Al-Azhar Bulletin of Science

Volume 21 | Issue 2 Article 22

12-1-2010
Section: Chemistry

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## How to Cite This Article

ABOUL-FETOUH, M.; NASSAR, F.; and TANTAWY, A. (2010) "ALKYL OLEATE SUCCINIC ANHYDRIDE AS A NEW MODIFICATION OF INTERNAL PAPER SIZING AGENT," *Al-Azhar Bulletin of Science*: Vol. 21: Iss. 2, Article 22.
DOI: https://doi.org/10.21608/absb.2010.7382

# ALKYL OLEATE SUCCINIC ANHYDRIDE AS A NEW MODIFICATION OF INTERNAL PAPER SIZING AGENT

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## Abstract

There are two common synthetic sizing agents which are used in neutral-alkaline paper making: alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). However both show many disadvantages on application. Using alkyl oleate enabled us to improve the performance of the sizing chemicals. Two alkyl oleate succinic anhydride: methyl and ethyl oleate succinic anhydrides have been prepared, converted to aqueous emulsion and used in sizing of paper hand sheets at laboratory scale. The sizing performance of each was compared with that of the commercial sizing agents.

## Introduction

Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are used in paper sizing. Each of them has advantages and disadvantages but ASA has been established to be more as a cost effective compared to AKD. However it has two major problems on application as paper sizing agent:

1. Its instability in emulsion.
2. Faster hydrolysis leading to higher risk of sticky deposits of hydrolyzed ASA calcium salt.

ASA hydrolyzes easily in aqueous emulsion to form alkenyl-succinic acid, which is ineffective in paper sizing.

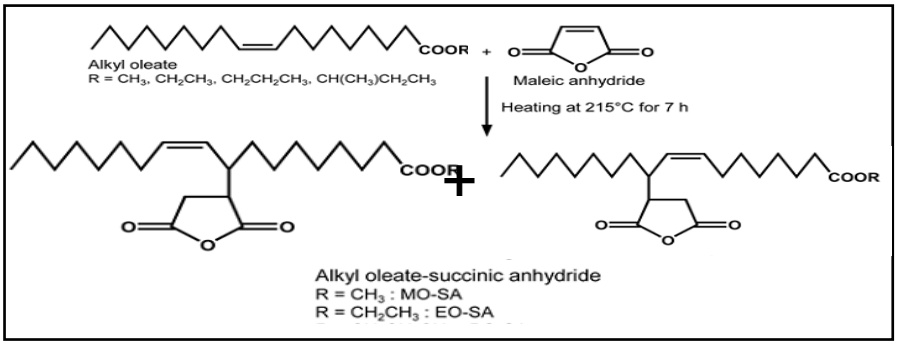



**Fig1: Reaction scheme for preparing alkyl oleate succinic anhydrides from alkyl oleate and maleic anhydride.**

ASA is synthesized from a mixture of internal olefins with 16-18 carbons. These olefins react with maleic anhydride at high temperatures. The reaction which take place at carbon – carbon double bond of the anhydride, is illustrated in fig.1, where

R represents one of the hydrocarbon group. Smith[1] reported that ASA has higher sizing efficiency when the internal olefins have their double bonds at the center position of the hydrocarbon chains.

The objective of this study is to avoid all these disadvantage by modifying the chemical structure of the alkylating chain by reacting two alkyl oleate esters with maleic anhydride to prepare alkyl oleate succinic anhydride (AOSA), then evaluating their sizing performance in terms of the alkyl group used for blocking The carboxyl group of oleic acid. The results were compared with those obtained using commercial ASA.

**Materials and methods**

a. Chemicals used :

Some of the chemicals used in this work, including oleic acid, ethanol, methanol, sulfuric acid, $TiO_2$ catalyst and maleic anhydride were laboratory grade.

