An Experience of Alkaline Sizing with AKD

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ABSTRACT

In the early 1800's, the water resistance was imparted to many papers by Alum-Rosin Sizing. The 1980's saw the break through of NeutralAlkaline Papermaking. The primary reason in changing from Acid (pH usually 4-5.5) to Neutral-Alkaline (pH 6.5-8.5) Papermaking was to use of Calcium carbonate to achieve the benefits of improved Paper permanency, optical and finishing properties. A conversion to Alkaline paper making with AKD or ASA size offer the Paper Maker an opportunity for improving the Product quality, system cleanliness and retention. The present paper highlights the effects of AKD (Alkaline) sizing vis-à-vis Alum-Rosin (Acidic) sizing. Based on lab trial, Process trial was conducted in wheat straw based furnish with 16 Kg/t of AKD, 400 gm/t of Coagulant and 220 gm/t of Retention aid which were optimized to 14 Kg/t, 350 gm/t and 180 gm/t in 60 GSM Ivory White segment respectively. It has been highlighted in process trial that AKD sizing has many advantages over Alum-Rosin sizing like improved cleanliness of system, helped in keeping clothing clean, 15.5% and 36.4% increase in FPR and FPAR respectively, improved drainage, approx 1.8 % increase in dryness after press, 50% reduction in defoamer consumption, improved opacity by 1.8 %, considerable increase in Bulk and marginal increase in Breaking length. It was also experienced that residual Chlorine in pulp has detrimental effect on optical properties due to increase in Cationic demand which in turn resulted in higher consumption of Coagulant, AKD & Retention aid in order to maintain the Cobb with in the desired limit.

INTRODUCTION

Paper making fibers have a strong tendency to interact with water due to hydrophilic nature of cellulose fiber. This property is important to the development of strong inter fiber hydrogen bonds during paper making and is also the reason that paper loses its strength when saturated with water. This behavior is an advantage for certain adsorbent grades such as toweling and tissue, but such type of behavior are not common for most paper grades like offset printing paper; writing paper, cereal boxes etc where some liquid penetration resistance is required. The process that impart resistance to water penetration in paper are called sizing processes. The purpose is to modify the surface of fiber to control the penetration of aqueous liquids in to the paper.

In the early 1800's, this water resistance was imparted to many papers by Alum-Rosin sizing. The 1980's saw the break through of NeutralAlkaline papermaking. The most common synthetic sizing agents are Alkyl Ketene Dimer (AKD), introduced in 1956 and Alkenyl Succinic Anhydride (ASA), introduced in 1974 (2). The primary reason in changing from acid (pH usually 4-5.5) to neutral-alkaline (pH 6.5-8.5) paper making was to use of calcium carbonate to achieve the benefits of improved permanency, higher levels of sizing, increased dry strength, improved tear strength, reduce energy usage, allows more extensive reuse of white water, reduced corrosion, easier effluent treatment and increased production (3).

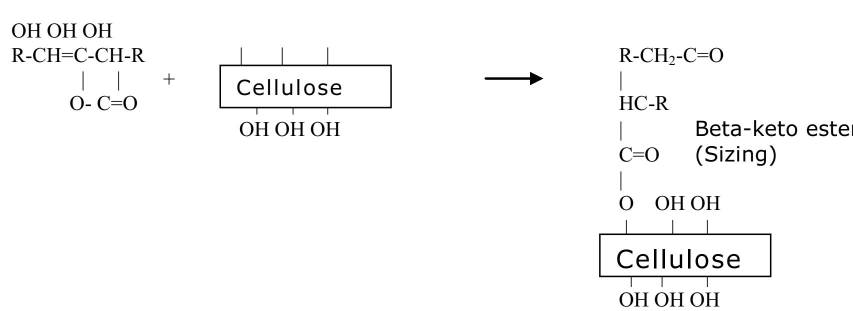
Any sizing agent must be (4):

- ✓ Hydrophobic
- ✓ Retained on fiber
- ✓ Distributed
- ✓ Anchored

The difference between conventional rosin sizes and alkaline sizes is in the way these four requirements are met. Rosin size functions by reacting with alum to form the size precipitate and the attachment of rosin ppt. to fiber by electrostatic attraction, which is the primary mechanism for rosin sizing. The retention, distribution and anchoring functions of rosin-alum are completed in the wet end of the machine.

