Identification and quantification of the causes of the paper yellowing for the Navigator brand

Characterization of commercial samples of ASA

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Abstract

Hydrophobicity is an important property for printing and writing paper regarding water resistance. It is enhanced by adding chemicals to the stock, referred to as internal sizing agents, before it enters the paper machine. Alkenyl succinic anhydride (ASA) is a key element in the sizing process and is one of the major factors in the production cost in the factory. It belongs to a very competitive market, where there is shortage of information on composition, raw materials and emulsification techniques. This means that it is difficult for paper producers to make choices on the purchase of ASA technology. In this master's thesis, commercial samples of ASA were detailed in order to study its influence on paper yellowing for the Navigator brand. Also, industrial emulsification conditions were optimized, leading to advantages when negotiating with suppliers. Information was obtained on the composition and structure of the ASA samples based on infrared spectroscopic analysis, high efficiency liquid chromatography and nuclear magnetic resonance spectroscopy. In addition, other factors were determined, among them binding efficiency, water and ash content. Accelerated ageing tests were made using UV and condensation cycles to assess the impact of ASA in the yellowing of paper. The tests undertaken show that the quality and purity of ASA depend fundamentally on the type of olefin used in its production, which influences the kinetics of paper yellowing. The kinetic and emulsification techniques show that it is possible to reduce the quantity of ASA used if respect is maintained for the interval when the hydrolysis is still slow, but when the average size of the droplet allows for greater efficiency.

Keywords: ASA, kinetic, emulsification, yellowing.

1. Introduction

During paper production, sizing chemicals are used to hydrophobize paper. Sizing hinders penetration of water into the sheet. This repellence is needed for durability and other desired paper characteristics, such as printability. For this purpose, amphiphilic molecules are used. They are able to attach to the cellulosic fiber surface with their hydrophilic, polar side, whereas their hydrophobic, apolar side is directed away from the surface and repels water, thus hindering water penetration into the paper sheet. If the sizing chemicals are added to the paper stock before sheet formation it is called internal sizing. Today, alkenyl succinic anhydrides (ASA) is the most common chemical used for this purpose in neutral to slightly alkaline paper production, mainly due to its shorter curing time and higher cost efficiency.

ASA is highly reactive and the reactions proceed rapidly and irreversibly in the papermaking process. ASA's high reactivity is attributed to the functionality of the anhydride ring which can split on either side of single-bonded oxygen and form an ester linkage with cellulosic hydroxyl groups. This leaves a hydrophilic carboxylic acid group on the molecule which is sterically shielded by the large hydrocarbon chain originating from the alkene. This means that most of the hydrophobizing effect is achieved before the size press of the paper machine. The hydrolysis of ASA is undesirable, since partly hydrolyzed ASA has the tendency to form detrimental deposits. In this process the succinic anhydride group is converted into succinic acid. As paper machine do not retain fibers and chemical additives completely, some of the added ASAs will be released into the white water, where they circulate, hydrolyze completely and accumulate. Then it forms sticky calcium salt deposits.

ASA is applied as emulsion in an aqueous polymer solution, often cationic starch. Stability of the sizes in these emulsions and efficiency of the emulsified sizing agents are two crucial factors determining appropriateness and quality of ASA. Due to hydrolysis behavior, ASA emulsions have to be reacted with cellulose fibers within 30 minutes of their preparation, otherwise ASA will be hydrolyzed. By modification of emulsion particle size and concentration, the emulsification process can be optimized. It should be noted that in papermaking, notable cost savings can be gained by using a correct sizing agent and right sizing properties.

This study focuses on characteristics crucial for the industrial application of ASA in paper mills: stability and reactivity properties, hydrolysis behavior and emulsification. Eight types of ASA will be compared and their different performances will be discussed in terms of different molecular structures and composition – the presence of

stabilizers and surfactants. Additionally, the tests undertaken will show ASA influence on the kinetics of paper yellowing for the Navigator brand.