As reference ASA we used commercial ASA from Nalco company commercial name N.7542 ASA. Other chemicals used in this study were commercial grade such as cationic starch having quaternary subistitute D.S. 0.03, and polyquaternary amine ( coagulant ) Buckman company.

b.Row materials

100% waste office paper with different commercial grads sorted to:

1st grade (best collected and clean waste), and 2nd grade have some contamination such as plastic bags and colored paper. The two grades were pulped, de-inked, bleached and beaten to 45° SR.

**Methods of preparation:**

**preparation of ethyl and methyl oleate – succinic anhydride[3]**

Methyl and ethyl oleate-succinic anhydrides have been prepared from laboratory grade methyl and ethyl oleate ester (one mole for each) by reacting with maleic anhydride (one mole) at 215°C for 7 hr under nitrogen atmosphere.

**Emulsification of Alkyl oleate succinic anhydride.**

For emulsification we have two methods.

a) Emulsification with cationic polymer, commercial name "N.7541 from Nalco Co."

"Cationic emulsifier Commercial Name N.7541 = "water- acrylamide -dimethyl amino ethyl methyl acrylate co-polymer"

- The Cationic emulsifier to alkyl oleate succinic anhydride ratio was 1:1.

- The alkyl oleate succinic anhydrides were poured together with the cationic emulsifier into the mixer (laboratory blender) and have been emulsified for 10 minutes at 1000 rpm. The total volume of each emulsion was 200ml.

- For standard alkyl oleate succinic anhydride the emulsion has been diluted with deminerlaized water.

The emulsion stability hase been measured starting after mixing.

b) Emulsification with cationic starch:

- 1% starch solution was prepared. Afterwards, the ethyl and methyl oleate succinic anhydrides were poured together with the cationic starch into the mixer and have been emulsified for 10 minutes at 1000 rpm. The total volume of each emulsion was 200 ml.

For standard alkyl oleate succinic anhydride the liquid cationic starch and the emulsion has been diluted with deminerlized water.

The starch to alkyl oleate maleic anhydride ratio was 1:1.

The emulsion stability hase been measured starting after mixing.

Internal sizing application for Hand sheets:

Designed amount of the ethyl oleate succinic anhydride emulsion, methyl oleate succinic anhydride emulsion, poly quaternary amine and Cationic Starch solution were added to pulp slurries under continoues stirring at 500 rpm

Hand sheets were prepared from the pulp slurries with tap water.

The pH of the pulp slurries was 8.

The wet pressed hand sheets were dried at 115°C for 5 min. in lab. oven.

**Evaluation and Measurements:**

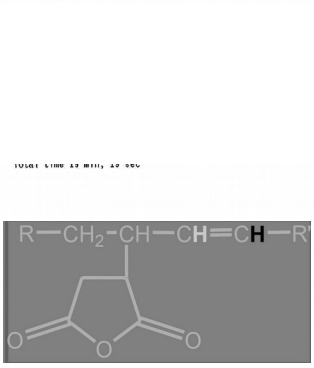
To evaluate a new product the sizing process is carried out by internal sizing method for hand sheet at laboratory scale and the degree of sizing was measured in seconds indicating the time of wettability.

**Instrumental Measurements:**

IR spectrometer: IR spectra were recorded on FT-IR 5300 spectrometer and perkin Elmer spectrum RXIFT-IR system (v, cm-1). All samples were analyzed at room temperature in the range 400 - 4000 cm-1.

$^{1}$HNMR Spectrometer: The $^{1}$HNMR spectra were recorded in DMSO-d6 at (300) MHz on Varian Mercury VX-300 NMR spectrometer (δ, ppm).

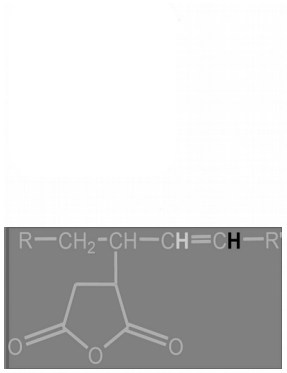
IR spectra and $^{1}$HNMR spectra were carried out at the Microanalytical Center of Cairo University, Cairo.