Cellulose reactive alkaline sizes such as AKD meet the requirements of sizing agent by a more circuitous route, AKD anchors with cellulose by the covalent Beta-keto ester bond (2) as show below.

It is the strong link in this mechanistic chain. But, in order to form this bond these nonionic hydrophobic organic compounds, which are not soluble in water, must be compatible with the aqueous paper making system. This is done by emulsifying them using dispersants and stabilizers as necessary. Generally, the supplier provides readymade AKD emulsion whereas ASA is prepared at the mill site owing to having high reactivity towards hydrolysis. Utilization of cationic stabilizers gives the emulsified particles a net positive charge, which provides a retention mechanism similar to that of the rosin size precipitate. However, the attractive forces usually are weaker because the emulsion particles are relatively large (0.2-1



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micrometer) as compared to rosin size ppt. (0.1 micrometer). Once the particle is retained on the cellulosic fiber surface, it must be distributed (4). This occurs only during the wet pressing and drying operations on the paper machine. Unlike the rosin size precipitate which achieves distribution by formation of the proper dimension precipitate in the wet end, the cellulose reactive sizes spread over the fiber down to molecular dimension prior reaction with cellulose. This very effective monomolecular coverage is one reason for the high efficiency of cellulose reactive sizes. Finally, after retention and distribution, the reaction with cellulose occurs and the sizing is obtained.

So, sizing completes in four steps

- Rapid mixing of size with stock.
- Attachment to fiber
- Retention in sheet by controlling over all first pass retention.
- Curing (Reaction of size with cellulose after melting)

Systematic development of sizing has been shown in fig-1. Out of four steps, Retention plays a very important role in Alkaline Sizing. Generally, The preferred feedpoint of Retention Aid is either just before or just after the pressure screen. After feeding will give best retention i.e good sizing with minimum AKD but if improved formation is a goal, feed before the screen will give the best formation at a cost of reduced retention (5). Poor retention allows free size, which is subject to hydrolysis and can lead to machine deposits severely affecting the machine runability (6). Cationic AKD and highly anionic additives such as fluorescent dyes do not perform well when added together in the wet-end (7). So, AKD have been assumed to impart sizing by reacting with cellulose to give ester product. These reactions orient the size in the fibers so that hydrophobicity i.e Sizing is imparted (8). The covalent ester bond is very strong and is extremely resistant to hydrolysis. The formation of covalent size cellulose bonds is generally accepted as the mechanism of imparting sizing. AKD is considerably less reactive than ASA size. So, AKD hydrolysis occurs only to limited extent in the paper machine wet end, but on the other hand, it is difficult to achieve high onmachine sizing and substantial curing must be needed off machine.

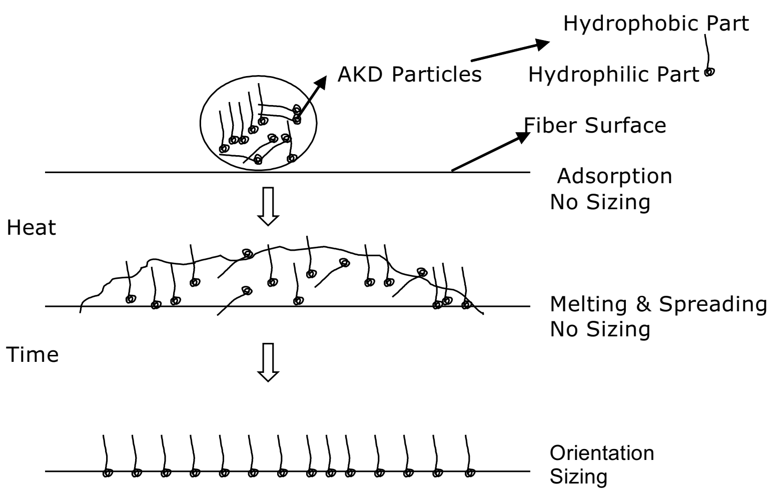

Fig-1: Schematic illustration of the mechanism of Sizing.

Table-1 AKD Dose vs $Cobb_{60}$

AKD Dose, kg/t as such	Cobb60 , gm/m2
14	24.3
16	23.2
18	22.1
20	20.3
22	19.5

By keeping in view the advantages of alkaline sizing with AKD, ABIL has decided to change over from acid to alkaline sizing with AKD in July-07.

