

# Influence of Anionic Trash Catcher Pretreatment on the Effectiveness of Dry Strengthening Agent

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Cationic dry strength agents (DSAs) are commonly used for paper strengthening. However, before they are applied, another chemical called an anionic trash catcher (ATC) is often used to pretreat pulp to neutralize the negative dissolved and colloidal substances (DCS), increasing the effectiveness of the subsequently added cationic DSA. However, in many cases, the negativity of the fibers is also neutralized by the ATC. Under such circumstances, it remains unclear to what degree the effectiveness of the DSA will be affected. In this paper, a deinked pulp was first pre-treated with a polyamine ATC; then, the effectiveness of two subsequently-added DSAs, anionic polyacrylamide (APAM) and cationic polyacrylamide (CPAM), were compared. Results showed that when the ATC was used alone, it deteriorated paper formation, resulting in a decrease of paper strength. When the DSAs were used alone, the CPAM was effective but the APAM was not. However, when the ATC was used to pretreat the pulp, the effectiveness of the CPAM clearly decreased, while that of the APAM clearly increased. The reason for this could be that the adsorption of APAM onto fibers was promoted by the pretreatment of ATC, possibly through the formation of an ATC and APAM polyelectrolyte complex.

*Keywords:* Anionic trash catcher (ATC); Dry strength agent; Polyamine; Dissolved and colloidal substances (DCS); Polyelectrolyte complexes

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## INTRODUCTION

With the increasing use of secondary fibers and with whitewater recirculating systems being more tightly closed, high amounts of dissolved and colloidal substances (DCSs) are often accumulated in papermaking systems. DCSs, which in most cases are highly negative and are thus also called anionic trash, severely affect the effectiveness of many cationic chemical additives, including cationic dry strength agents (DSAs) (Gill 1996).

Many methods have been utilized by papermakers to counteract the detrimental effects of anionic trash. Using fixing agents to neutralize the anionic trash and “fix” them onto pulp fibers is a commonly used method. The fixing agents are characterized by high cationic charge density and relatively low molecular weight; some typical ones include polyamines (PAs), polyvinylamines (PVams), polydimethyldiallylammonium chlorides (PDADMACs), polyethyleneimines (PEIs), and specially-made highly cationic starches, also called starch-based fixing agents (SBFs) (Miao *et al.* 2003). Because they are

effective at “catching” the anionic trash, they are also referred to as “Anionic Trash Catchers (ATCs).”

Using ATCs to promote the effectiveness of other paper chemicals has been widely adopted. Examples demonstrated previously include the following: When a bleached chemithermomechanical pulp was pretreated with a starch-based fixing agent (SBF), the adsorptions of fluorescent whitening agent, tinting dye, wet strengthening agent, dry strengthening agent, neutral sizing agent, and retention agent onto fibers were all improved, and the improved adsorptions resulted in higher brightness, better tinting, higher wet and dry strengths, better sizing, and higher retention and drainage (Wang *et al.* 2011). For a deinked pulp used for newsprint manufacturing, a synergistic effect was found for the addition of PDADMAC (to thick stock) followed by the use of a CPAM retention agent (to the diluted stock), which resulted in extremely better microstickie’s controlling effects compared to what can be achieved by the addition of PDADMAC or CPAM alone (Wang *et al.* 2005). Polyaluminum chloride (PAC), polyamine (PA), polyamido-amine-epichlorohydrin (PAE), polyethyleneimine (PEI), and polydiallyldimethylammonium chloride (PDADMAC) were used as ATCs to control the anionic trash in an alkaline peroxide bleached mechanical pulp (APMP), and they were found to have the ability to promote the neutral sizing efficiency of AKD to different extents, with the most effective one being PEI, which could improve the sizing degree by more than 64%, and the least effective one being PAC, which could still improve sizing by more than 18% (Wang *et al.* 2010).

