Alkaline Sizing – Have We Got it Wrong?

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Many words have been written regarding alkaline sizing of paper. The learned works often launch directly into cellulose-size reactions. Starch – a carbohydrate with a similar surface chemistry to cellulose – rarely features in the considerations. Yet the contact of size with the starch may be far more intimate and extensive than the contact with cellulose. It is suggested that the reaction of the size with starch is an important and overlooked contribution to our understanding of sizing.

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Reactive Size -

Reams of technical literature have been published on emulsified synthetic sizing agents and their reaction with cellulose. The accepted reaction mechanism with cellulose is formation of an ester linkage by the anhydride group. Such a mechanism is shown in Fig. 1 for the case of alkenylsuccinic anhydride (ASA) sizing agent. Generally in the literature no role or impact, with respect to the reaction, is assigned to the emulsifying agent.

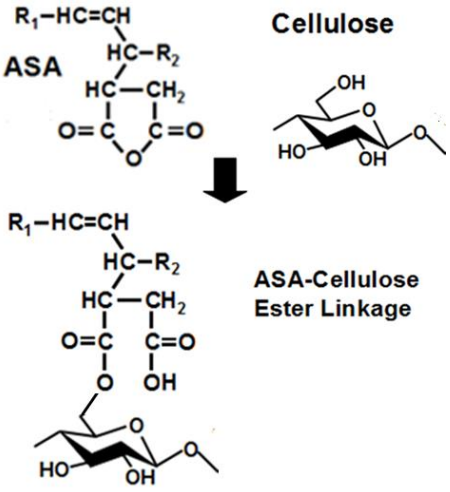

Fig. 1. Reaction scheme as commonly depicted in publications

Cellulose is a D-glucose polymer. The D-glucose monomers within cellulose are linked via β-1,4-glycosidic bonds. As shown in the Fig. 2, such bonding means that each successive D-glucose unit is "flipped" relative to its predecessor.

Starch is the most common emulsifying agent used for on-site emulsification of the sizing agents ASA and alkylketene dimer (AKD). Starch, as shown in Fig. 2, is also a D-glucose polymer. The D-glucose monomers in this case are linked via α-1,4-glycosidic bonds to form amylose.

Amylose and cellulose are isomers, both materials being 1-4 linked D-glucose polymers. They differ in the anomeric configuration, with sequential rotation of the 1,4-glycosidic bond in cellulose; they share the same surface chemistry. All the reactions postulated for sizing cellulose may also take place with starch.

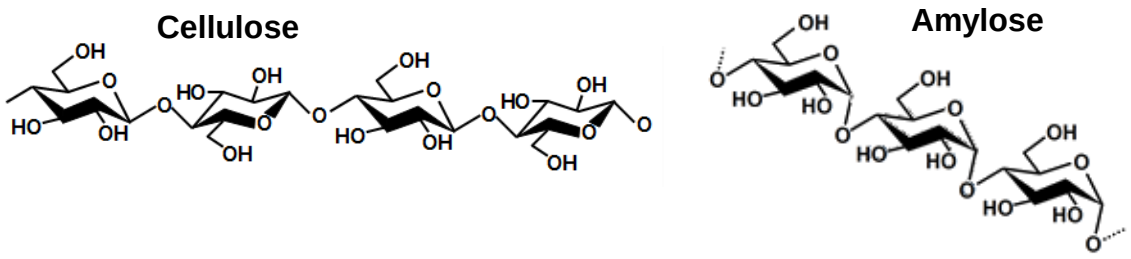

Fig. 2. Chemical structures of cellulose and amylose.

The purpose of emulsifying reactive sizing agents is threefold, firstly to produce a stable, dispersed emulsion, secondly to provide a cationic charge to the emulsion particles to ensure attraction to and retention on the furnish components, and thirdly to provide a protective barrier against hydrolysis. To do this, each emulsion droplet must be fully encapsulated.

Cationic starch is the cheapest and generally preferred on-site emulsifying agent. The recommended starch:ASA ratio is 4:1. The emulsion droplet size is 95% below 2 µm; such emulsions have a specific surface area of 6 to 7 m^2 per cm^3. This then is also the areal contact between starch and ASA.

Starch is in intimate contact with size from the moment of emulsification. The size has considerable exposure to starch hydroxyl groups before introduction to the papermaking stock. By comparison, the specific surface area of a papermaking furnish is 0.2 to 0.5 m^2 /g.

On retaining the emulsified size, it is the encapsulating starch that contacts the fibre, the sizing agent only being exposed when the emulsion capsule ruptures. The exposed size sits atop the adsorbed capsule wall; *i.e.* an intervening layer of starch exists between the fibre and the size. Additionally, the underlying fibre often has a covering of cationic starch added for strength and retention purpose. This raises the question, "Does the size ever actually contact the cellulose fibre?" Is it not the starch surface that is sized?

When neutral-sized paper is re-pulped, washed, and then reformed into handsheets, there is a low level of sizing development in the paper. If the re-pulped paper is treated with amylase to remove the starch before washing, then there is no sizing developed in the subsequent formed handsheets. In other words, the sizing is lost when the starch is removed.

Japanese publications were fairly early in suggesting that the size-cellulose reaction theory was in error. At that point the question involved whether the reaction took place at all. However, maybe the question has been somewhat misdirected all these years. Perhaps we have been looking to the wrong carbohydrate substrate for the sizing reaction.