2. Material and methods

2.1. Source of chemicals

Eight types of commercial ASA samples, supplied by The Navigator Company, were used as sizing agents. The grades identification is the following: Mare ASA 220 VS, Mare ASA 31 EX, Mare 31 NE from the Mare supplier, Fennosize AS 1000 and Fennosize AS 3000 from the Kemira Chemie supplier, Ivax 111 S and I sample, from the IVAX supplier, and S sample from the Solenis supplier. Cationic corn starch and carboxymethyl cellulose were supplied by RAIZ, Forest and Paper Investigation Institute, and linseed oil was provided by Resiquímica. Ethyl acetate (>99%) and deuterated chloroform, $CDCl_3$, (99.8%) were supplied by Carlo Erba and Aldrich, respectively.

2.2. Emulsification

2.2.1. Emulsion preparation

In the first step of the emulsion preparation to analyse its stability, a water-to-ASA- ratio of 1.8 was used for all the commercial samples. 5 g of ASA were mixed with 9 g of deionized water with a VV3 Vortex mixer, VWR, during 1 minute at position 3 on the scale of 1 to 6. Subsequently, the emulsion breaking kinetics were analyzed over 30 minutes with further characterization of the layers formed.

To analyse industrial emulsification, cationic corn starch stabilizer solution was prepared containing 4% of starch and deionized water. The cooking was carried out in a three neck 1L reactor with a Heidolph mixer system. The reactor was immersed in an oil bath which was pre-heated to 75°C. A thermopar (with an on-off control) was placed in one of the necks. The solution was cooked for 30 minutes at temperature 80°C under good mixing. After cooking, a UFESA BS4704 blender of 800 ml was used for emulsification. It emulsified the stabilized solution and the ASA sizing agent with continuous mixing of 1 minute. The starch –to-ASA ratio varied between 1.0 and 3.0 during the experiments for all ASA commercial samples.

2.2.2. Emulsion measurements

Emulsion particle size measurements were done with NANO-flex device by Microtrac – Europe GmbH. This technology relies on dynamic light scattering to determine the particle-size distribution. The refractive index of ASA was chosen to be 1.52 and for the continuous phase, water, 1.333 was used. The measurements were done straight after emulsification.

2.3. Rancimat Method

The 679 Rancimat, Metrohm-Herisau, determines the oxidation stability and reactivity of commercial ASA samples. The heating block is heated up to 80°C and the measuring vessel is filled with 70 mL of deionized water and placed on the Rancimat device together with the measuring vessel cover. The tests duration was of 8 hours.

Sample preparation. A sample size of 3.0 g was used. At first, a sample composition with 90% linseed oil and 10% ASA sample was prepared. Subsequently, to reproduce the hydrolysis kinetics of ASA, a sample with 89% linseed oil, 10% ASA sample and 1% deionized water was made and then tested.

2.4. Characterization of ASA samples

To characterize the commercial ASA samples several techniques were applied. The water content was determined by the Karl Fischer method with an 831 KF Coulometer, Methrohm. Ash content was determined with a muffle furnace by Naberthem. Additionally, to study the ASA behaviour during the freezing period and the frozen stability after thawing, the samples were frozen to -13°C for 3 hours.

2.5. FT-MIR spectrometer

Mid InfraRed spectrums were collected using a FT-MIR spectrometer from BOMEM FTLA2000-100, ABB CANADA equipped with a SiC light source and a DTGS detector. The spectra were analysed by means of the BOMEM Grams/32 software. The spectral range is from 4000-650 cm^{-1} and a resolution up to 16 cm^{-1}. One drop of the ASA sample was placed on top of the probe head and the measurement was started immediately.

2.6. High performance liquid chromatography (HPLC)

HPLC analysis allows the identification of compounds according to their molecular weight. The HPLC system was composed of an Alliance 2695 HPLC chromatography unit (Waters, part# WAT270008 and WAT270852).

Sample preparation. For HPLC analysis, 25mg ASA sample was diluted in 25 ml ethyl acetate, which was followed by a second dilution of 25 μl from the previous solution in 25 ml ethyl acetate.

2.7. Nuclear magnetic resonance (NMR) spectroscopy

Specta were recorded at 300 MHz for ^{13}C using a Bruker Avance II instrument, with $CDCl_3$ as solvent. Topspin software was used for spectra acquisition and MestReNova software for its treatment.

Sample preparation. In total, 200 mg of the sample was dissolved in 200 μl of $CDCl_3$ for NMR analysis.

2.8. Accelerated ageing test

For testing QUV resistance, a QPanel QUV/BASIC 230 V 50 Hz accelerated weathering tester was used during a 24 hour

period at 60℃. Two UV/condensation tests were done in this study.

