Alkaline Papermaking

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ABSTRACT

This paper describes the alkaline and acid papermaking process in more details. Basically the alkaline papermaking is carried out at pH of 7·0 to 9 0. The acid papermaking is carried out at pH of 4 0 to 5.0, with rosin, and is being presently used in India. The advantages of alkaline papermaking are both economic and quality.

It is now evident all over the world that alkaline papermaking is the current trend. In the United States and Europe more than 75% of the printing and writing paper maufactured today is by alkaline papermaking. Most of the conversions to alkaline papermaking have happened in the United States during the last seven years. Some other countries have started using alkaline process at few of the mills. Most other countries are either experimenting with it or seriously looking into it.

This paper will explain sizing mechanism, chemicals and fillers used in both alkaline and acid papermaking. It will also discuss manufacturing process of alkaline papers.

The economic and quality advantages occur because with alkaline system other fillers like precipitated and ground calcium carbonates can be used. The major quality advantages are permanence, higher brightness, higher opacity and improved print quality.

The paper industry has been making printing paper since before 1950's only by what is called acid sizing. Sizing is defined as resistance to water and is required for printing papers to make paper resistant to water in the offset printing process. Without sizing the paper will be weakened by water and break during printing operations.

In offset printing the fact that images can be made by making the printing plate accept water or ink is used. The ink acceptable area is the print area. Figure 1 shows schematic of the offset printing process. The print roll is first passed over the water applicator roll and the non-image areas accept water. Then the print roll is passed over the ink applicator roll which then accepts ink in the image areas. The print roll comes in contact with the blanket roll and accepts the ink from the print roll. The blanket roll then transfers the ink to the paper to create the image on the paper.

In acid sizing (pH of 4 to 6.5), rosin and alum are used. The rosin-alum complex has hydrophobic and hydrophyllic components. The hydrophyllic component attaches to the cellulose and the hydrophobic component is stretched out to make fiber surface hydrophobic as shown in Figure 2. There can be two basic reactions of the hydrophobes with the cellulose fibers:

1. The uncontrolled deposition of the hydrophobes on the cellulose which lead to what are called pitch problems on a paper machine.

2. The controlled deposition of the hydrophobes on the cellulose which leads to what is called acid sizing.

In alkaline sizing (pH 7 to 9), the hydrophyllic part of the alkaline sizing agents reacts with the cellulose fibers. The hydrophobic component of the sizing agent sticks out to make the cellulose fibers

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repel water. Figure 3 shows the chemical reactions that take place with Alkyl Ketene Dimer (AKD).AKD can react with the cellulose to create sizing of the cellulose or can react with water to get hydrolysed and not create sizing of the cellulose. The reactions with other alkaline sizing agent, Alkenyl Succinic Anhydride (ASA) are quite similar.

