Loading and Filling of Paper For Economy and Excellence— Theory & Practice

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INTRODUCTION

Escalating cost of raw materials, machinery, and man power and high capital investment, coupled with our stringent government regulations for producing huge quantum of cultural papres at uneconomical prices fixed by them, has brought down considerably the profitability of paper industry. All efforts are now geared up to bring down the cost of production, so as to increase the economic viability of the industry.

Many strategies have been adopted to achieve this objective and loading of the paper, by replacing the more expensive cellulose half stuff with cheaper minerals has proved to be one of easier and best methods to bring down the cost of production.

An attempt has been made in this review to highlight the various aspects involved in the use of fillers—the economy, effect on strength and optical properties, effects on printability of the paper, the ways and means of achieving maximum retention and the understanding of the electro kinetic phenomena involved in the retention of fines and fillers. Some of the more recent developments have been dealt with in more details, as we find that there is paucity of a critical review in this important field in recent years.

FILLERS

In fact, loading or filling of papers with finely powdered mineral materials has been in vogue for quite some time, although in the initial stages it was regarded as an adulteration. However, now it is widely practiced and it has been recognised that fillers make paper more suitable for various uses. The fillers improve the printing properties of paper by increasing its brightness and opacity, decreasing its show through, giving more body and better formation to the sheet. They also improve the 'feel' of paper and result in better finish on calendering.

Talc, Clay, Titanium dioxide and Calcium Carbonate are the principal filler pigments used in Indian paper indusrty. As stated earlier, in loading and filling of paper, 12% to 15% ash in paper would replace as much quantity of the parent pulp at one fifth cost (at 55%-60% filler retention). However, it is to be pointed out here that titanium dioxide filler is much more expensive than cellulose half stuff. Thus an optimum filler pigment retention is very important both for economy (covering the input values) and for effective utilisation. We also present in this paper some of the efforts made by us to improve the retention of fillers.

Willets[1] has enumerated the qualifications of an ideal filler as follows :

1. It should have a reflectance of 100% in all wave lengths of light.
2. It should have very high refractive index.
3. It should be free from grit or extraneous matter and have a particle size distribution close to 0.3.
4. It should be soft and non abrasive.
5. It should be able to impart to paper a surface capable of taking any furnish upto the highest Gloss.
6. It should be chemically inert and insoluble.
7. It should be reasonable in price.

Probably, a perfect filler pigment, conforming to all these specifications will never be available. While talc and clay are not so prohibitive in cost, titanium dioxide is expensive and calcium carbonate has its limitations since it must be used in

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alkaline conditions. A few typical properties of typical filler pigments are tabulated in Table 1[2].

TALC

Talc, a hydrated magnesium silicate theoretically containing 31.7% MgO, 63.5% SiO_2 and 4.8% H_2O is the most common filler used in Indian paper industry. It imparts a characterististic soapy and greasy feel to the papers. Also it improves sheet formation.

Talc frequently contain relatively coarse material and have other minerals[3] like tremolite [$CaMg_3 (SiO_3)_4$], serpentine (3 MgO. 2 SiO_2 . 2 H_2O) anthophyllite ($Mg_7OH)_2$ $(Si_4OH)_2$ and chlorite. Impurities such as dolomite (Ca, $MgCO_3$) calcite ($CaCO_3$), Iron oxide and manganese oxide may also be present. Presence of calcium carbonate is harmful to sizing and to certain dyestuffs.

CHINA CLAY also known as Kaolin is hydrated aluminium silicate and is used in paper as a filler because it is inexpensive, white in colour, soft and non abrasive and increases the opacity of the sheet. It is used as a coating pigment to improve the printing characteristics of the paper, by improving ink receptivity providing the contrast billiance and detail necessary in today's colour printing.

TITANIUM DIOXIDE is the most expensive filler pigment but ranks more important among the other pigments. The major characteristic of titanium dioxide is its high optical scattering power resulting from its high refractive index and uniformly fine particle size.

Titanium dioxide has carved out its unique place because of this important optical property which imparts opacity and whiteness unattainable otherwise. Speciality papers such as opaque waxing, opaque glassine, opaque air mail and decorative resin laminates, require their use. Light weight paper requiring high opacity incorporate titanium dioxide in their furnishes.

