

Charge Measurement and its Importance in Wet End Chemistry- A Review and Experience in Bagasse Paper Making

Moses Paul, Thirumalachary Praburaj, Swaminathan Rajesh, K., Gopalswamy Venkoba Rao

Tamil Nadu Newsprints and Papers Ltd., Kagithapuram-639 136, Tamil Nadu

Abstract

Reducing the cost of production by optimized chemical application and reduced processing losses is the urgent need to make the paper production globally cost competitive. Improving the paper machine wet end performance with wide range of additives and retention chemicals has come to stay. Optimizing the wet end chemistry through effective charge control has been acclaimed to be the scientific promising approach which in turn results in effective utilization of process chemicals and additives and reduction of fibre and filler losses. The charge measurement and control technique for better-wet end retention control has been discussed. Our practical experiences with charge measurements have been shared. Online measurement and control of system charge appears to be the most effective approach to control retention in modern high-speed paper machine. Investments on such systems cuts down the cost of production and improved productivity.

INTRODUCTION

The theory and application of the electro-kinetic techniques in research and process control in mill, is a subject of utmost interest to paper chemist since they play a major role in the fibre and filler flocculation during the stock preparation. By and large major paper mills worldwide have conclusively agreed that fibre and filler retention systems are necessary for meeting the environmental standards towards the effluent treatment, quality requirements and at the same time reduction of cost of production (1). This paper discusses some of the basic features for effective Retention system viz. Charge measurements, Ionic Demand Measurement, on-line measurement of charge and ionic demand.

EXPERIMENTAL

The need for electro kinetic measurements

A paper making stock consists of particles ranging

in size from 2-3 mm in case of soft wood fibres, 0.8-1.2mm in case of hardwood/agro residue fibres, to filler particles at a few microns to colloidal particles and even dissolved substances (Table 1). One of the challenges in papermaking is to form these disparate particles into a coherent sheet that can be printed, folded, glued, coated and otherwise used. Chemical additives used for retention, strength improvement, and water drainage are among the smallest components of the furnish.

In general, the flocculation is governed by the charge on the individual particles since opposite charges attract each other and like charges repel each other. Most of the pulp fibres and as well as most of the fillers have a net anionic charge. During the process of sheet formation these fibre particles tend to disperse and those particles which are small enough to pass through the wire will not be retained on the sheet unless mechanically by the filtering action of the web as it forms.

Among the different variables that have a

striking influence on papermaking process, are pH, Head Box and tray consistency, freeness, and Zeta potential, which are cited most often (2). Many of the papermakers indicate that some type of charge measurement should be considered to control the wet end. Much research has been carried out to find a correlation between wet-end charge and retention on the wire. It has been reported that the magnitude and total quantity of charge have a significant effect on the efficacy of chemical additives and on physical sheet forming parameters such as retention, drainage, and response to vacuum (3). However, it has also been observed that no single charge measurement method can reliably predict retention in all pulp systems. The question is what is the most important factor that is meaningful in the control of retention - viz. Measurement of absolute charge or measurement of off-line charge demand or measurement of on-line charge demand. This paper attempts to find this factor.

Electrokinetic measurements

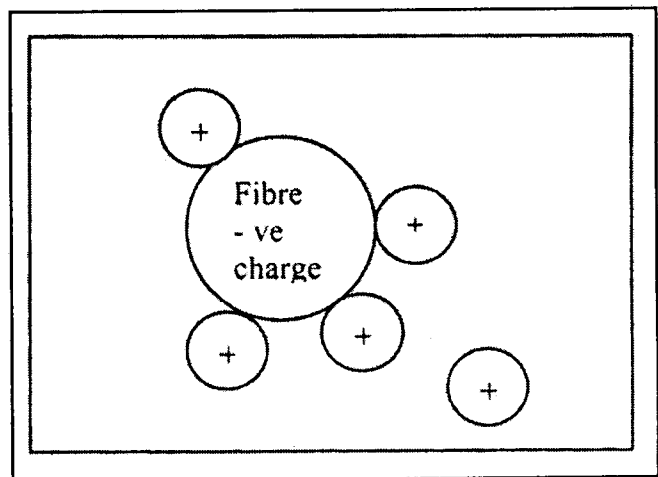
The Electrokinetic measurements provide insight into the important parameters, which have striking in the papermaking process (4). The electrokinetic measurements are of two types: 1) Magnitude or intensity of the electrokinetic charge (mobility or Zeta potential or Streaming potential charge) in absolute values. This dictates the mutual attraction or repulsion of the furnish components.