However, for paper strengthening with ATC pretreatment followed by the use of a dry strength agent (DSA), the situation might be more complicated (Hubbe 2006). While many detailed points related to strengthening mechanisms remain unclear, it is generally reasonable to recommend using an ATC before using a cationic dry strength agent such as cationic starch or cationic polyacrylamide. For example, a starch-based fixing agent was used to treat the anionic trash in a peroxide-bleached thermomechanical pulp and it was found that the pre-treatment increased the adsorption of a cationic starch dry strength agent onto fiber and that its strengthening effect was better (Bobacka *et al.* 1999). For an ATC, using it at its proper dosage is very important. Ideally, the ATC neutralizes all the anionic trash while the negativity of the fiber is not affected, so that the fiber can take as much of the subsequently added cationic chemicals to ensure their effectiveness. However, in most cases, the ATC would not operate so ideally, that is, it will also neutralize the negative charges of cellulosic fibers at the same time. The following question then arises: when a pulp is partly neutralized with ATC, will a subsequently added chemical, such as a DSA, still work properly? Logically, there is some conjecture that the effectiveness of the later-added cationic chemical will be negatively affected. Unfortunately, enough clear answers cannot be found for this question because in many relevant publications it is often difficult to see clearly to what extent the fibers were neutralized.

In this study, a deinked pulp was sampled from a real mill line. Analysis of its charge characteristics showed that its fiber had high negativity but its anionic trash content in the water phase was low; therefore, the pulp water phase was actually very easy to be neutralized with ATC. The partial neutralization of fiber was performed by adding a designated amount of ATC. Then, two polyacrylamide DSAs, one cationic and another anionic, were subsequently but individually added to the ATC pre-treated pulp. The differences in their effective paper strengthening are compared, and the related reasons are discussed.

## EXPERIMENTAL

### Materials

The pulp used in this study was a deinked pulp (DIP) taken from the stock chest for making the bottom layer of white manila board in a mill belonging to the Zhejiang Yontai Paper Manufacturing Co. Ltd. The pulp consistency was 2.1%, the beating degree was 62.5°SR, the conductivity was 473  $\mu\text{s}/\text{cm}$ , and the pH was 6.9.

The ATC used in this study was a polyamine (PA) in liquid form prepared by Linyi Obei Chemistry Co. Ltd. Its solid content was 52.5%, the intrinsic viscosity was 17.33 mL/g, measured with a 4-0.55/16 Ubbelohde viscometer in a 30 °C water bath, with the PA being dissolved in a 1M NaCl solution, and the charge density was 6.176 meq/g, measured with a charge analysis system (CAS) by AFG Analytic GMBH, Germany, using polyethylene sodium sulfonate (PES-Na) as standard titrant.

The two polyacrylamide DSAs, were supplied by Hangzhou Hanghua Harima Chemical Co., Ltd. Polyelectrolyte titration with PDADMAC (polydiallyl dimethyl ammonium chloride) or PES-Na at pH 7 showed one had positive charge density of 0.420 meq/g and another had anionic charge density of -0.016 meq/g. However, they were actually amphoteric in nature, as shown in Fig. 1, where the streaming current device output (mV) and pH of the polymer solutions were recorded with the CAS instrument with 0.01 M HCl being continuously titrated into the measuring cell. In most cases, the DSA1 was anionic, because its positive charge appeared only when the pH was lower than 4. On the contrary, the DSA2 was cationic in most cases because its anionic charge only appeared when the pH was greater than 7.6. Considering that the pH value for papermaking generally ranges from 5.0 to 7.5, the DSA1 and DSA2 were simply noted as APAM and CPAM, respectively, in the following discussion.