CALCIUM CARBONATE

Precipitated calcium carbonate is high in purity, brightness, and has controlled particle size, shape and is less abrasive, Though calcium carbonate is a very good filler pigment, its use has been limited due to its high reactivity with acid furnishes. Precipitated calcium carbonate is primary filler in cigarette papers, where particle size is critical in order to regulate the burning rate.

EFFECT OF FILLERS ON STRENGTH PROPERTIES OF PAPER

Despite their beneficial effects, filler pigments impair the strength especially clay Titanium pigments have little or no effect when used upto 6%.

It is our experience, however, great many varieties of papers can be manufactured at an ash content level of 15-17% meeting the Indian Stanard Specifications, provided the bleached pulp viscosity is above 8 cps (0.5 in CED), which we are maintaining without difficulty.

The loss of strength properties occurs presumably because the fibrous material having inter fibre bonding being replaced by an amorphous material which hinders interfibre bonding.

RETENTION OF FILLERS

Efficient utilisation of filler pigments is most important. Because of the very low particle size of the filler material; the possibility of its passing through the mesh into the drains in the wire part of paper machines exists. Ways and means will have to be found for effective retention of the filler material in the paper mat.

TABLE—I SOME TYPICAL PROPERTIES OF IMPORTANT FILLER PIGMENTS

		Clay	Talc	Titanium dioxide	Calcium carbonate precipitated
1.	Brightness %	75–85	Upto 90	94–98	95
2.	Refractive index	1.56	1.57	2.55 to 2.7	1.56
3.	Average particle size μ	0.5–1.0	1–10	0.3–0.35	0.2–0.5
4.	Specific gravity	2.5–2.8	2.7	3.9–4.2	2.7–3.0
5.	Solubility in water gm/1000 ml.	Negligible	Negligible	Negligible	0.0014
6.	Solubility in dilute acid	—do—	—do—	—do—	Soluble.

Casey has given an excellent review on retention of fillers and loading materials(5).

MECHANISM OF RETENTION OF FILLERS

The mechanism of filler retention depends on a combination of electro chemical and mechanical factors which play an important part not only in holding the filler in the web but in effecient white water usage.

Retention can be achieved by a number of mechanisms and not all of these mechanisms involve electrostatic interactions. Haslam and Steel (6) postulated three mechanisms of filler retention.

a) filteration by the fibrous mat
b) entrapment in the fibre pores and lumens
c) co-flocculation and coagulation.

The first two mechanisms are difficult to separate experimentally as both involve mechanical entrapment or entanglement. Thus we can broadly classify retention mechnisms into mechanical and colloidal. The effect of particle charge on the mechanical retention processes should be minimal, and they matter most in the colloidal retention mechanism.

In recent years, the use of Zeta potential—the electrokinetic charge on a colloidal partical and its importance in paper making especially in filler and fines retention have been looked into in detail.[8—13]

Paper making fibres, fillers assume normaly a strong negative charge in soft water. The fibres fines and pigment particles tend to repel each other and remain in a dispersed condition. Such surface charges attract a thin layer of oppositely charged counter ions in the liquid. The electrical potential between these thin layer of counter ions and the bulk of the liquid is known as the Zeta potential. If the surface of the particle is negative its Zeta potential, is negative. The higher the Zeta potential, the greater the repulsion and therefore greater the stability, with consequent poor retention. Repulsion prevents agglomeration/flocculation on the wire and the particles, therefore, go through to to the white water. The Zeta potential is expressed in millivelts.

As the Zeta potential approaches zero the charge 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 2. Table 3 gives the Zeta potential of common filler materials. It has been pointed out that for paper making a Zeta potential at near zero as the furnish hits the wire is only the theoretical optimum, with a practical working range of —5 to +5 millivolts.