Offset Printing Process

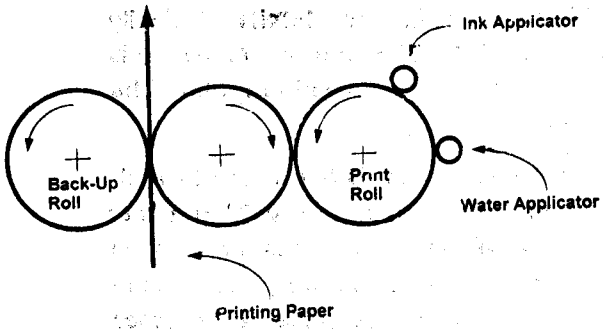


Figure 1

Reactions Between Rosin and Cellulose

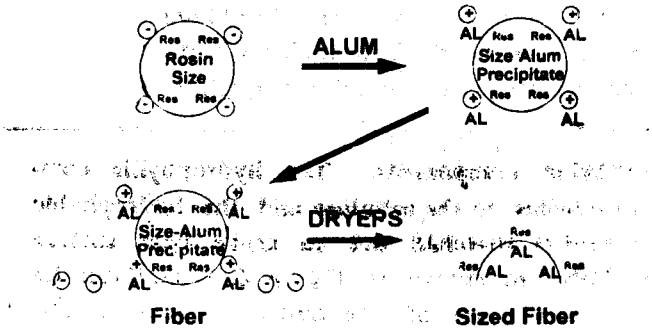


Figure 2

Reactions Between AKD and Cellulose

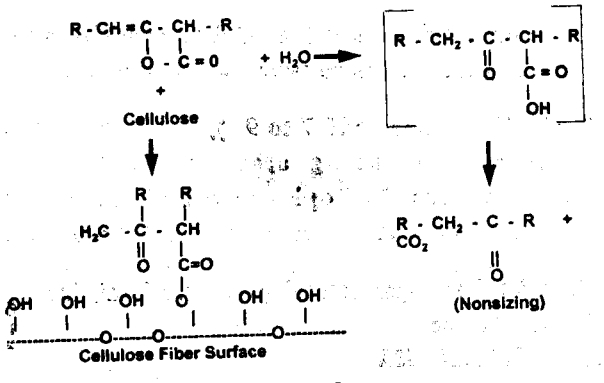


Figure 3

Paper making is quite complex, both mechanically and chemically and hence changing from acid sizing to alkaline sizing is quite critical. The chemical complexity is due to the electrochemistry involved Each component used to make paper has its own zeta potential (electrical charge, either positive or negative. To obtain the best finished paper properties, the knowledge of zeta-potential of the components used and at all critical points during papermaking process, is essential The Figure 4 shows the importance of the zeta-potential of all the components and their effect on drainage, retention, pressing, drying etc. Hence, a thorough knowledge of the effect of all variables, is necessary to manufacture paper of superior quality.

Impact of Wet End Chemicals

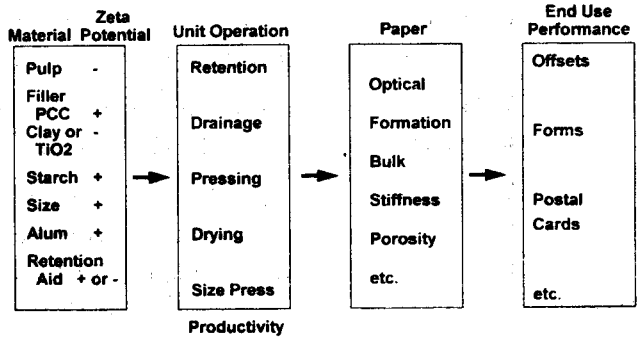


Figure 4

When acid sizing is used to size papers, alkaline fillers like precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) could not be used and only clay and titanium dioxide are used. In the 1950's when alkaline sizing was developed, the alkaline fillers could be used.

The acid sizing of paper has been rapidly replaced all over the world by alkaline sizing. In alkaline sizing, as the name suggests the sizing of the paper is done under alkaline conditions. It has been shown over the last 35 years that alkaline sizing is better than acid sizing because of significant savings, enhanced paper quality and permanence. The following table shows the merits of alkaline papermaking over acid papermaking.

The following table shows the principle difference between acid and alkaline papermaking.

	ACID	ALKALINE
Sizing Chemical	Rosin Alum	AKD or ASA
Filler	Clay Soapstone TiO_2 Talc	PCC GCC TiO_2 Clay
Retention Aid	Cationic	Anionic/Cationic
Operating pH	4.0-6 5	7.0-9 0
Operating Electrochem. (Zeta-potential)	—15 to —25 mev	—10 to neutral

	ALKALINE	ACID
Optical properties	Higher	Lower
Physical properties	Stronger	Weaker
Energy required	Less	More
Corrosion	Less	More
Makeup water required	Less	More
Effluent treatment	Less	More
Permanence	More	Less
Recyclability	More	Less
Filler options	Unrestricted	Restricted
Microbiological activity	More	Less