About the Mill

M/s Abhishek Industries Ltd., (ABIL) is an integrated pulp and paper mill situated at Dhaula, District Barnala, Punjab. It is a part of Trident group of companies. The mill produces Eco-friendly paper varieties using wheat straw, an agro based residue.

The paper division of ABIL was established at Dhaula, Punjab in the year 1993 with an installed capacity of Paper 75 tpd. After 1993, Division upgraded its paper mill to expand the capacity towards continuous growth & development and commissioned Soda Recovery Plant with an installed capacity of 165 tpd of black liquor solids in the year 1998. Presently the mill produces 110 tpd of Printing and Writing paper grades utilizing the Continuous digester pulp of uniform quality. Division is going for massive expansion to increases its total capacity to 375 tpd with state of art latest Eco-friendly technologies. Expansion plan includes, New Environment friendly Fibre line supplied by the world leader Metso Sundsval AB., Sweden, with an ECF bleaching sequence of $OD_1E(OP)D_2$ to get bleached Wheat Straw pulp Brightness of 88+%ISO, Installation of New Paper Machine of 265-tpd capacity, Two stage Causticization Plant of TAA about 100 tpd with Lime-mud reburning kiln of capacity 140 tpd, Power Plant of 40 MWH capacity & Conversion of current agro pulping line into hard wood pulping with capacity 90 tpd.

EXPERIMENTAL APPROACH

Laboratory studies were conducted by taking 100% plant washed bleached Wheat straw pulp with different doses of AKD for target $Cobb_{60}$ 22-23 gm/m2. The dose of AKD was varied from 14 Kg/T to 22 Kg/T along with wet end chemicals that are used in process and 350 gm/t of ATC and 200 gm/t of retention aid. The pH was kept around 7.5 to 7.7 before addition of AKD. Dryed 60 GSM hand sheet were cured for 10 min. in oven at 105^{o}C and thereafter $Cobb_{60}$ was measured as per standard method. Results are given in table-1.

PROCESS TRIAL

Based on laboratory findings, process scale trial was planned with 16 KG/T of AKD by keeping in target Cobb 22-23 gm/m2 in Ivory white. Table-2 explains the Chemical preparation and point of addition of AKD, Coagulant and Retention aid.

AKD was initially added in thick stock i.e inlet to primary centricleaner pump, coagulant in machine chest and retention aid in inlet to primary pressure screen. The main reason of adding retention in inlet to primary pressure screen is to avoid severe turbulence of fan pump.

After one day, it was observed that AKD and OBA consumption have been increased. For controlling the same, dosing point of AKD and coagulant were changed. AKD has been shifted to thin stock i.e primary centricleaner accept line. It gave two advantages, one is uniform distribution of AKD with cellulosic fibers and other is saving of AKD, which was being wasted with centricleaner rejects. Coagulant or fixative additive was shifted in CLB drop leg, which is going to primary centricleaner pump. The main purpose of adding coagulant in CLB drop leg was to give sufficient time to OBA with pulp, because it has been observed that cationic polymer quench the effect of OBA.

Doses of AKD was controlled by on-machine 10 Min. oven curing Cobb. The target of on machine Cobb of paper was 26-27 gm/m2 for all varieties. This was optimized by 24 hr natural Cobb of paper.

Coagulant was controlled as per the cationic demand of tower straw pulp and head box slurry. Head box cationic demand was tried to maintain in the range of 20-35 meq/lit. Alkalinity of backwater was controlled by addition of alum in machine chest and kept around 300-325 ppm as CaCo3. The best performance from AKD is achieved in systems containing moderate levels of alkalinity (150-250 ppm as $CaCo_3$). Alkalinity helps in improving the reactivity because the fiber swells to produce an additional & more reactive surface. High alkalinity (in excess of 400 ppm) should be avoided. It is most often due to high concentration of hydroxide ions favoring the hydrolysis of AKD, and can also cause reversion of sizing (= loss of size response with time after the paper has been made). The loss of sizing can be the result of hydrolysis of unreacted AKD into Ketone.

As retention of AKD plays a very important role in order to control the system deposits and hydrolysis of AKD, First pass retention (FPR) was controlled in the range of 73 to 75% by optimizing the dose of retention aid.