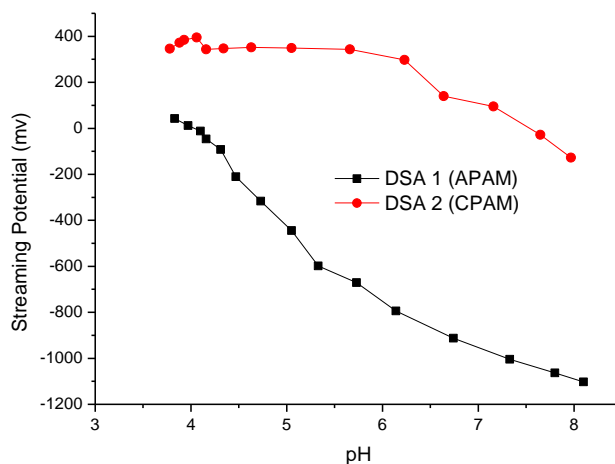


Fig. 1. Charge characteristics of two dry strength agents under different pH conditions

### Methods

#### *Measurement of the anionic trash content and streaming potential of DIP*

To determine the content of anionic trash in the DIP, a set volume of DIP was filtered through a 200-mesh stainless wire. The filtrate was then filtered again through a 1.0- $\mu\text{m}$  Whatman GF/C microfiltration membrane. Micro-filtrate (10 mL) was put into the measuring cell of the CAS (AFG Analytic GMBH) mentioned above, titrated with a

0.001 N PDADMAC standard cationic solution to iso-electric endpoint, and the content of anionic trash was calculated (Scott 1996). Based on this, the dosage of ATC required for neutralizing all the negative charge of anionic trash in DIP was calculated.

Streaming potentials of the DIP, before and after being treated with different volumes of the ATC solutions, were measured with a Fiber Potential Analyzer by AFG Analytic GMBH. The main procedure was as follows: firstly, 200 mL of DIP (2.1% pulp consistency) was subjected to  $\zeta$ -potential measurement. Then, a portion of ATC solution, equivalent to a dosage of 0.12% calculated as a percentage of dry ATC to that of dried pulp (hereafter denoted as 0.12% d/d), was added to the pulp suspension, which was agitated for 45 s before measuring the  $\zeta$ -potential. The procedure was continuously repeated with other portions of ATC at the same 0.12% d/d dosage intervals until the  $\zeta$ -potential of the fiber changed from negative to positive. The amount of ATC required to neutralize the whole pulp could thus be estimated.

#### *Handsheet preparation and mechanical property measurement*

For handsheet formation, TAPPI Standard T 205 sp-02 was referenced. First, a pre-determined volume of DIP was taken and a certain amount of ATC solution was added. The mixture was stirred for 45 s, and then a predetermined volume of DSA solution was added. The new mixture was stirred for another 45 s and finally diluted to be 0.3% consistency for the production of handsheets. The handsheet properties, including basis weight, brightness, and tensile and bursting indices, were tested according to TAPPI Standards T 205 sp-02, T 525 om-02, T 494 om-01, and T 403 om-02, respectively. The formation indices of the handsheets were measured with a LPA07 formation tester made by OPTTEST Co., Ltd, Canada.