The ionic demand (normally Cationic as the papermaking fibres are anionic). The ionic demand indicates the capacity of the system to absorb materials having a charge opposite to that being measured. This is important because the detrimental effects of anionic water-soluble substances present in the system interfere with performance of most of chemical additives. These substances are known as anionic trash, which inhibit the action of retention chemical additives. It has been reported that a correlation exists between charge and retention because retention aids are consumed in an ineffective

manner when there is no systems established to level the anionic charges of colloidal dissolved substances (5).

Origin of charge in the pulp furnish

Fibres are generally negative charged, mainly due to the presence of carboxyl groups (-COOH) on the surface. Because of the negative surface charge, positive ions like Na⁺ + Al³⁺ concentrate around the fibres, building up the "so called" current of counter ions. For each negative charge on the fibre surface, on positive ion becomes bounded electrostatically. In the case mechanical pulps another factor is different additives that are added during the lignin preservative bleaching.



Formation of Carboxylic Acid Groups

These carboxylic acids form during processing of the cellulose raw materials both in pulping as well as in bleaching. Depending on the pulping process, if it is sulphite pulping process sulphonic acid groups are also formed, which also contribute to the negative charge. In the bleaching process, the carboxylic-COOH groups are created both in cellulose as well as hemicelluloses. The hypo bleaching contributes significantly to this. Trying to reach higher brightness levels by hypochlorite bleaching results in more creation of carboxylic acid groups in cellulose as well as hemi-cellulose (non-cellulosic

carbohydrates). In the case of high yield and lignin rich mechanical pulps, the chromophoric groups when oxidized by oxidizing agents such as Hydrogen peroxide during bleaching form carboxylic groups which induce negative charge. In the pulps bleached by lignin specific bleaching agents like chlorine dioxide, the formation of carboxylic acid groups is considerably reduced.

In some of the raw materials, saccharinic acids form part of the hemicelluloses. Examples of such types of raw materials are, agricultural residues like bagasse. In short growth cycle raw material like hardwoods, due to incomplete biosynthetic pathways, the hemicellulose contain more carboxylic acid groups in the non-crystalline lattices of the fibre which also contribute to more negative charge as more carboxyl groups are exposed to the media for reaction. Charge on pulp slurry will also be affected by absorption of ionic substances on the surface of the pulp or fines.

Types of charge measurement

There are two basic types of charge analysis

Those that measure the charge on a given particle

Zeta potential and its equivalent, Streaming current potential, measure the charge of the particle or rather the average charge of the system. Therefore this type of measurement gives the papermaker the average intensity of the charges on the particles in a given system. Therefore streaming current potential and Zeta potential will tell what charges are on the particle (6). Zeta potential and streaming current potential can also tell when the charges on the particles in a system have been neutralized. The primary weaknesses of the intensity measurements is that it cannot be used to predict the reactivity of the system changes in bleaching. This can change the intensity of the charges on the particles of a system and this will change the Zeta potential/ Streaming current potential of that system. Especially

when we use precipitated Calcium carbonate (PCC), these charge measurements are misleading. This is because the charges are created due to the method in which PCC is manufactured. (Specifically the residual lime in PCC can change the intensity of the charge on these particles and this will affect Zeta potential and Streaming current potential).

Measurements that evaluate capacity of the system

This measures the capacity of the particle or system to sorb material having a charge opposite to that being measured (7). These measurements have found widespread acceptance in wet end control. This measurement done with automatic titrators, by measuring the total quantity of the materials that is absorbed to a Zeta potential of Zero.

Intensity measurements or absolute charge measurements

There are types of measurements a) Zeta potential measurements, which are more popular and b) Streaming current potential measurements (8).

Zeta potential

Zeta potential is an electro-kinetic potential existing between the fibres and the surrounding liquid, in the slurry of pulp. This is one of the forces that tend to hold the fibres in stable slurry. Reducing the variation in electro-kinetics of furnish, improves the stability and in turn improves the machine run ability. Since Zeta potential refers to a more dynamic situation, it has found more applications in charge measurements as a part of wet end chemistry. This is the one involved in various no static electrical properties of solids to liquid interface and is the one responsible for the electrical effects observed in colloids. Since Zeta potential measurements are related to measurements with colloids, it can be used to measure the charges of small particles in a given system, not those of the large particles.