Because of the reasons mentioned above the alkaline paper making has spread all over the World. In Europe, because of the availability of chalk, the alkaline papermaking conversion was achieved sooner. By 1985 approximately 70% of the production of fine papers, which includes printing, writing and copy papers, had been converted to alkaline sizing. In United States the alkaline papermaking had been used only in speciality paper mills untill 1986 and was only 10% of the fine paper production. Before 1986 the main reasons for not going alkaline were the non-availability of good sizing agent and low cost fillers. But since that time till today the conversion has been 75% because of the availability of good sizing agents and precipitated calcium carbonate (PCC) from on site PCC facilities. The progress in alkaline papermaking in United States is shown graphically in Figure 5. Countries like Mexico, Indonesia, Colombia, Thailand, Brazil have also partially converted or have been very seriously looking into alkaline papermaking.

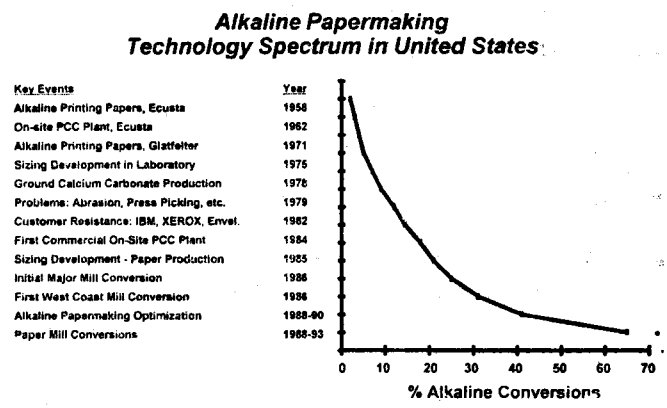


Figure 5

Since the world is getting smaller, and because of global competition, alkaline papermaking has to be accepted as the most logical way to make fine papers in the future. It is time for rest of the countries in the world to start looking into converting its fine paper production from acid sizing to alkaline sizing.

Based on the above tables it is necessary to look at the savings and quality aspects for alkaline papermaking.

Savings :

Normally acid sized papers are made with lower percent fillers and to get increased opacity, expensive fillers like titanium dioxide are used. In alkaline sizing lower cost fillers at higher percent is used, which represents savings in raw material costs. For papers presently being made by alkaline sizing these savings have been significant.

The paper under alkaline conditions produces increased and stronger fiber bonding. This increase strength can be capitalized in several ways. One approach is to reduce fiber refining and get a sheet that is faster draining and easier to dry. This provides higher production rate and lower energy requirement in producing paper. The other approach would be to

make lighter-weight paper of equal strength. Yet another approach is to use higher per cent filler by replacing the higher cost fiber.

The principal filler for alkaline system is precipitated calcium carbonate (PCC). The difference between the fillers commonly used clay, PCC, ground calcium carbonate (GCC) and titanium dioxide (TiO_2) are as follows; *(Shown below)

Another way of looking at the savings is to increase profits by following ways :

* Manufacturing Value added grades of paper.
* Manufacturing higher quality papers which will bring significantly higher selling price.

Quality Aspects :

As mentioned above in advantages of alkaline vs acid papermaking the following quality aspects further mention :

Permanence :

With the use of PCC in alkaline papers the degradation of fibers is minimized. The atmospheric oxidizing components attack PCC before it can attack the fibers and hence the degradation of fibers, reduction in strength and discolouring is suppressed. This permanence is quite essential for printing papers used for books.

Brightness :

Normally acid sized printing and writing papers used clays with brightness of 76–90%, which gives low brightness papers. To increase the brightness sometimes titanium dioxide is used, which is very expensive. But in alkaline sized papers the use of PCC, with very high brightness 95–98%, increases the brightness of the paper by 2–5%, which is very significant. This can be seen in Figure 6, where the brightness of papers made by acid and alkaline sizing is shown.