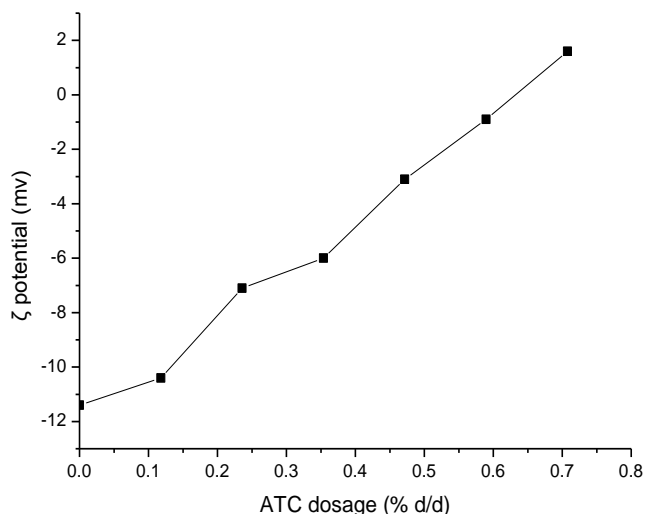
## RESULTS AND DISCUSSION

### **Effect of ATC Dosage on the Electrokinetic Characteristics of DIP**

Anionic trash content and fiber streaming potential are the two main parameters to generalize the electrokinetic characteristics of a pulp. As described in the experimental section, in this study, the DIP was filtered through a 200-mesh wire and a 1.0- $\mu\text{m}$  GF/C microfiltration membrane, during which fibers and fines in the pulp suspension were removed and the dissolved and colloidal substances were left in the microfiltrate; these could thus be considered “real” anionic trash. With the CAS instrument, the cationic demand of the microfiltrate, *i.e.*, the anionic trash content, was determined to be 0.052 meq/L. As the cationic charge density of the PA fixative was already known to be 6.17 meq/g, the theoretical dosage of ATC required to neutralize all the anionic trash in the filtrate was 8.43 mg/L. Because the pulp consistency was 2.1%, *i.e.*, around 21 g/L, the dosage of PA required to neutralize all the anionic trash in the pulp water phase was calculated to be 0.040% d/d.

However, the dosage calculated above is only an ideal one. In fact, when a portion of ATC is added to a pulp suspension, a part of it will react with the anionic trash in the water phase, and the other part will be adsorbed onto the fibers, increasing the fiber zeta potential. Figure 2 illustrates the change in the fiber  $\zeta$ -potential as the pulp was treated with ATC. Clearly, it was seen that the  $\zeta$ -potentials increased as the dosage of ATC increased. Surprisingly, the amount of ATC required to completely neutralize the pulp (contributed by fibers as well as anionic trash) was as high as 0.63% d/d, 15.75 times

larger than that required to neutralize all the anionic trash, which was only 0.04% d/d, as stated above.



**Fig. 2.** Change in fiber  $\zeta$ -potential with the ATC dosage

Therefore, for this DIP, the fiber was highly negative but the water phase was not, *i.e.*, its anionic trash content was low. In the following, the ATC dosages were set at 0.15% d/d and 0.30% d/d. Under these conditions, the anionic trash in the pulp water phase barely survived, but the fibers remained negative, so that cationic DSA could still be adsorbed to a certain degree.

### Effect of a Single ATC Treatment on Paper Properties

ATC is a polyelectrolyte with a high cationic charge density and low molecular weight. The main purpose of using ATC is to eliminate the interference of anionic trash present in the wet-end of papermaking systems. The anionic trash, after being fixed onto fibers and finally “dispersed” in the paper webs, will inevitably affect paper strength. For instance, it has been reported that due to the hydrophobicity of anionic trash, inter-fiber bonding can be impaired, and thus fixation incurs a detrimental effect on paper strength (Tay 2001; Francis and Ouchi 2001; Rundlöf 2002; Zhang 2000). Another factor that leads to the same result is that fixing agents, having the ability to agglomerate fines and fibers, may negatively affect paper formation, thus adversely affecting paper strength (Nazhad *et al.* 2000).

Exceptions reported include the fact that polysaccharide-based anionic trash may contribute to the increase of paper strengths, if they are well fixed, for example, by starch-based fixing agents (Vihervaara 1994; Luo and Wang 2010), and that some of the DCS components present in recycled pulp may improve the paper strength through sheet drying, much like the addition of cationic latex to the wet-end of a paper machine (Alince 1999; Wang *et al.* 2006).

No matter what is happening inherently, in this study, it was first necessary to clarify the effect of a single ATC treatment on paper properties. The results are shown in Table 1.

