current systems sometimes include; apparent high cost, production and quality problems and in some cases a negative effect on formation.

The next generation multi-component organic/inorganic systems have demonstrated their ability to decouple the effects of retention and drainage and to improve the formation and print quality for the same retention and in some cases higher retention levels.

It is now possible to optimize independently retention, drainage and formation effects with the same high return on investment of current microparticle systems.

## Introduction

When novel microparticle systems were introduced in the early 1980's it quickly became apparent that these new systems created challenges as well as delivering significant benefits to the papermaker. High total and first pass ash retentions coupled with rapid initial drainage tended to set the sheet too early in the forming

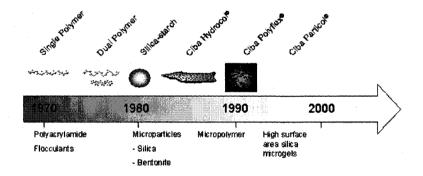
zone and created the potential to adversely effect sheet formation

Papermakers had to work with these systems to adapt the paper machine to take
full advantage of the new opportunities reconfigurating the wet end to increase fan
pump speeds to carry more water into the forming zone, adjusting drainage
elements and reducing headbox solids to take advantage of the rapid drainage
characteristics microparticle systems created.

Many mills benefited from extra production or lower steam usage, increased total and first pass ash retention, higher sheet ash levels, improved colloidal retention, reduced starch and size usage and in many cases improved formation.

Not every application could make all these changes successfully and so the advantages in running these microparticle systems were never fully achieved on these machines.

## Major Developments in Retention Aid Technology



#### **Early Retention Aids**

Polymers used for retention improvements were primarily based on acrylamide chemistry with the aim of producing high molecular weight linear chain molecules to increase ash and finesretention and contribute to drainage improvements. The use of polymers based on polyethyleneimene (PEI) has been seen to

significantly improve drainage, particularly in mechanical paper grades and waste based board furnishes. (1)

The use of these high molecular weight polymers gave high total first pass and ash retention, thus reducing significantly white water and headbox solids and enabling the paper maker to improving sheet formation.

#### Silica-Based Microparticles

In the late 1970's and early 1980's the first microparticle system was introduced using Colloidal Silica along with cationic starch, (2) and later cationic polymers, (3) for use as retention and drainage aids in the manufacture of paper and board. The primary targeted activity was in highly filled alkaline paper.

The colloidal silica-based microparticle system gained acceptance in the early years of the 1980's, particularly in alkaline/neutral sized and unsized coating base papers.

(4) In these grades, the ability to increase internal strength with the high retention of cationic starch improved Scott Bond and reduced picking, linting, and enabled

coating formulas to be changed with quality and cost benefits.

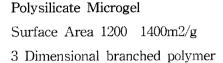
The microparticle effect was achieved for many paper and board applications. This effect gave high total and first pass ash retention and significantly increased free drainage, drainage in the vacuum section and in the press section. As a result machine speed increases in the order of up to 20% contributed significantly to the cost effectiveness and the early acceptance of this new Microparticle Technology.

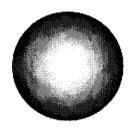
The first silica used was colloidal silica having a spherical shape with an average diameter of 5 nm, with a surface area of 500-800 m2/g and exhibiting a very high anionic surface charge. Further developments in this area have seen the development of surface modified silica and silica with increasing levels of structuring.

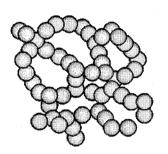
The most recent silica particles are structured Polysilicate Microgels with the

surface area increased to approximately 1200-1400 m2/g. (5) These polysilicate microgels are significantly more effective than their lower surface area counterparts. Below is a representation of the two silica structures.

Colloidal Silica Surface Area 500 to 800m2/g 5nm diameter







At first, the cationic component of the silica-based systems was cationic starch, which gave additional benefits in providing high internal bond strength. Progressive developments in starch chemistry provided more effective products with higher degrees of cationic substitution.

While cationic starch is typically present, cationic polyacrylamide is used to improve the overall cost effectiveness and performance of the system.

#### Bentonite-Based Microparticles

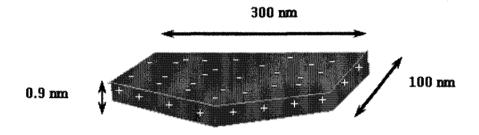
The silica-based microparticle system demonstrated the benefits of high retention and increased drainage on paper and board quality and machine efficiency.