Streaming current potential measurements

The streaming potential is the potential developed as the fluid passes through a capillary or a porous plug. As the fluid passes through the capillary, charges in the mobile part of the electrical double layer are carried in the direction of flow. The streaming current 'e' causes an accumulation of charge in the direction of the flow and creates an electric field. The electric field then induces current in the opposite direction. When the two currents achieve a steady state, the resulting electrostatic potential between the two ends of the capillary is called Streaming potential

Measurement of Zeta potential

The instruments used in paper industry to measure Zeta potential (Z), is based on electrophoretic mobility. Fig. 1 how a basic Electrophoretic mobility unit.

The unit is basically an Electrophoretic cell with a microscopic attachment that enables the operator/ tester to visually observe the rate of movement of suspended/colloidal particles. The operator first filters, usually through a piece of paper-machine wire, the stock sample, to remove the long fibres and any other large particles while keeping the fine particles in filtrate. The filtrate is placed in the cell and power is applied to the electrodes and the time taken for the given particle to move over a given distance is recorded. Several particles are measured and the average electrophoretic mobility is calculated.

$$U \text{ (Electrophoretic mobility)} = t/E.l$$

Where t = Time taken for the particle to move over a distance l

E = Applied potential

The Zeta potential (ζ) is related to the Electrophoretic mobility by the following equation.

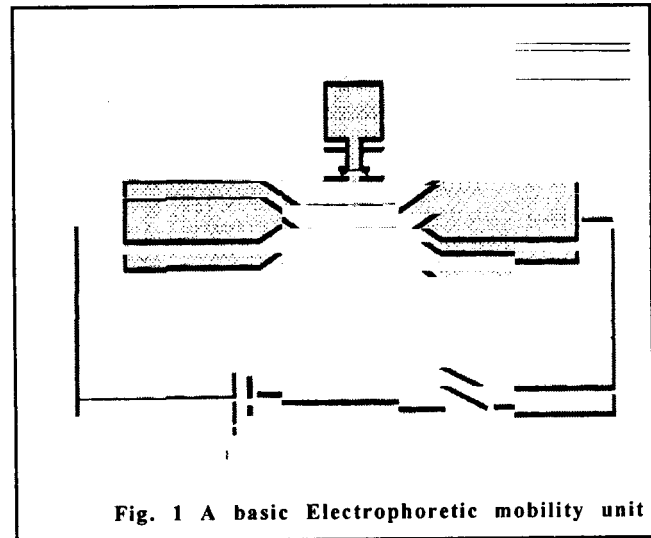


Fig. 1 A basic Electrophoretic mobility unit

$$\zeta = \eta u/\epsilon$$

Where η = viscosity of the fluid

ϵ = Dielectric constant of the medium (fluid)

Streaming current potential measurement

For the measurements of streaming potential, a stock containing all furnish components (after filtration) is forced through a screen, forming a porous plug, as shown in the Fig. 2.