The performance of wet-end was monitored by Alkalinity & pH of back water, cationic demand before & after addition of coagulant, first pass retention & first pass ash retention and head box ^{o}SR. Wet-end and Dry-end parameters have been compared between Acidic and AKD sizing in table-3 and table-4 respectively.

Table-2 Chemical Preparation and dosing points

Chemicals	Preparation	Point of Addition
OBA	Added as such	Mixing Chest
Alum	Prepared by Aluminium hydrate and sulphuric acid of 600 gpl that contains 7.0% Alumina.	Machine Back Water
Coagulant	Received in viscous liquid form. Diluted to 250 gpl	CLB drop leg
AKD	Added as such	PCC accept line
Retention Aid	Received in granular powder form. 1 gpl solution is prepared by homogeneous mixing of granular powder with water by automatic preparation system.	Pressure screen inlet

Table-3 Wet-end Parameter (Ivory White, 60 gsm)

Wet-end Parameters	Unit	Acid Sizing	AKD Sizing
Back water pH	-	4.3	7.8
Back water Alkalinity	ppm as CaCo3	-	346
Head box Cy.	%	0.96	0.82
Backwater Cy.	%	0.36	0.24
Backwater ash	%	65.0	59.0
FPR	%	62.5	72.2
FPAR	%	33.0	45.0
Head box freeness	^{O}SR	49	46

Table-4 Dry-end Parameter

Parameters	Unit	Acid Sizing	AKD Sizing
Steam Consumption	t/t of paper	2.7	2.5
Dryness after Press	%	40.2	42

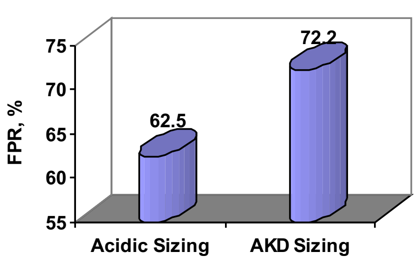

Fig.2: FPR in Acidic vs AKD Sizing

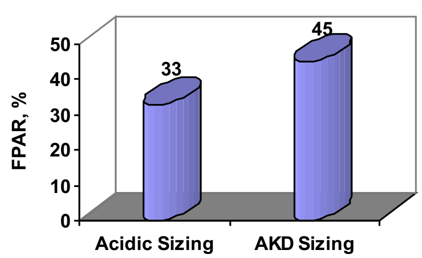

Fig.3: FPAR in Acidic vs AKD Sizing

RESULTS AND DISCUSSION

Wet-end Performance

Table no.3 differentiate the Wet-end parameters in Acidic & AKD sizing for Ivory White 60 gsm. If we compare Wet-end parameter, as illustrated in fig-2-5, with respect to Acidic sizing, we find that the Head box & Backwater consistency are reduced by 15% & 33% respectively, FPR & FPAR are increased by 15.5% & 36.4% respectively, Head box ^{o}SR is decreased from 49 to 46 i.e drainability of stock improved significantly. Good drainability of stock has contributed in

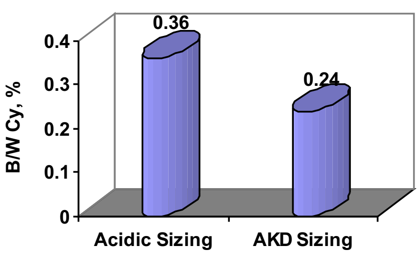

Fig.4: B/W Cy in Acidic vs AKD Sizing

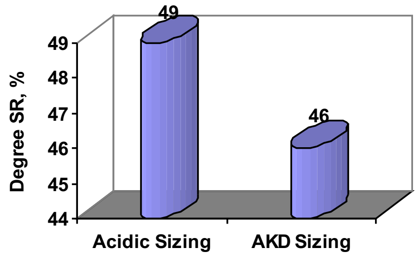

Fig.5: Degree SR in Acidic vs AKD Sizing

Table-5 Paper Properties (IVORY WHITE 60 GSM)