**Methyl oleate succinic anhydride**




**Fig.2: $^{1}$H NMR spectrum of methyl oleate succinic anhydride**




**Ethyl oleate succinic anhydride**




**Fig.3: $^{1}$H NMR spectrum of ethyl oleate succinic anhydride**

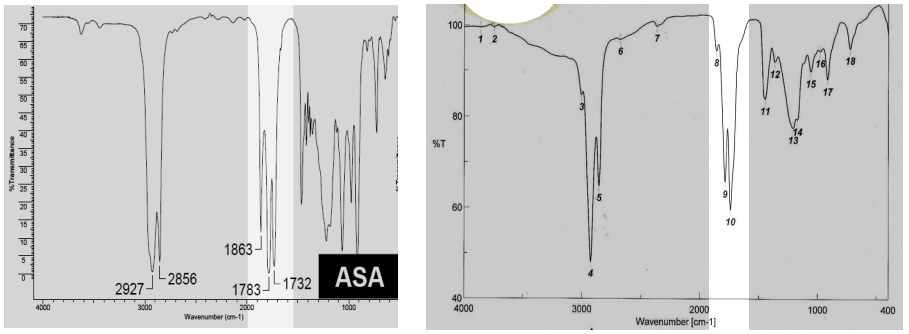



**Fig.4: IR spectrum of reference ASA and ethyl oleate succinic anhydride**

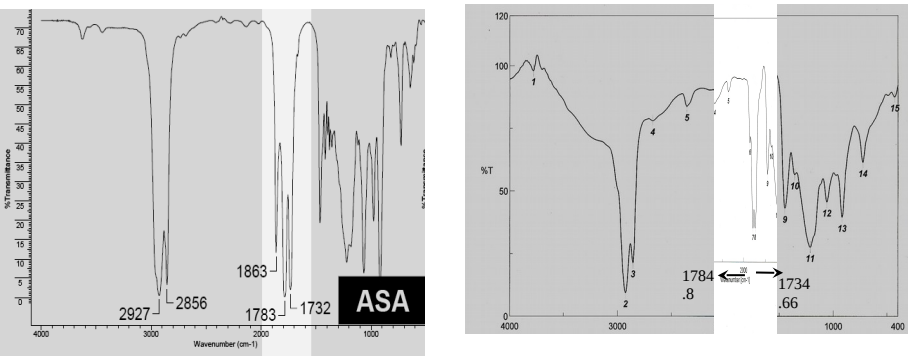



**Fig.5: IR spectrum of reference ASA and methyl oleate succinic anhydride**

**Results & Discussions**

**1-Sizing performance of alkyl oleate succinic anhydride:**

The sizing performance of ethyl and methyl oleate succinc anhydride has been evaluated against commercial ASA.

The results are summarized in the table 1. the results outline the time of wettability "sizing degree (Sec.)" for hand sheets prepared by adding alkyl oleate succinic anhydride aqueous emulsion and commercial ASA.

**Table 1, Summarize the sizing degree, (sec.) for hand sheets sized by commercial ASA and that sized by new products.**

| No. | Sizing agent | Emulsifier | Sizing agent : Emulsifier ratio | Time of wettability sizing degree,s |
|---|---|---|---|---|
| 1 | Commercial ASA | Cationic polymer | 1 : 1 | 5 |
| 2 | EOSA | Cationic polymer | 1 : 1 | 5.5 |
| 3 | EOSA | Cationic starch | 1 : 1 | 10 |
| 4 | MOSA | Cationic starch | 1 : 1 | 17 |
| 5 | MOSA | Cationic polymer | 1 : 1 | 10 |

Comparing the sizing performance of commercial ASA and Alkyl Oleate Succinic Anhydride for hand sheets showing that:

i) Among the kinds of AOSA compounds, methyl oleate succinic anhydride with cationic starch emulsifier has the highest sizing efficiency, and

ii) The difference in sizing performance is attributed to different chemical structures of AOSA compounds used, which have been brought about not only by the hydrophobicity of each compound but also, by the degree of molecular orientation on the paper surface or the coagulation behavior of the molecules in sheet structure.