TABLE—2 EFFECT OF ZETA POTENTIAL MAGNITUDE ON RETENTION

Retention characteristics	Zeta potential in millivolts
Excellent retention	±5
Fair retention	± 10 to ± 20
Poor retention	± 20 to ± 40
Out of control	± 40 plus

TABLE—3 ZETA POTENTIAL FOR FILLERS [1]

Filler	Zeta potential in millivolts (Appelton city water)
Calcium sulfate	—5
Titanium dioxide Anatase	—8.9
Coating clay	—9.2
Talc	—11.2
High brightness Talc	—12.0

TABLE 4 ZETA POTENTIAL SURVEY OF PAPER MACHINE SYSTEM.[11]

Material	Zeta potential in millivolts
Wet strength resin (Parez 631)	+6
Defoamer	0
No ionic rewetting agent	0
Broke	+4
Northern HW sulphate	—9 to —15
Canadian SWK	—9
Southern SWK	+5
Western SWK	+5

The importance of Zeta potential determinarion hinges on the particle charge, in colloidal retention mechanisms. In the colloidal mechanism, co-flocculation can easily be envisaned to depend strongly on particle charge. This mechanism is really at least two separate mechanisms. Coagulation and flocculation. Co-flocculation is implemented through the mechanism of :

a) collapse or compression of electrical double layers of the particles, as described in the theory of stability of hydrophobic colloids.[14]

b) development of polymer bridges as enunciated by Lamer etal [15,16] and combination of (a) and (b).

The first mechanism is called coagulation and the second is called flocculation.

When the particles are charged, a priori their interaction will be affected by the nature of that charge. In addition the behaviour of these particles in the presence of long chain polymers which also carry a charge will similarly be determined to some extent by electrostatic interactions. Therefore, control of zeta potential should be important to the extent that the colloidal retention mechanisms are governed by it. In practical terms the colloidal mechanism becomes quite important and has been described by Williams as the 'dominant mechanism are retaining pigment fillers and pulp fines'.[9]

We would also like to point out here that the predominant mechanism of sheet formation on paper machine is hydromechanical. As described in the preceding paragraphs chemical and colloid chemical factors influence nonetheless, the behaviour of the furnish especially that of the fine material present. Thus a better understanding of the physical and mechanistic surface chemistry of fines and pigments in the furnish should improve the machine performance by increasing drainage rate, by improving pigment utilisation and by illuminating environmental and energy problems. In addition correct manipulation of the fines and pigments contribute to the improvement of the machine stability, a vital aspect of paper making economics.

FACTORS AFFECTING RETENTION AND WAYS AND MEANS OF ACHIEVING BETTER RETENTION

Many factors have bearing on the retention of filler materials. It is documented that the following effects increase the retention :

a) increased sheet weight
b) increased beating
c) increased sizing (this may be attributed to the alum used)
d) increased fibre length of the stock
e) increased recirculation of white water.

In contrast, the following factors adversely affect the retention.

a) increased machine speed
b) increased shake or turbulance
c) very high pH values.

FACTORS AIDING INCREASED RETENTION

Increased alum dosage increases retention till a particular limit is reached, after which further addition, in fact, brings down the retention. Willets found that 3% alum to be most effective with titanium pigments[5]. Roschiler[5] found 5% alum to be most effective when the pH was maintained constant at 5 to 6. Roschiler found that pH had an important effect, even with constant alum. Alum without alkali is not very effective, since no alumina is formed. The optimum pH appeared to be between 5 to 6.

In a recent communication Avery[18] using alum analysis to monitor the head box furnishes found retention aid efficiency can be maximised by maintaining the soluble alum content at the lowest practical level.

An excessive amount of alum in paper machine head box reduces the effective of the retention aids. Laboratory studies by other workers ([19],[20]) revealed that alum levels in excess of 5% is detrimental to retention. Further, zeta potential studies [21] have pointed out that the addition of 6 0% alum resulted in a bleached kraft furnish becoming positively charged,

USE OF RETENTION AIDS FOR ACHIEVING BETTER RETENTION

Many types of synthetic polymers are now used to improve drainage and retention in paper making systems. The commercial polymers used for this purpose are mostly poly-acrylomides. They are either cationic, anionic or amphoteric, and cover a wide range or charge densities and molecular weights ([7],[22]) Commercial cationic starch has also been found to be a good retention aid. Several publications have dealt with the mechanisms by which these work ([12],[20],[23]). Although earlier work laid greater importance on charge neutralisation of the substrate surfaces ([24],[25]) more recent investigations on drainge and retention improvement with polymers have shown the other factors can dominate over charge effects. ([13],[20],[26],[27])

Britt and Unbehend ([27]) have used dual polymers, a cationic and anionic resin to obtain higher levels of retention than was possible with single polymer. Moore ([22]) has also used a combination of cationic and anionic polymers with a proper balance of charge and concentration to obtain a very high levels of retention with high shear resistance for a given alum level and pH. There were additional beneficial side effects like increased wet strength. A combination of cationic starch and hydrolysed polycrylomide was used by Moore.