Properties	Unit	Acid Sizing	AKD Sizing
GSM	g/m2	60	60
Bulk	cm^3/g	1.20	1.22
Tear factor MD		37.6	37.5
CD		41.2	41.0
Breaking Length MD	meter	4050	4200
CD		2100	2200
Cobb60 TS	g/m2	23.4	23.2
WS		25.6	26.5
24 Hrs $Cobb_{60}$ TS	g/m2	_	21.4
WS			24.2
48 Hrs $Cobb_{60}$ TS	g/m2	_	20.8
WS			22.6
ISO Brightness	%	85.1	85.2
Whiteness	%	131.4	133.4
Opacity	%	88	89.8

Table-6 Effect of Acidic & AKD Sizing, Coagulant dose and Residual Chlorine on Paper B'ness

Particular	Acid Sizing	AKD Sizing				
Residual Chlorine	Nil	Nil	Nil	Nil	Nil	3 ppm
OBA	6 kg/t	6 kg/t	6 kg/t	6 kg/t	6 kg/t	6 kg/t
Fortified Rosin	20 kg/t			0		
Coagulant	0	200 g/t	200 g/t	400 g/t	200 g/t	200 g/t
AKD	0	14 kg/t	18 kg/t	18 kg/t	22 kg/t	18 kg/t
Retention Aid	200 g/t	200 g/t	200 g/t	200 g/t	200 g/t	200 g/t
pH	4.4	7.5	7.5	7.5	7.5	7.5
Alkalinity	-	375	375	375	375	375
Brightness	84.2	85.2	84.6	84.3	83.7	82.4
Whiteness	110.5	115.4	113.2	112.8	110.2	104.5
Fluoresence	7.11	7.65	7.45	7.42	7.1	6.6
$Cobb_{60}$	22.7	22	20.5	19.5	19	24.5

Table-7 Effect of OBA type on Paper Brightness

Particular	Unit	Tetra Sulpho	Di Sulpho
Brightness	%	83	83.5
Whiteness		107.8	111.9
Fluoresence		6.92	7.38

increasing the dryness from 40.2% to 42%, which has resulted in decreasing the steam consumption. It has reduced to 2.5 t/t from 2.7 t/t of paper. Positive impact of Wet-end parameter is due to the good performance of Retention aid programme in AKD sizing. Defoamer consumption in wet end is also reduced by 50%. It has been seen physically that AKD sizing helps in maintaining the cleanliness of clothing a longer time than acidic sizing.

Backwater alkalinity was varied from 325 to 360 with an average value 346 ppm as $CaCo_3$. We have not observed any fugitive sizing owing to higher alkalinity. Alkalinity was controlled by alum, however it could not be reduced to the level of 250 ppm. Higher alkalinity in stock is due to high alkalinity of straw pulp.

Paper Properties

Table-5 compares the paper characteristics of IVORY WHITE 60 gsm manufactured under acidic sizing and AKD sizing.

Although, there is no significant increase in brightness at constant dose of OBA but there is significant increase in Opacity and Bulk i.e from 88 to 89.8 % and 1.20 to 1.22 cm^3/g respectively. No improvement in Tear factor observed, while slightly increase in Breaking length noticed.

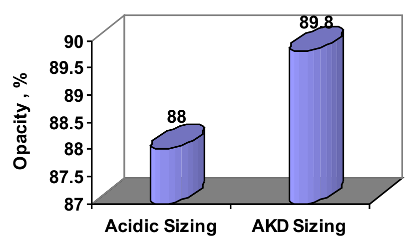

Fig.6: Opacity of Ivory White 60 gsm in Acidic vs AKD Sizing

Input Chemical Consumption

Input chemical consumption for achieving the paper properties are more or less same in AKD sizing as compared to Acidic sizing except low consumption of filler to maintain the % Ash in paper and higher consumption of OBA approx. 2 kg/t to maintain the brightness as per specification. In order to study the cause of higher consumption of OBA, laboratory experiments were carried out to study the effect of Acidic & AKD sizing, fixative dose and Residual chlorine in

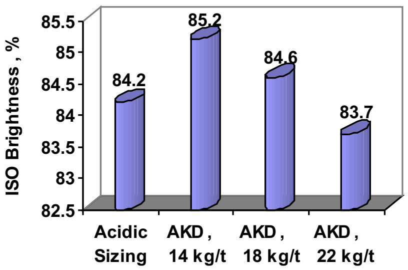

Fig.7: Effect of Acidic and AKD Sizing on Brighntess.