A bentonite-based system had already been developed in the late 1970's for use as a retention/drainage aid in difficult to treat newsprint and mechanical printing grades which were characterized by a high cationic demand. (6) This was not however a microparticle system in the true sense of the definition.

After the introduction of silica as a microparticle, it was quickly realized that bentonite had many similar characteristics to that of colloidal silica. (7) The member of the bentonite family that performed the most effective as a microparticle component was the smectite crystal. (8)

When bentonite, or the smectite crystals are hydrated in water, they too have a very large surface area, up to 800 m2/g and a very high anionic surface charge.

Below is a representation of a hydrated smectite crystal.



Hydratedsurfacearea=800m2/g

The bentonite microparticle is used in conjunction with cationic polyacrylamide, which is added as the first component. Important characteristics governing the choice of polymer are cationic charge density, molecular size and molecular architecture.

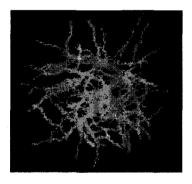
In addition to providing the microparticle retention and drainage effect, bentonite also has the additional capability to adsorb anionic and non ionic colloidal materials onto the its surface thereby contributing to a system cleaning effect. This results in a reduction of pitch and stickies type material in the stock system with a consequent improvement in sticky breaks, runnability and machine productivity. This is particularly true in recycled and mechanical containing grades.

#### Micropolymer-Based System

With silica and bentonite systems protected by patents, further development of

novel microparticles was through polymer chemistry. A new and novel answer to this situation was the invention of Polyflex micropolymer. (9) This unique technology produced polymer architecture with sub-micron three-dimensional constrained structured microparticle or micropolymer, creating a high anionic surface area and a very high anionic charge.

The micropolymer is designed to incorporate the performance aspects of both inorganic microparticles (highly anionic surface, sub-micron dimensions, and a 3-dimensional constrained structure) and of polymeric flocculants & coagulants (flexible polymer chains of controlled ionic charge) and this is achieved with the anionic micronetwork structure. Its dry particle size is 60 - 80 nm and the reported polymer microemulsion droplet size as measured by DLS is 130 nm. A computer simulation is shown below.



Surface area ~1000m2/g High and controlled anionic charge

The anionic micropolymer-based system performed similarly to the silica and bentonite-based systems, with some of the characteristics of a linear polymer retention aid. With the silica and bentonite-based microparticle systems some form of cationic or in one system an anionic polymer, is required to react with the inorganic component. In the silica based system this could be cationic starch or a cationic or anionic polymer, but in the bentonite-based system in all but a very small number of applications, a cationic polyacrylamide is required.

In the micropolymer system, the cationic species could be alum, polyaluminum chloride, aluminum chlorohydrate, cationic starch, polyamine or polyDADMAC. The micropolymer system can give a high total first pass and especially high ash retention, but does not always give the very rapid free drainage and dewatering characteristics exhibited by the inorganic systems.

#### Advantages and Disadvantages of Microparticle/Micropolymer Systems

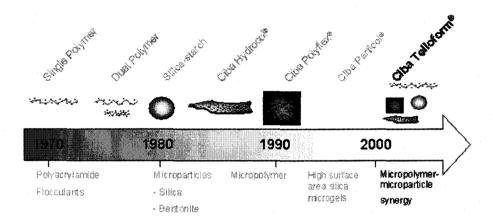
There are advantages and disadvantages to high first pass retention and high rates of dewatering, (10) and these can manifest themselves as formation or print quality problems. The basic mechanism of all retention and dewatering systems is coagulation and predominantly flocculation. The majority of paper and board machines could not run efficiently without some sort of retention system and many would run slower without dewatering or drainage aids. However the mechanism by which these systems work can very often over flocculate the thin stock in the process of attaining acceptable filler retention. Rapid initial draining furnish can freeze the stock early on the wire and stops the activity that often helps formation. The wet end chemistry will always determine the retention/drainage aid mechanism required.

There has to be a balance between retention and drainage to give good formation, but this is not always achievable. Some furnishes will flocculate easily and not defloculate sufficiently in the shear zones in the headbox and still give good retention, while some headboxes are poorly designed for good formation. Furnishes that react strongly with the microparticle system selected are the most susceptible to formation problems.

Former design and machine running conditions are another challenge. Fourdrinier machines can in many cases be modified to run fast draining stocks as can top wire formers. Twin wire machines drain rapidly because of their design and require

powerful retention systems to give acceptable ash retention. This can, and does in some cases, create formation problems through the use of the very powerful current microparticle/micropolymer retention/drainage aid systems.