Sample preparation. One drop of the ASA sample was placed on top of the cellulose sheet bale. This procedure was repeated for all the samples.

3. Results and Discussion

3.1. Analytical methods results

Using various analytical methods including infrared spectroscopy, high performance liquid chromatography, ^{13}C nuclear magnetic resonance spectroscopy the commercial ASA samples were comprehensively analysed.

3.1.1. Infrared spectroscopy results

Figure 1 presents the spectrums of the commercial ASA samples and shows that IVAX sample has been hydrolysed to a very small extent. The most intense band in the spectrum of the pure anhydride (Figure 1 (a)) is υ(C=O)=1782 cm^{-1}. On passing from anhydride to acid, the IR spectrum shows characteristic changes connected with the disappearance of the succinic anhydride grouping and the appearance of COOH groups resulting from the ring opening. Both the carbonyl bands (1782 and 1860 cm^{-1}) start to disappear and in place of these, an intense band appears at 1709 cm^{-1} (the A band) corresponding to the stretching vibration of the C=O bond of the COOH group. The loss of intensity of the C-O-C bond when the anhydride is converted into the acid and the formation of two C-O bonds, giving rise to complex vibrational interactions in the single COOH group, are accompanied respectively by the loss of intensity of the 1065 cm^{-1} band and the appearance of an intense band at 1288 cm^{-1} (the B band).

The presence of acid in the IVAX sample is mainly due to the fact that the FT-MIR acquisition cell provides greater contact surface with atmospheric moisture.

3.1.2. High performance liquid chromatography results

Figure 2 shows HPLC chromatograph for the identification of compounds in ASA samples. The A and B bands correspond to solvent and ASA molecule, respectively. Surfactant (the D band) is present in samples S, Mare ASA 220 VS and Fennosize AS 3000. In the case of the Fennosize AS 1000 sample, it can be observed the presence of a compound with a long retention time (the E band), which probably corresponds to a stabilizer.

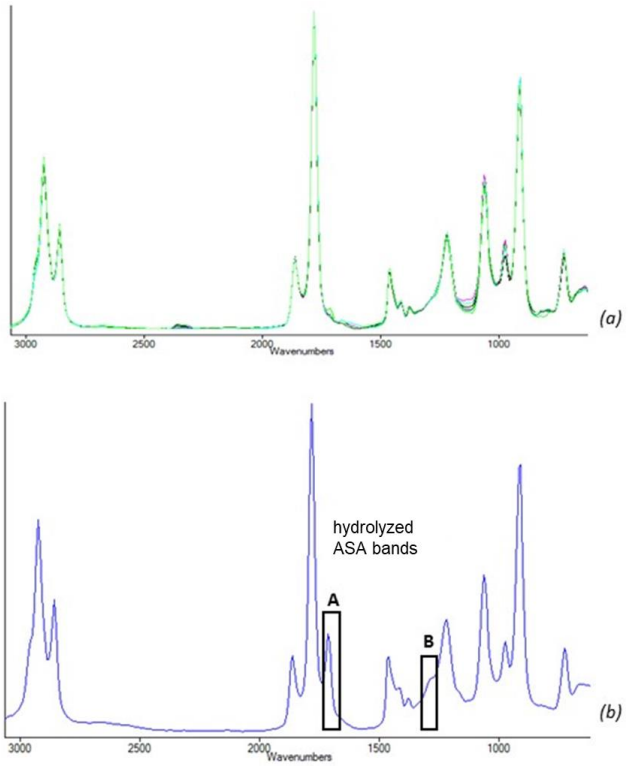


Figure 1 – FT-MIR spectra of ASA samples: (a) superposition of Mare ASA 220 VS, 31 EX, 31 NE, Fennosize AS 1000 and 3000, I and S samples; (b) Ivax 111 S samples (A – carboxylic acid C=O stretch 1709 cm^{-1} and B – carboxylic acid C-O stretch 1288 cm^{-1}).