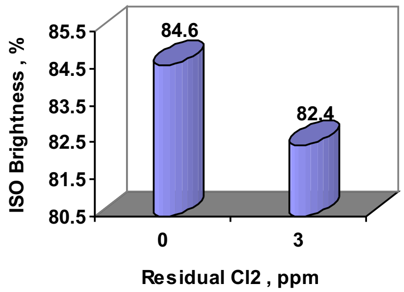

Fig.8: Effect of Residual Cl_2 on B'ness

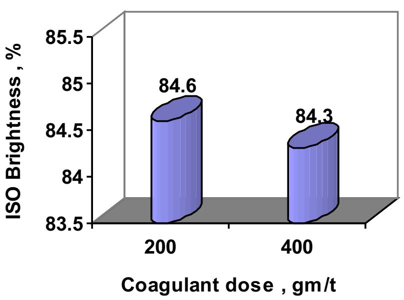

Fig.9: Effect of Coagulant on B'ness

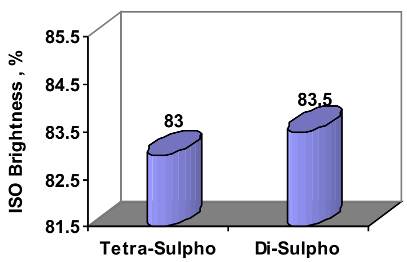

Fig.10: Effect of OBA type on B'ness

pulp on paper brightness. Experimental conditions and results are depicted in table-6.

Straw pulp was taken from H.D tower and diluted with M/C backwater to maintain the same process alkalinity. One experiment was also carried out with Disulpho & Tetrasulpho OBA. Results are given in table-7.

If we compare the % ISO Brightness between Acidic & AKD sizing as shown in fig-7, we find that brightness increases by 1% in AKD sizing for the approx. same Cobb i.e from 84.2% to 85.2%. However, brightness decreases by 0.9% on increasing the AKD from 18 kg/t to 22 kg/t and in this case brightness is lower than that of acidic sizing i.e 83.7% against 84.2%. So, to maintain the same brightness, we will have to increase the dose of OBA. This may be the reason of higher consumption of OBA.

The Cationic demand during process trial was varied from 60 to 250 meq/lit owing to residual chlorine in pulp. High variation disturbed the performance of AKD and in turn higher consumption of AKD. Effect of residual chlorine in pulp studied in lab. Results are given in table-6. If we compare the brightness at nil and 3 ppm residual chlorine at 18 Kg/t AKD & 6 Kg/T OBA, we find that approx. 2 % brightness is dropped and Cobb is increased from 20.5 to 24.5 g/m^2. This is quite evident that not only it has consumed AKD but also it has quenched the performance of OBA. So, we had to increase the dose of AKD as well as OBA to achieve the desired Cobb and Brightness.

Fig-9 reveals that brightness decreases by 0.3% by increasing the dose of Coagulant, while Fig-10 indicates the fact that Disulpho gives good performance in alkaline medium as compared to Tetra-Sulpho at same dose. Brightness and Whiteness increases by 0.5 % and 4% respectively by using Di-sulpho instead of Tetra-Sulpho in AKD sizing.

Based on these findings, we concluded that higher AKD & Coagulant consumption due to residual chlorine in pulp impacted the brightness of paper. After controlling the nil residual chlorine in pulp, we could get less OBA consumption 0.5 to 1 kg/t for the specified brightness and less AKD consumption 1 to 1.5 kg/t for the desired Cobb.

CONCLUSION

A conversion to alkaline sizing with AKD from Alum-Rosin sizing in Agro based furnish is fully compatible for producing good quality of paper without affecting the Machine runnability, provided well controlled charge balance throughout the stock by fine tuning the dose of Coagulant and Retention aid at suitable point of addition in stock. Best performance can be achieved only by carefull control of nil residual chlorine in pulp, 20-30 meq/lit cationic demand in Head box and good first pass retention. Cationic demand of pulp is a very crucial factor in controlling the consumption of Coagulant, AKD and Retention aid for maintaining the desired Cobb and shade of paper. Residual chlorine in pulp has a very serious impact on AKD sizing as it leads to higher cationic demand that resulted in higher consumption of Coagulant, AKD & OBA for maintaining the desired Cobb and Brightness.

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