# The Latest Advance-Ciba Telioform System



# Decoupling Retention, Drainage and Formation Laboratory Evaluations

The challenge to decouple the effects of retention and dewatering has been recognized for sometime. In the course of laboratory evaluations, it was discovered that a synergistic effect is observed between the various microparticle systems and anionic linear polymers and micropolymers. (11) It was well understood that an anionic polymer-based retention system will drain more slowly than a microparticle system and that in most cases the micropolymer system drains more slowly than the inorganic microparticle systems.

The addition of a mixture of the anionic polymers and inorganic microparticles as the second component of a microparticle system generated interesting results. The first effect observed was the total first pass and ash retention increased significantly.

More detailed laboratory evaluations concluded that there was indeed a significant increase in retention and even more interesting there was no adverse effect on formation. (12) In fact, in some instances formation was improved.

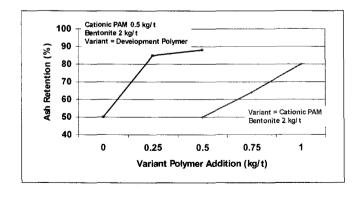
This effect can be seen in the results of a laboratory evaluation detailed in the graphs below.

In graph 1 the addition of a third component the developmental polymer and also the addition of the cationic PAM is increased resulting in an increase in first pass ash retention.

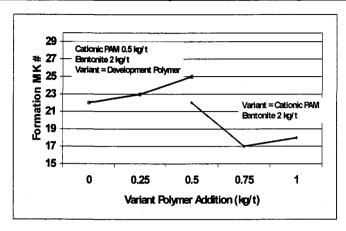
However, in graph 2 with the addition of a third component, the developmental polymer, formation of the sheet improved, but with the increased addition of the cationic PAM, the formation was decreased.

This effect is seen for both silica and bentonite based systems.

Graph1, Ash Retention Against Addition Rate for Bentonite Microparticle System



<u>Graph2FormationAgainstAdditionRateforBentoniteMicroparticleSystem</u>

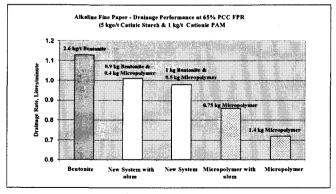


Graph 3 details the ability of the new system to decouple the drainage effect from the retention level. In this case a constant PCC retention of 65% has been selected. This is achieved using different ratios of inorganic and organic microparticles and the effect on the dewatering is measured.

The drainage rate for the micropolymer can be increased with the addition of a small quantity of alum. The new systems drainage rate has increased the drainage rate over the micropolymer, and again, with a small quantity of alum giving a still higher drainage rate is seen. The bentonite microparticle system exhibits the fastest drainage rate of all the three systems.

Graph3 Ability to moderate drainage at constant retention.

Alumaddition level is 2.5kg/t.



How could this be, and what is the mechanism at work here?

It is hypothesized that the addition of anionic micropolymer reacts in a synergistic manner with the inorganic microparticleto increase the retention of fines, ash and colloidal material in the thin stock, but did not increase the long fiber flocculation. At the same time the initial, or free drainage rate has been reduced, resulting in a more even formed sheet. This effect is seen with both the silica and the bentonite-based microparticle systems. Could this effect be translated to an actual machine application?

Machine trials have in fact proved this to be possible.

#### Paper Machine Case Studies

- 1, A paper machine in North America used a cationic PAM and a micropolymer to make coated and uncoated freesheet grades. The Fourdrinier forming section had an excess of free drainage and vacuum dewatering. Ash retention was on the low side and any efforts to increase retention by the addition of more cationic PAM polymer or anionic micropolymer resulted in a decrease in formation. The addition of 0.2 kg per ton of silica increased ash retention by 10 percentage points without increasing drainage or having an adverse effect on formation. (13)
- 2, A world-class twin wire machine making uncoated freesheet trialed a retention system using a cationic PAM and anionic micropolymer against a silica based system. It was decided to investigate the new technology during this trial. The addition of <1kg/t of bentonite microparticle reduced the addition rate of both the cationic PAM and the anionic micropolymer while maintaining the same tray solids and increasing formation 2-3 points. This also made the system more cost effective.
- 3, A medium sized Fourdrinier machine making uncoated freesheet and running a micropolymer system had the requirement to improve formation. By substituting 0.2

kg/ton of micropolymer with 0.2 kg/t of silica, the paper machine maintained the same retention and improved formation by 4-5 points.