**Table 1.** Effect of a Single ATC Treatment on Paper Properties

ATC (%odp)	Basis Weight, (g/m <sup>2</sup> )	Thickness, (μm)	Formation Index	Brightness (%ISO)	Tensile index, (N·m/g)	Bursting index, (kPa·m <sup>2</sup> /g)
0	57.32±0.44	152.9±3.3	29.5±1.6	40.08±0.58	26.35±1.02	1.84±0.08
0.15	61.40±1.56	156.1±5.2	24.0±1.0	37.73±0.36	24.35±1.42	1.60±0.05
0.30	62.04±1.32	158.9±4.1	18.0±1.0	36.58±0.10	23.52±1.29	1.64±0.07

The basis weight and thickness of the handsheets increased with increasing ATC dosage, providing a strong indication that ATC itself has a good retention effect for paper stock. It is also clear that paper formation was worsened by ATC treatment, supporting the idea that the ATC had an agglomerating effect that improved retention but deteriorated formation. Furthermore, brightness was also decreased by ATC treatment, indicating that the ATC retained a significant amount of fines as well as DCS components, as the small components in deinked pulp were darker than fibers (Zhang *et al.* 1999; Hubbe *et al.* 2012). Finally, regarding paper strength, it was also seen that a higher ATC dosage corresponded to lower strengths. These results indicated that a single treatment with ATC resulted in a loss of paper strength because its agglomeration deteriorated paper formation (Nazhad *et al.* 2000) and the successful fixation of DCSs impaired inter-fiber bonding (Tay 2001; Francis and Ouchi 2001; Rundlöf 2002; Zhang 2000).

### Effect of a Single DSA Treatment on Paper Properties

Similarly, the effects of a single DSA treatment on paper properties were investigated, and the results are shown in Table 2. It can be seen that while the APAM DSA had no significant effect on the basis weight and thickness, the CPAM did, indicating that the retention effect of CPAM was prominent. The strengthening effect of the CPAM DSA was significant despite the fact that it deteriorated paper formation and brightness (lower brightness means more retention of fines and DCS components). On the other hand, the strengthening effect of APAM DSA was null. This phenomenon is actually reasonable, as the CPAM DSA surely can be better adsorbed by the pulp fibers, which contributes to better strengthening.

One unexpected result was that the APAM DSA also decreased paper formation and brightness, indicating that an anionic polymer can also agglomerate fibers and fines to some degree, possibly due to the functioning of inter-molecular forces such as Van der Waals' forces between the polymer and fiber cellulose (Scott 1999; Hubbe 2006).

**Table 2.** Effect of a Single DSA Treatment on Paper Properties

DSA	Basis Weight, (g/m <sup>2</sup> )	Thickness, (μm)	Formation Index	Brightness (%ISO)	Tensile index, (N·m/g)	Bursting index, (kPa·m <sup>2</sup> /g)
None	57.32±0.44	152.9±3.3	29.5±1.6	40.08±0.58	26.35±1.02	1.84±0.08
APAM	58.41±0.78	150.0±3.2	25.7±2.2	38.38±0.33	26.03±4.93	1.80±0.17
CPAM	60.55±1.20	154.0±4.6	24.5±0.7	36.65±0.17	28.93±2.33	1.90±0.05