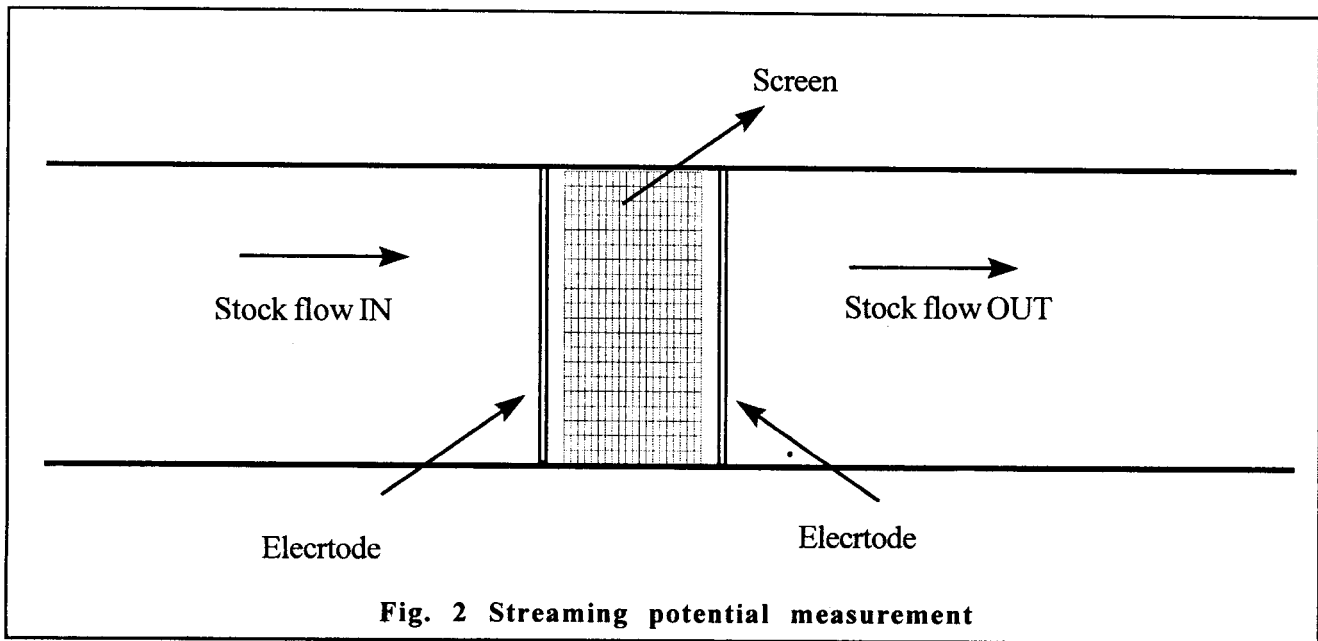
As the liquid passes through the plug, charges in the mobile part of the electrical double layer are carried in the direction of flow, creating a streaming current. The accumulation of electric charge creates an electric field, which then induces an induction current equal and opposite to that of the streaming current. When the two currents achieve a steady state, the resulting potential difference between the electrodes is called streaming potential.

The Zeta potential is related to the Streaming potential through the equation-

$$\zeta = \eta (\lambda_D - 2 \lambda_E - /r)^E / pE$$

λ_D is the specific conductance of the fluid

λ_E is the specific surface conductance of the fluid.



r is the radius of the capillary
 p back pressure of the fluid.

However from the extensive studies conducted by J.G. Penniman of Paper consultancy laboratory Inc, a leading consultant from the official lab of Electrophoresis in paper industry, it has been clearly shown that the correlation between Zeta potential and streaming current potential is very poor with a correlation coefficient of only 0.152.

Thus both these measurements give the idea of the intensity of the charge ie whether the charge is positive or negative. In conducting the Streaming current potential determination, care has to be taken. Because of possible adsorption of the hemicelluloses and the other materials on the cell surface and the measured potential is relative to the potential of the adsorbed material on the surface. Therefore, a proper cleaning of the cell is very important. Therefore cleaning the system is especially important with online units since they are expected to provide reliable signal with little maintenance.

Measurement of charge demand

Charge demand is dictated by the capacity of the

paper making system to absorb charged chemical species.

Two types of capacity measurements are made

- a) Cationic demand
- b) Anionic demand

They are defined similarly, being the quantity of the charged polymer (Cationic for cationic demand and anionic for anionic demand), a given paper making process absorbs before reaching electro neutrality or Zeta potential near Zero or Streaming current potential near Zero.

The measurements usually involve a sample of the process water (after filtration) with the appropriate polymer and recording the volume of the polymer required to reach the electrical neutrality. The end point is usually measured with SCD (Streaming current detector) or PCD (Particle Charge Detector) or Zeta meter. The demand is expressed as volume of polymer per unit of fluid (6).

Common Titrants used in ionic demand estimations

Cationic Demand Titrant- Poly DADMAC (Poly Diallyl Dimethyl Ammonium Chloride)

Anionic Demand Titrant- PVSK (Polyvinyl Sulphuric Acid-Potassium salt) or PESNa Polyethylene Sulphonic acid-Sodium salt).

The manufacturers of this chemical also express the charge content of these solutions, just like we express the strength of standard solutions viz 0.1N HCl. The charge demand can be expressed as milliequivalents per unit of fluid (meq of polymer/ml of water).

Types of monitoring equipments available

Sensors for measuring charge demand and a retention control scheme that incorporates such sensors, along with consistency measurements are currently in use worldwide. However, they are more common in Europe than in the USA.