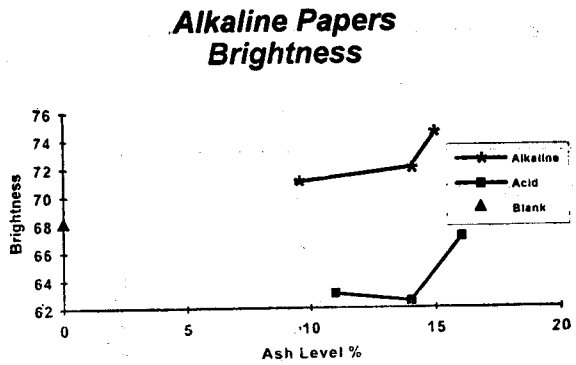


Figure. 6

Opacity :

Because of the use of PCC in alkaline sized papers the opacity of the papers is increased by 2–5% over similar acid sized papers, which is very significant. This significantly reduces the ink showthrough when the paper is printed. This can be seen in Figure 7, where the opacity of papers made by acid and alkaline sizing is shown.

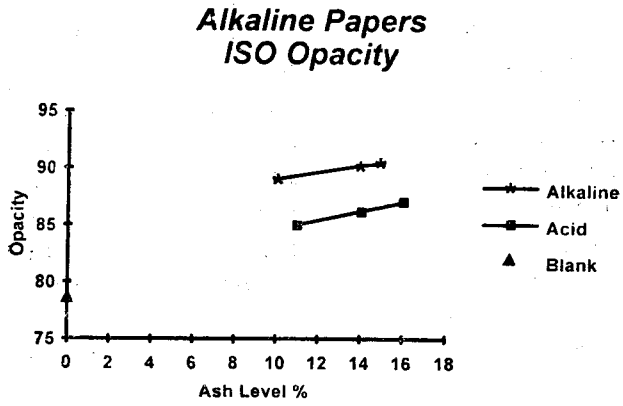


Figure. 7

Bulk, Caliper, Stiffness :

Because of the use of PCC in alkaline sized papers the bulk of the papers is increased by 5- 15% over acid sized papers, which is very significant. This also gives higher stiffness which is an advantage in handling

*	Clay	PCC	GCC	TiO_2
Brightness (ISO)	79.93	94-96	90-94	99
Scattering Coefficient	800-1200	1800-2500	1200-1800	4500-6000
pH	7.0	9.4	9.4	7.5
Prices in U.S. $/short ton	120	120	120	1800

printing papers. This can be seen in Figure 8, where the caliper of papers made by acid and alkaline sizing is shown.

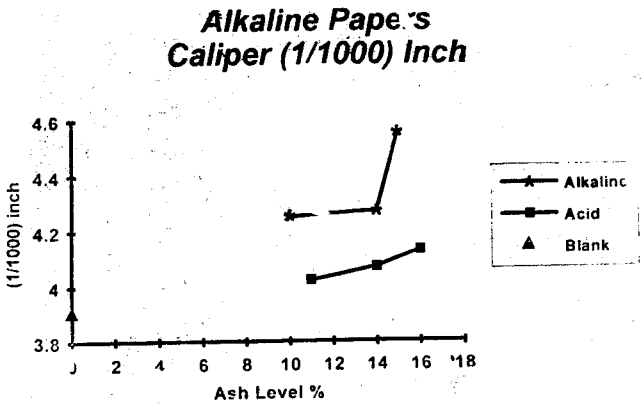


Figure 8

Microbiology :

There is more microbilogical growth in alkaline system but this has been studied and preventive measures are commercially available.

Other potential issues are :

* **Felt Filling** : Higher filler level can create felt filling but proper actions can be used to minimise this. The felt life is normally the same as in the case of acid sizing.

* **Press picking** : This can be minimized by using proper roll cover. It is also minimized by proper selection of sizing and retention agents.

* **Wire Life** : Due to the higher filler level, and especially with ground calcium carbonate, the particles can get entrapped at the foil or vacuum boxes. This can cause wire abrasion. This can be minimized by using Precipitated Calcium Carbonate.

* **Productivity** : is usually higher after the first year, when all the operating issues have been resolved.