EFFECT OF POLYELECTROLYTE MOLECULAR WEIGHT ON FILLER RETENTION

Arvela etal[23] have investigated the effect of retention aid molecular weight on the filler retention and sheet formation. They found that increasing the molecular weight of the polymer at constant dosage did not enhance the tenacity of retention, increased the filler retention only slightly and produced poorer formation.

FACTORS AFFECTING ADVERSELY THE RETENTION—EFFECT OF STOCK AGITATION ON FILLER RETENTION

Increased turbulance decreases the efficiency of retention. The added polyelectrolytes however, help in minimising the losses and increase the retention even under turbulent conditions. Various flocculating agents or 'retention aids' have highly different degrees of effectiveness in the retention of fines under turbulant conditions. Of particular interest is that the differences among flocculating agents are shown up principally in the higher degrees of turbulence (hydraulic shear) typical of fast running paper machines. At low levels of shear the various flocculants are not greatly different but at higher levels they tend to form two groups those which display high tenacity in resisting redispersion of fines and those in which the flocculation is readily broken up by dispersive forces (soft flocculation). The tenacious flocculation requires a relatively long chain polymer either as a sole additive in which case it is a cationic polymer, or as a final step after the stock has been preconditioned to accept an anionic polymer. Short chain cationics, cationic starch and all anionics give soft flocculations.

The sorption and flocculation mechanism in paper stock systems in presence of poly electrolytes has been dealt lucidly by Britt and co workers in one of their recent publications.[28] Moore in examining the drainage and retention mechanisms of paper making systems treated with cationic polymers has demonstrated that bridging mechanisms can predominate over charge neutralisation effects in optimising drainage and retention with high molecular weight cationic polymers.[30]

EFFECT OF THE QUALITY OF PROCESS WATER ON THE RETENTION

The quality of the process water (as well as the ions built up in the backwater) plays an important part in the electrokinetics of the system. From his study Melzer concludes that 'even under the complicated conditions found in practice in paper mills, the action of retention aids is optimum in the range of isoelectric point'.

PRACTICAL APPLICATIONS OF ELECTROKINETICS OF THE PAPER MAKING

Electrokinetics of paper making viz Zeta potential measurements have been also shown to have practical application for increasing both the efficiency of chemical retention and physical properties of paper web on the paper machines. In the manufacture of photographic base paper at Eastman Kodak, Mckague and co workers[29] have found that the optimum electrophoeric charge was achieved through the use of an anionic dry strength resin which provided maximum retention of chemicals along with better drainage on fourdrinier wire with consequent easier drying. This improvement in performance permitted upto 25% increase in the machine speed in addition to lowering the BOD of effluent.

Anderson and Penniman[11] have shown that control of retention of drainage, physical properties and effluent waste rests upon optimising the coagulation chemistry of the wet end of the machine and this is accomplished by controlling the zeta potential at or near zero, at the isoelectric pH. An instrument called Laser Zee meter, developed by Penniman[10] was used to measure the zeta potential and thereby monitor the electro kinetics.

However, it is to be pointed out here that the use of this technique has not come yet in to wider practice.

OUR MILL EXPERIENCE

In our mill, we have found that polyacrylomides manufactured in India do not significantly increase the retention of fillers when they are used as a wet end additive. This may be attributed to the fact that these do not have either the molecular weight or the charge density needed for flocculations of the fines in the pulp from our raw materials.

However, we have used with considerable success some of the polyectrolytes for quicker setting in our settling type of Marx save—alls. An addition of about 6-8 ppm of polyacrylamine resulted in most efficient settling of fines and titanium dioxide so that save—all underflow can be recirculated again to the maximum extent. With this we have been able to go up to the retention of titanium dioxide upto 75-80%.

In this review, we have been able to present only a birds eye view picture of the loading of paper. However, the references furnished should enable the reader to go in greater depth in to this very important aspect of paper making.

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