It is to be stated that these charge measurements have to be done very carefully and subject to variations due to errors committed by operators and is subjective. King has observed "charge measurements are frequently difficult to conduct because the test is subjective, operator to operator, requires complicated filtration, the results are hard to interpret, the test, time consuming etc." (9)

Because of these factors to have a better control

of the machine, online automatic charge titrators, which determine continuously the system charge demand, have gained more acceptance and the particle charge detectors, which measure only the intensity of charge, as they have been used more in research studies and not in plant operations.

Let us now review some of these common equipments.

Electro kinetic charge titrator of M/s Chemtrac Electrokinetic Charge Titrator (ECT)

This measures the charge and the charge demand of the thick stock or head box sample. The technique involves titration with known normality and charge density. The titration is carried to the zero streaming current potential end point.

Table 2. Effect of zeta potential magnitude on retention

Retention	Zeta potential in millivolts
Excellent retention	+/- 5
Fair retention	+/- 10 to +/- 20
Poor retention	+/- 20 to +/- 40
Out of control	+/- 40 plus

Table 1. Smaller dimensions of furnish components

Component	Size	Dimensions
Fibre	10-20 m μ	Width
Fibril	< 1 m	Width
Non fibrillar fibre fines	< 2 m	Diameter
Filler particles	0.1 - 1.0 m μ	Diameter
Dispersed rosin size aggregate	< 1 m	
Dissolved polyacrylamide molecule	<0.1 m	

Table 3. Zeta potential for some fillers

Filler	Zeta potential in millivolts
Calcium sulphate	- 5
TiO ₂ Anatase	- 8.9
Coating clay (Kaolin)	- 92
Talc	- 11.2
High brightness talc	- 12

Table 4. Zeta potential of some imported pulps

Pulps	Zeta potential in millivolts
Broke	+ 4
Northern Hardwood sulphate	- 9 to -15
Canadian softwood	-9
Southern softwood kraft	- 9
Western softwood kraft	+ 5
	+ 5

Table 5

Pulp	Streaming Potential mV	Ionic Demand ml/Litre
Bleached Eucalyptus Kraft Pulp	(-) 143.8	67 (Cationic Demand)
Bleached Bagasse Kraft Pulp	(-) 95.4	63 (Cationic Demand)
Bleached Chemi-Thermo Mechanical Bagasse pulp	(-) 173.0	522 (Cationic Demand)
A typical Fine Paper furnish with Eucalyptus & Bagasse Kraft Pulps- Stuff Box- After Alum addition.	(+) 107.0	37 (Anionic Demand)
A typical Newsprint furnish with Eucalyptus Kraft pulp, Bagasse Kraft pulp and Bagasse CTMP stuff Box- After Alum Addition	(-) 79.0	66 (Cationic Demand)
A typical Fine paper furnish with Eucalyptus & bagasse Kraft pulps Head Box- After Polymer addition	(+) 52.0	15 (Anionic Demand)
A typical newsprint furnish with Eucalyptus Kraft pulp, Bagasse Kraft pulp and Bagasse CTMP Head Box- After Polymer addition	(-) 76.0	55 (Cationic Demand)

The two outputs are :-

Streaming current value before startup of the titration

Milliequivalents per litre of charge demand poly DADMAC

This is an online equipments currently Chemtrac has sold 18 units in North America and 1 Unit in South America and 4 units in the Europe.

Online particle charge titrator-mutek

The BTG/Mutek online particle charge titrator (PCT 15) has originated from Mutek laboratories and upgraded laboratory Particle charge detector. The principle employed, the method is same as lab tester. For consistencies greater than 1% the stock is filtered with a thick stock sampler, and filtrate is metered to the measuring cell and titrated to zero charge end point. Following the titration, the cell is emptied, cleaned with ultrasound and all wetted parts are rinsed with detergent solutions to ensure repeatable results.

There are about 80 PCT systems installed world wide with 75% of the installations in Europe.

Online cationic demand analyzer

Metso Automations online Kajaani CAT analyzer measures the cationic demand for consistencies less than 1%. The measurements are based on the titration technology and the streaming current is used to detect the titration end point. Titrating chemicals are Poly DADMAC and PVSK. Automatic cleaning of the cell is done by pressurized air, water cleaning chemical and ultrasonic energy to ensure reliable operations. There have been about 50 installations worldwide and of this 70% are in Europe.

