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Prepared Contribution - Some New Research in Alum Chemistry

Alum has been used in papermaking for about 200 years. Despite the enormous amount of theoretical work done, the chemistry of alum in the papermaking process is still not adequately understood. To explain the chemistry of aluminium salts, three basic approaches have been taken by the various investigators. One is the use of classical analytical techniques to identify the ionic species formed by hydrolysis of Al-salts. Another approach uses coagulation of extremely small anionic colloids, such as silver halides. The third approach is surface-chemical, whereby the structure of the complex aluminium ions is deduced from the interaction patterns with mono-molecular rosin films. Conclusions drawn from the hydrolysis studies dominate the explanations of alum chemistry in the papermaking process. Many authors have used the Hayden-Rubin distributions (1) as a basis for deducing that the octamer structures of type $Al_8^{+4}(OH)_{20}$ or $Al_8^{+4}(OH)_{10}(SO_4)_5$ are the active species in the papermaking process (2,3).

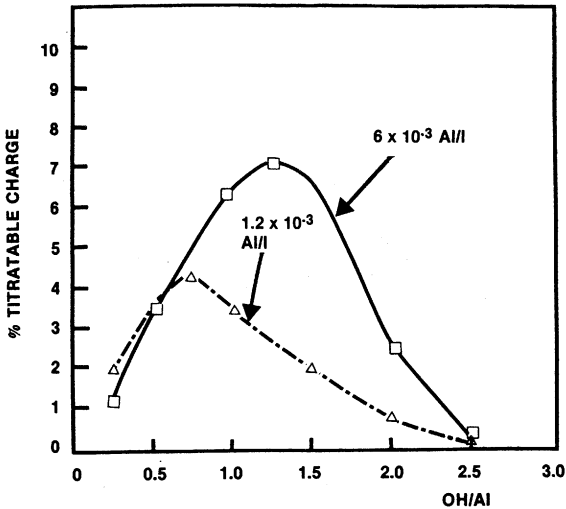


Fig 1—Titratable charge of Aluminium Sulphate as a function of the degree of neutralisation and Al - concentration

When it comes to explaining how alum acts in papermaking, the surface chemical approach is the name of the game (4). On the basis of the early work by Ekwall and co-workers (5) and by the author (4), it was deduced that the adsorbing cationic hydroxy-aluminum ions undergo lateral hydrogen bonding to form a quasi-polymeric network which brings about a profound stiffening of the mono-molecular rosin films. I will stress again that the virtue of the strong hydrogen bonding at the interface is a very crucial phenomenon in explaining the chemistry of alum in papermaking.

Since the work of Hayden-Rubin has captured the attention of many investigators, specific comments must be made in regard to the pertinence of this work in explaining the chemistry of papermaking. Several problems arise. Their distributions show simultaneous existence of about 20% Al^{+++} ion and about 20% of $Al(OH)_3$ which are hard to justify, especially due to the fact that a complex corresponding to a composition of $Al(OH)_{2.5}(SO_4)_{0.25}$ is thermodynamically preferred (6) since this composition forms over a broad range of alum neutralization (7). All the hydrolysis studies have been made in the absence of cellulose and other papermaking components, which are large anionic polyelectrolytes that are capable of interaction with the more active, smaller size hydroxy-aluminum cations, and those occur at lower degrees of Al^{+++} neutralization. Careful studies have shown that maximum effectiveness of alum in papermaking is achieved at about 30% to 50% neutralization (not at 83%, corresponding to octamer).

To explain the chemistry of alum in papermaking more concisely, we attempted to quantify the available cationic charge of alum by titrating with a polyvinylsulphate polyelectrolyte. The idea was that such interaction would adequately mimic the surface chemical interactions with the larger polyelectrolytes, such as cellulose and rosin. For illustration of the results obtained, one graph is attached. This shows the dependence of cationic charge as function of degree of neutralization for 6×10 and 1.2×10 Al/liter concentrations. If expressed as % for the trivalent charge of Al-ion, only about 8% of cationic charge can ion exchange under best conditions. This occurs

at 50% neutralization for the higher Al-concentration. If alum concentration is reduced, the cationicity of alum decreases along with a shift towards a lower degree of neutralization. This shows that hydrolysis and solubility parameters play an important role in these reactions. Other experiments have shown that if alum is allowed to form a floc, the available cationic charge decreases to about 1.8%, indicating that accessibility, rate of mixing and distribution are important parameters in getting maximum efficiency from alum under papermaking conditions. Other variables studied included the effects of stock temperature and co-ordinating anions. All results tie in with the actual performance of alum in papermaking under those conditions.

This work was reported at the 5th International Conference on Colloid Science and Surface Chemistry on 26th June, 1985 in Potsdam, N.Y., U.S.A. and will be published shortly in TAPPI.

Summary

The octamer does not appear an important species in the papermaking applications. The working species appear to be the more cationic, less neutralized hydroxy-aluminium ions which adsorb at the interfaces of large polyelectrolytes, such as cellulose or rosin, undergoing extensive hydrogen bonding, even at the expense of disproportionate hydrolysis. All this occurs via complex reactions, but the end product, that forms through ion exchange and all these other mechanisms, is a precipitate corresponding to the average composition of $\text{Al}(\text{OH})_{2.5}(\text{SO}_4)_{0.25}$.

References

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Acknowledgements

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Marton It is difficult to make a short response to a long standing controversy on alum chemistry, so all I will say is that this is a refreshing new approach. However, I would not necessarily agree that it is completely correct because the presence of these highly charged aluminium polymers have been demonstrated by using electrophoretic techniques. You are completely right in the sense that these were not materials co-flocculated with cellulosic components and fines. So, I think it is valuable to further discuss this whole area, but we should not just ignore the important contributions of Hayden, Rubin and Matijevic respectively.