Note: the dosage of the DSAs was 0.2% d/d

### Effect of ATC Pretreatment Followed by DSA Dosing on Paper Properties

The effects of dual treatment, *i.e.*, ATC pretreatment followed by DSA dosing, are shown in Table 3. Compared to the situations when the DSAs were used singly, where the effect of the CPAM DSA was clearly better than that of the APAM, the dual treatments showed that the APAM DSA was more effective than the CPAM DSA. For the APAM DSA, the pretreatments by the anionic trash catcher contributed by increasing the basis weight and thickness, indicating that retention and fixation were better. Despite the fact that paper formation uniformity and brightness were decreased, tensile and bursting strengths were apparently increased. However, for the CPAM DSA, the ATC pretreatment had no significant influence on the basis weight and thickness, indicating the failure of retention and fixation. Decreases in strength for “ATC + CPAM DSA” treatments were apparent and were larger with increasing dosage of ATC. The “ATC + CPAM DSA” treatment also decreased paper formation and brightness; however, it is thought that this cannot be the main reason for strength loss, as the two sets of dual treatments, “ATC + APAM DSA” and “ATC + CPAM DSA,” had similar results on formation and brightness. Instead, the primary reason for the different paper strengthening results is that ATC pretreatment promoted the adsorption of anionic DSA but impeded the adsorption of cationic DSA onto paper fibers, possibly due to the effective formation of a polyelectrolyte complex between the ATC and the APAM DSA. The formation of polyelectrolyte complexes (PDADMAC/carboxymethyl cellulose complexes) and their deposition onto fiber surface resulting in higher paper strengths have been well elucidated in several works (Hubbe *et al.* 2003; Lofton *et al.* 2005; Hubbe *et al.* 2005; Hubbe 2006). However, in these studies, more attention was paid to the situation where the dosages of the first added cationic polymer PDADMAC were exceeding the adsorption capacity of the fibers. While these fundamental works are undoubtedly interesting, we suggest that research should also focus on those dosages below the fiber adsorption saturation point, since lower dosages are more economically realizable. Moreover, the dosage of PADMAC at 0.5 multiples of fiber saturation point also showed significant breaking length improvement (Lofton *et al.* 2005), much like the phenomenon we found in this study where the dosages of polyamine were apparently far below the saturation point or the fiber charge reversal point. Our future research will look at whether polyelectrolyte complexes are formed in the fiber suspension when the first cationic polymer is used at relatively low dosages.

**Table 3.** Effect of ATC Pretreatment Followed by DSA Dosing on Paper Properties

ATC (%odp)	DSAs	Basis Weight, (g/m <sup>2</sup> )	Thickness, (μm)	Formation Index	Brightness (%ISO)	Tensile index, (N·m/g)	Bursting index, (kPa·m <sup>2</sup> /g)
0	APAM	58.41±0.78	150.0±3.2	25.7±2.2	38.38±0.33	26.03±4.93	1.80±0.17
0.15		62.20±1.09	154.3±4.3	25.0±1.4	36.30±0.18	27.82±1.27	1.90±0.08
0.30		62.46±1.71	157.9±5.2	19.5±0.7	35.88±0.35	27.79±2.69	1.87±0.15
0	CPAM	60.55±1.20	154.0±4.6	24.5±0.7	36.65±0.17	28.93±2.33	1.90±0.05
0.15		59.74±1.19	154.0±4.4	21.5±0.7	36.00±0.18	27.72±3.66	1.59±0.09
0.30		59.47±1.97	155.9±4.4	19.5±0.7	35.65±0.25	25.80±3.78	1.79±0.08

Note: the dosage of the DSAs was 0.2% d/d following the ATC treatment.

The strengthening effect of a single CPAM DSA treatment (0.2% d/d) was better than the “ATC + APAM DSA” (ATC 0.15 or 0.30% d/d + APAM 0.2% d/d) treatment; however, it can be seen that the retention effect of the latter was better than the former (inferred from the higher basis weight). This means that through proper optimization work, the “ATC + APAM” dual treatment can be more suitable. Therefore, in cases where ATC is used to pre-treat the pulp, either for controlling anionic trash content or for purposes such as higher retention, the use of an anionic DSA may be better than a cationic one. A related study using pulp with a much higher anionic trash content is being carried out; similar results have been found and will be reported later.

## CONCLUSIONS

1. A single treatment of an anionic trash catcher (ATC) on deinked pulp improves retention and fixation but deteriorates paper formation, lowering paper strength.
2. The strengthening effect of a cationic dry strengthening agent is superior to that of an anionic one when they are used alone, simply because the former can be better adsorbed onto fibers than the latter.
3. The partial neutralization of fibers by ATC during the pretreatment of pulp adversely affects the adsorption of cationic dry strength agent, and the effectiveness of the dry strength agent is therefore greatly impeded. On the contrary, the adsorption of anionic dry strength agent can be improved, possibly by the “on-site” formation of ATC-APAM polyelectrolyte complex, and the strengthening effect of the anionic dry strength agent can thus be improved.

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