* **System variability** : is significantly reduced by alkaline sizing. This is dependant on the proper use and quality of chemicals.

As can be seen from the above discussions, for alkaline sizing to be successful one needs good source of suitable quality and economical filler, sizing agents and retention aids.

Fillers for Alkaline Papermaking :

Evaluations of the fillers available for alkaline papermaking has been done quite extensively in the laboratory and on paper machines. The fillers evaluated were clay, ground calcium carbonate, titanium dioxide and precipitated calcium carbonate. It has been concluded that precipitated calcium carbonate is the filler of choice because of its higher optical properties per unit cost.

Precipitated calcium carbonate is the raw material of biggest importance after the fibers. PCC is available all over the World but special grades of PCC are required for fiine paper manufacture.

Precipitated Calcium Carbonate (PCC) :

PCC is chemically the same as limestone, marble, chalk and ground calcium carbonate. In the PCC process the limestone is calcined to give quicklime, which is then hydrated to calcium hydroxide. The carbon dioxide which is evolved in the calcination step is now reacted with the calcium hydroxide to obtain PCC with desired quality The slaking and carbonation steps and design of the equipment are used to control the quality of PCC along with the source of the limestone and its calcination. Figures 9 and 10 show the different shapes that can be made with this process. All different sizes in these shapes also can be made.

The advantage of PCC over chalk and ground limestone is that the particle size distribution is unimodal and very narrow. This control of the particle size distribution is quite important for its use in paper because that allows the papermaker to control the desired paper properties more precisely,

Chemicals for Alkaline Papermaking :

Since alkaline papermaking is carried out at elevated pH of 7.0 to 9.0 it requires different chemicals which are compatible at alkaline pH. The system strategy is also quite different and requires special knowledge and testing. The paper machine also needs to have minor equipment modifications and additions.

Precipitated Calcium Carbonate (PCC)

Calcite Rhombohedral

Aragonite Needle

Figure 9

Szing Agents :

The Sizing agents used in alkaline papermaking are reactive chemicals which interact under appropriate conditions with cellulose to provide a water repellant quality to paper. There are two main synthetic sizing agents:

1. Alkyl ketene dimer (AKD)
2. Alkenyl Succinic Anhydride (ASA)

Operating pH :

Since the equilibrium pH of precipitated calcium carbonate is 9.4, the papermaking system tends to equilibrate in the range of 7.0 to 9.0 for an alkaline system. For most of the alkaline paper machines PCC buffers the system and therefore no additional chemicals for pH adjustment are needed.