**2. Stability of alkyl oleate succinic anhydride in emulsion;**

To evaluate the stability of alkyl oleate succinic anhydride in aqueous emulsion, we studied the effects of emulsion storage time. The results are given in Fig.6 :

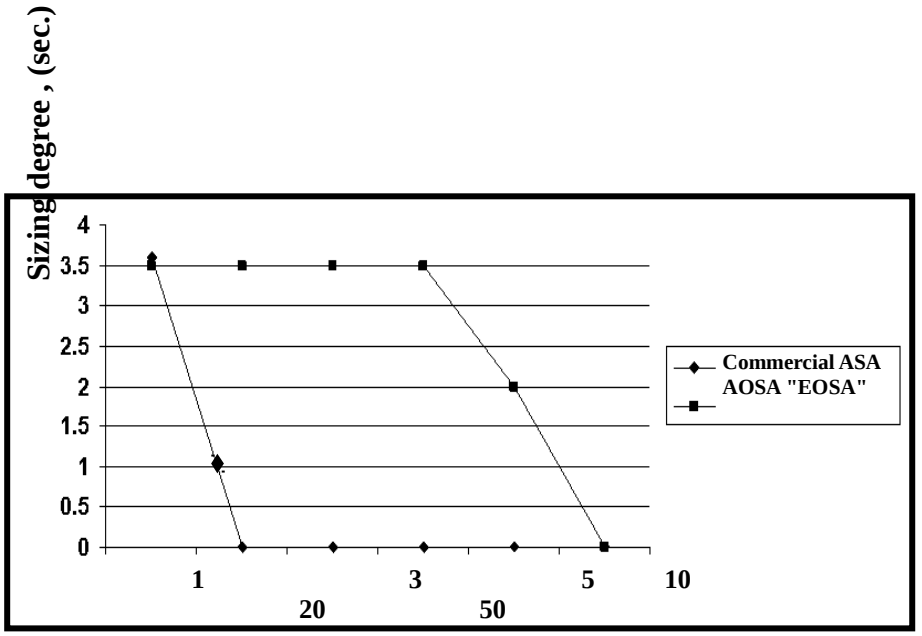


**Fig. 6: sizing degree of hand sheet prepared by internal addition of 0.3% ASA or EOSA, with different storage time.**

- The degree of sizing of the hand sheet prepared with commercial ASA dropped to nearly zero after the ASA emulsion had been stored for two hour. In contrast a high degree of sizing was maintained for hand sheet prepared with the AOSA emulsion when the emulsion was stored for one day.
- This result indicates that the Maleic anhydride group of AOSA has higher stability or higher resistance to hydrolysis in the emulsion state than commercial ASA has.

**3. Stickiness of hydrolyzed AOSA calcium salt:** 12-13-14

- When an aqueous solution of $Ca(OH)_2$ was added to either commercial ASA or AOSA emulsion, white precipitates formed with the chemical structure of calcium salts of either hydrolyzed commercial ASA or hydrolyzed AOSA.
- The calcium salt of hydrolyzed AOSA in water was not as sticky as the calcium salt of Hydrolyzed commercial ASA.

## Conclusions

Succinic anhydride – linked Methyl oleate (MOSA) show the highest sizing efficiency compared with the commercial ASA.

The stability of the anhydride group in aqueous media is much higher than that of the commercial ASA, which is reflected in the wetting time.

The succinic anhydride group of (AOSA) in aqueous emulsion is more stable against hydrolysis than commercial ASA.

Alkyl oleate succinic anhydride represents a new, efficient, stable size for internal sizing of paper.

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