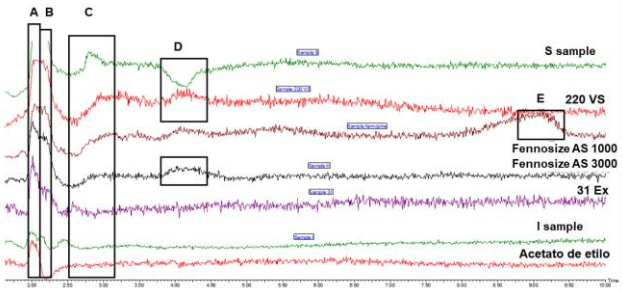


Figure 2 – HPLC chromatograph of six ASA samples diluted in ethyl acetate and of ethyl acetate (solvent).

3.1.3. 13C nuclear magnetic resonance spectroscopy results

NMR allowed structural elucidation of commercial ASA samples. The assignments of the resonances to structural elements are given in Table 1 for the ^{13}C domain. The resonances between 29.7 and 27.1 ppm originates from the aliphatic chain. The olefinic protons of the double bound were found around 126.4 and 136.9 ppm, respectively. The resonances at 173.2 and 170.3 are assigned to carbonyl carbon atoms from the succinic anhydride ring.

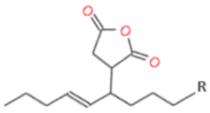
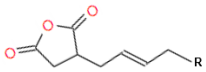
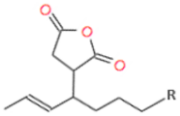
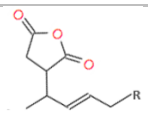
Table 1 – ^{13}C NMR peak assignment for ASA molecule.

Chemical shift (ppm)	Structural element
14.1	CH_3
22.6	CH_3-$\underline{C}H_2$
28.6-29.7	$\underline{C}H_2$-$\underline{C}H_2$
30.2	CH_2 in succ.
31.8	CH_3-CH_2-$\underline{C}H_2$
32.6-32.7	CH (succ.)-CH-CH=CH-$\underline{C}H_2$
42.6	-$\underline{C}$H-CH (succ.)-
45.5	$\underline{C}$H in succ.
126.4-136.9	CH (succ.)-CH-$\underline{C}$H=$\underline{C}$H
170.3-173.2	C(=O)-O-C(=O) in succ.

Through subsequent analysis of the ^{13}C chemical shift of the succinic anhydride ring, the number of different ASA molecules presented in the commercial samples were determined. The Mare ASA 220 VS, 31 EX, Fennosize AS 3000, S and IVAX 111 S samples have 2 types of molecules, while the Fennosize AS 1000 and I samples contain 3 different forms.

The resonance in the terminal methyl groups of a branched-chain varies according to its length. Table 2 shows the chemical structure of the commercial ASA samples. The Fennosize AS 3000, Mare ASA 31 EX, and S samples are the only ones with a straight-chain.

Table 2 - ^{13}C NMR chemical structure assignment for the commercial ASA samples according to the terminal methyl groups

Chemical shift (ppm)	Commercial samples	Chemical structure
13.7	Fennosize 1000 Mare ASA 220[a] Mare 31 NE[a] S sample IVAX 111 S I sample[b]	
14.1	Fennosize 3000 Mare 31 EX[a] S sample	
16.5	Fennosize 3000 Fennosize 1000 IVAX 111 S	
17.0	Fennosize 1000	

[a] Two ASA molecules with this structure
[b] Three ASA molecules with this structure

3.2. Characterization of commercial ASA samples

Table 3 presents the water and ash composition of the commercial ASA samples and its unfreezing time. As shown, the samples have residual moisture content (0.001 and 0.01%). However, it is unlikely that moisture is caused by the handling of samples or during its storage. In addition, it is worth mentioning that the analyses of inorganic matter aim to identify the presence of catalysts used in the synthesis of ASA. Based on this, the methods used to prepare the Mare ASA 220 VS and I samples do not use catalysts.

Table 3 – ASA samples water and ash composition and its unfreezing time

	Moisture (ppm)	Ash (%)	Unfreezing time (min.)
Mare ASA 220 VS	29.39	0	01:51
Mare ASA 31 EX	41.80	0.21	02:42
Mare 31 NE	13.34	0.04	02:52
Fennosize AS 1000	59.88	0.31	19:49
Fennosize AS 3000	96.48	0.21	17:50
I sample	84.81	0	05:59
S sample	20.35	0.32	03:24
IVAX 111 S	35.80	0.13	05:25

Then, it was studied the unfreezing time of frozen ASA samples at -13°C. The first samples to unfreeze have shorter side, branched or unsaturated chains, which it is the case of the Mare ASA 220 VS, the Mare ASA 31 EX, the Mare 31 NE and the S samples. On the contrary, the samples with the highest unfreezing time are more crystalline, therefore, more stable, and are probably obtained from a longer and saturated olefin. The samples with this behaviour are Fennosize AS 1000 and 3000.