RESULTS AND DISCUSSION

Application of charge measurements in paper machine operations

In Retention aid systems

As the zeta potential approaches zero, the charges becomes less effective in keeping the particles apart, and conditions approach optimum agglomeration, flocculation and consequent retention. The relationship between zeta potential and retention is shown in Table 1- in the next two tables, Table 2, 3 the zeta potential values of some of the fillers and also zeta potential of pulp/fibres are given.

Measurements in paper making system

As a measure of the charge balance in printing and writing furnish system and newsprint furnish systems, in order to regulate the addition of coagulant and flocculent, for optimum performance, colloidal charge was determined with lasertrim streaming current tester (SCT). The soluble charge, which varied widely, could indicate only the potential difference and could not tell anything about the capacity of the system charge. The charge of various furnish components are provided in Table 5. It can be observed that for similar charge (or streaming potential) the two pulps namely hardwood pulp and bagasse mechanical pulp exhibit extremely different ionic demands. As it can be observed it appears that it is the ionic demand rather than the absolute charge is meaningful. The soluble charge measurement thus could not tell us the quantity of retention aid required for neutralization, so as to have better flocculation and better retention of fillers and fines.

Charge demand determination was carried out using polydadmac and PVSK. The charge demand values expressed as ml/ml for individual pulps and for stock blend is provided in Table-5. The cationic charge demand varied from 0.026 to 0.186 ml/ml for

hardwood pulp while for chemical bagasse pulp it varied between 0.056 to 0.114 ml/ml. The higher charge demand for hardwood pulp can be attributed to two stage hypochlorite bleaching resulting in more formation of carboxylic acid groups. Also the hypochlorite addition is also more in hardwood due to higher kappa number of unbleached pulp.

The cationic demand was highest for mechanical bagasse pulp 0.442 to 0.572 ml/ml, mainly due to the presence of high amount of anionic trash. The consumption of the cationic standard reagent is a measure for the content of anionic substances in the tested solution and may be taken as an indicator of the anionic trash level. However, the charge demand of the blended stock at the machine head box, has been consistent at 0.015 to 0.094 ml/ml during the production of fine paper. During fine paper run, the machine head box pulp was cationic and its anionic demand was 0.012 ml/ml. During newsprint run the pulp was anionic and the cationic demand varied between 0.028 to 0.110 ml/ml. This shift in value during newsprint run is due to reduced alum dosage. Continuous measurements of ionic demand in both the systems indicated constant fluctuations. Therefore online measurement of ionic demand is more effective for optimizing the retention.

CONCLUSION

Comparison of charge demand values and charge measurement values, it is clear that they are not directly proportional to each other. The charge measurement will give only limited information and charge demand is also required additionally to make the measurement more meaningful. For best retention and wet end control, charge should be near zero and the soluble material should have a cationic or anionic demand close to zero. Online systems of charge measurements and control hooked up to retention aid dosage will be the best practical approach, helping the industry to save chemicals and cut down the

cost of production.

ACKNOWLEDGEMENT

The author wishes to thank the Management of TNPL for giving permission to publish this paper.

REFERENCES

1. Junhua Chen, Martin A. Hubbe, John A. Hetmann, Paper Makers Conference, Proc. Tappi Press Sess. 5, (2001).
2. Brouwer, P.H., Tappi J, 1, 171 (1991).
3. Springer, A.M., Taggart, T.E. 5, p. 116, (1986).
4. Lindstrom, T., Paper Chemistry, Roberts, J.C., Ed., p-25-43, (1991).
5. Bley, L., Pulp and Paper Canada, 99 (5), p165, (1998).
6. Jain L., Bharati, R., Vijay Kumar Bharati, S., Aggarwal, S.K., IPPTA J. 3, 46 (1991).
7. Patton, P.A., and Lee, D.T. Tappi J. 76(8), p- 107-115 (1993).
8. Tanaka, H., Ueda, I., Ichiura, H., and Kitaoka, T., Proc. Inter. Symp. Environmentally Friendly and Emerging Technologies for a sustainable pulp and paper industry, Taipei, Taiwan, April, p- 68-71 (2000).
9. King, C.A. Paper Makers Conf. Proc. Tappi Press, Atlanta, p. 507 (1992)