4. A Wood Free coated paper machine producing art base paper in the Asia Pacific region using GCC and AKD sizing was running a silica based microparticle retention system. The mill trialled and are now continuously runningthe Ciba Telioform

retention system based on a cationic PAM, an inorganic microparticle and an anionic micropolymer. The advantages gained using this system included improvements in FPAR, improved runnability and less machine downtime due to an improved wet-end stability, improved FPR and an increase in machine speed by approximately 120m/min to help achieve machine speeds of up to 1470m/min.

- 5. A Gap former machine in Scandinavia making uncoated Freesheet with 20 24% sheet ash was running the CibaHydrocol system. After trials of the 3 component Telioform System, results clearly showed an increase in sheet formation of up to 10 % whilst maintaining retention levels from pre Telioform System. The results clearly demonstrated that Formation improvements can be achieved with high sheet ash levels.
- 6. A Fourdrinier machine in Eastern Europe producing 45 to 120gsm white top board using the Ciba Hydrocol system. After extended trials the Ciba Telioform system gave the mill improved machine runnability, improved machine speed, more water was added to the headbox giving improved sheet formation whist the total retention was maintained.
- 7. A Fourdrinier machine with top wire in Africa producing 120 000 tpa of Linerboard using the Ciba Hydrocol system. Trials with a 3 component Ciba Telioformsystem gave the mill significantly improved wet end stability and colloidal

retentions were significantly improved. The system turbidity improved from 1000 to <100 NTU. The benefits to the papermaker were: production increase of >25%, reduced size consumption of 18% and improved sheet formation.

The overall chemical costs on the machine were reduced.

# Conclusion

This new and novel Ciba Specialty Chemicals patented technology named - The TelioformSystem has demonstrated in both laboratory evaluations and in machine trials that it is possible to decouple the effect of retention, drainage/dewatering and more importantly, formation/sheet print quality results. The system will work equally well for both silica and bentonite based microparticle systems. It is particularly cost effective when used on high-speed twin wire paper machines where it has at times proved difficult to achieve good ash retention without adversely effecting formation. It has also proved to be valuable on smaller machines with former configurations that exhibit rapid free drainage/dewatering characteristics that can contribute to poor sheet formation.

Results from recent trials and ongoing customers have demonstrated that this next generation retention and drainage system can be applied across a wide range of grades with significant benefits to our customers.

# References

- 1. Pask, M. D., Lorz, R., *TAPPI papermakers Conference*, Atlanta, GA. TAPPI Press, Atlanta, p 247 (1990)
- 2. Sunden, O. Batelson, Per G. Johansson, H. E. Larsson, H. M. and Svending, Per
- J. U.S. Patent 4,388,150 (1983)
- 3. Rushmere, J. D., U.S. Patent 4,954,222 (1990)

4. Moberg, K. 1987 TAPPI Advanced Topics in Wet End Chemistry Seminar, Memphis TN. TAPPI Press,

Atlanta, p 7 (1987)

- 5. Rushmere, J. D., U.S. Patent 4.954.220 (1990)
- 6. Langley, J. G., Litchfield, E. U.S. Patent 4,305,781
- 7. Langley, J. Holroyd, D U.S. Patent 4,753,710 (1988)
- 8. Knudson, M. I. 1993 Papermakers Conference, Atlanta, GA. TAPPI Press Atlanta, p 141 (1993)
- 9. Honig, D.S. and Harris, E.W., U.S. Patent 5,167,766 (1992), (b) Honig, D.S. and Harris, E.W., U.S. Patent 5,274,055.
- 10. Ford, P. A. 1991 TAPPI Papermakers Conference, Seattle, WA., TAAPI Press Atlanta, p.501 (1991)
- 11 (a) Heard, M.B. and Chen, G.C.I., U.S. Patent 6,406,593 (2002), (b) Chen, G.C.I. and Richardson, G.P., U.S. Patent 6,395,134 (2002), (c) Hjalmarson, B., Asberg, H., Eriksson, P., Ljungvist, T., Richardson, G.P., and Chen, G.C.I., U.S. Patent 6,391,156 (2002), (d) Chen, G.C.I., U.S. Patent 6,454,902 (2002). Chen, G.C.I. and Richardson, G.P., World Patent Application WO 20020066540 (2002),
- 12. Internal Laboratory Evaluation Reports
- 13. Internal Paper Machine Trial Reports