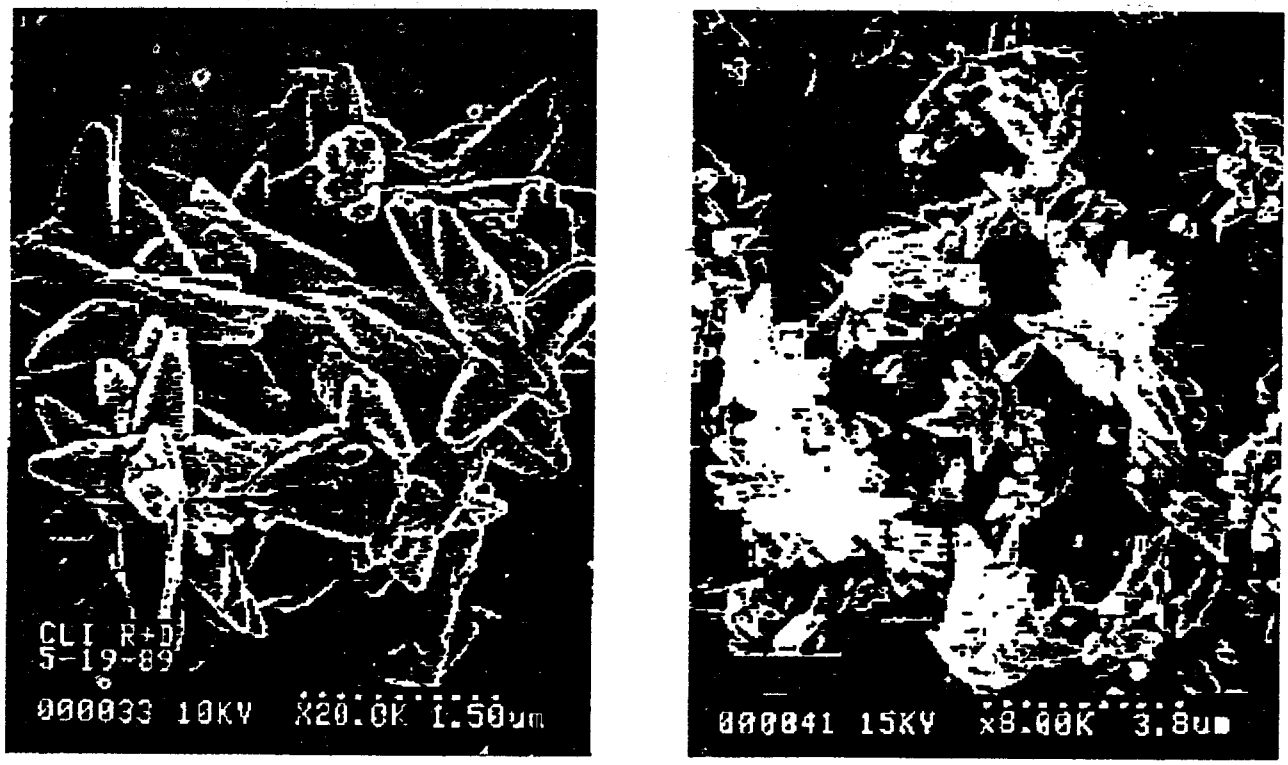
Electrochemistry :

Due to its crystal structure and the action of ions PCC requires a residual positive Zeta potential. This could, however, be dependant on the mill water composition, etc. Due to its positive charge and absence of large quantities of eletronegatively charged clay, the system charge tends to equilibrate in the range of-10 to neutral. It is critical to control the electrochemistry of the system.

Retention Aids :

Since PCC is electropositive, cationic (+ve) in nature, the retention aids usually need to be switched anionic (—ve). The retention also depends on the anionicity of the fibers used for paper making. The retention of fiber fines and filler is critical for the success of the program.

Precipitated Calcium Carbonate (PCC) Calcite Scalenohedral (Rosette)



Large Particle Size **Small Particle Size**

Figure 10

Key factors affecting Successful Conversion :

Most of the potential issues metioned above have been solved and most alkaline mills world-wide enjoy most of the advantages. However, several factors influence the success :

* Pulp quality and variability
* Paper machine configuration
  ** Press section
  ** Dryers
  ** Size press
* Quality of alkaline chemicals (namely sizing agents, retention aids, PCC and biocides)
* Delivery systems for-new wet-end additives
* Technical level of mill and operating personnel.

Recommendations for Hardware :

The detailed and more specific recommendations can be developed only after a pilot machine trial, mill audit and paper machine trials. However, some general comments can be made at this stage.

* The wet end system needs to be properly designed based on what is available now. Separate tanks with agitators, motors and flowmeters for preparation and delivery of the following chemicals :
  ** Precipitated Calcium Carbonate
  ** AKD/ASA
  ** Starch
  ** Alum

** Retention aid

** Biocide

Manufacturing Strategy and Implementation :

The program will be developed in the following stages :

* Preliminary evaluation
* Phase I : handsheet study, Technoeconomic feasibility.
* Phase II: Pilot trails – Paper quality and performance evaluation
* Phase III : Pretrial preparation to get paper machine and personnel ready for paper machine trials.

Production	Trial # 1	1 Day
	Trial # 2	3 Days
	Trial # 2	3-10 days

This will complete paper production trials for all grades.

Next will come the following stages:

* Paper Performance - Customer Evaluation
* Market Evaluation
* Total Economic Evaluation
* Install permanent system in place
* Conversion monitoring