In particular, the Fennosize samples present higher unfreezing times and this might suggest that these samples have higher molecular weight than the others, and are therefore more hydrophobic. Linear hydrocarbons are more hydrophobic than branched ones. However, the greater the hydrophobicity of the ASA molecule, the more difficult it is to prepare a stable quality ASA emulsion.

3.3. Rancimat method

The Rancimat method is an accelerated ageing test, in which the double bonds of the ASA structure are oxidized. At the end of the test, volatile, secondary reaction products are formed. The time until secondary reaction products are detected is called the induction period (IP). This value characterizes the resistance of the sample to oxidation. The longer the induction time, the more stable a sample is. Tables 4 and 5 summarize studies of ASA resistance to degradation using the Rancimat method.

Table 4 – Comparison between IP of ASA samples.

	IP (h)
Mare ASA 220 VS	2.52
S sample	2.76
Fennosize AS 3000	4.37
IVAX 111 S	4.43
I sample	4.60
Mare ASA 31 EX	5.10
Mare 31 NE	5.11
Fennosize AS 1000	5.51

OXIDATIVE DEGRATION BY ASCENDING ORDER

As shown in Table 4, the Fennosize AS 1000, the Mare 31 NE, the Mare ASA 31 EX are the most stable samples

against oxidative degradation, whereas the Mare ASA 220 VS and S samples are the least resistant.

Table 5 – Comparison between IP of ASA samples with 1% of deionized water.

	IP (h)
Mare ASA 220 VS	0.21
S sample	2.17
IVAX 111 S	2.98
I sample	3.72
Mare 31 NE	3.98
Mare ASA 31 EX	3.99
Fennosize AS 3000	4.02
Fennosize AS 1000	4.32

OXIDATIVE DEGRATION BY ASCENDING ORDER

As might be expected, the IP values decreased with the addition of water, since moisture speeds up the degradation process.

Table 6 – Comparison of induction periods of ASA samples with and without water

	Variation (%)
Mare ASA 220 VS	92
IVAX 111 S	33
Mare ASA 31 EX	22
Fennosize AS 1000	22
Mare 31 NE	22
S sample	21
I sample	19
Fennosize AS 3000	8

Table 6 shows that the Fennosize AS 3000 is the most resistant sample to hydrolysis. In fact, the emulsions prepared with this sample are expected to be more stable on the paper machine, which will result in a less intense formation of foaming and aggregation, but also to an increase in the hydrophobization effect, since the reactive anhydride group can be efficiently distributed onto the fiber surface for a longer period. Cellulose has a high surface area, which causes better binding of ASA small particles onto the fiber surface.

On the contrary, the Mare ASA 220 VS sample reveals a marked deterioration (92%), which shows quick hydrolysis in the presence of water on the paper machine, causing two types of problems: sticky deposit formation and less binding efficiency, since only a small amount of ASA molecules can now react with the cellulose fibers. It should be noted that the rate of the reaction of ASA with cellulose is of second order, therefore to achieve sizing the amount of unreacted ASA is important.

All the other samples present an acceleration of oxidation of approximately 20% (Table 6).

3.4. Emulsification

ASA is supplied practically in 100% active form having no charge or affinity for anionic cellulose fibers and needs to be protected from moisture. Because of the fast reactivity of ASA, it is emulsified on-site and dispersed in a cationic polymer solution, e.g., cationic starch, the most common ASA emulsion stabilizer, prior to its addition to the paper stock. To achieve a good sizing effect, the most important quality parameters of ASA emulsions are stability and particle size.

3.4.1. Emulsion stability

The procedure consists in a preliminar test of the industrial emulsification process without cationic starch. Emulsion visual characteristics shown in Figure 3 and 4 were observed in order to identify the existence of surfactant present in ASA samples and to analyse the emulsion breakage kinetics over time.

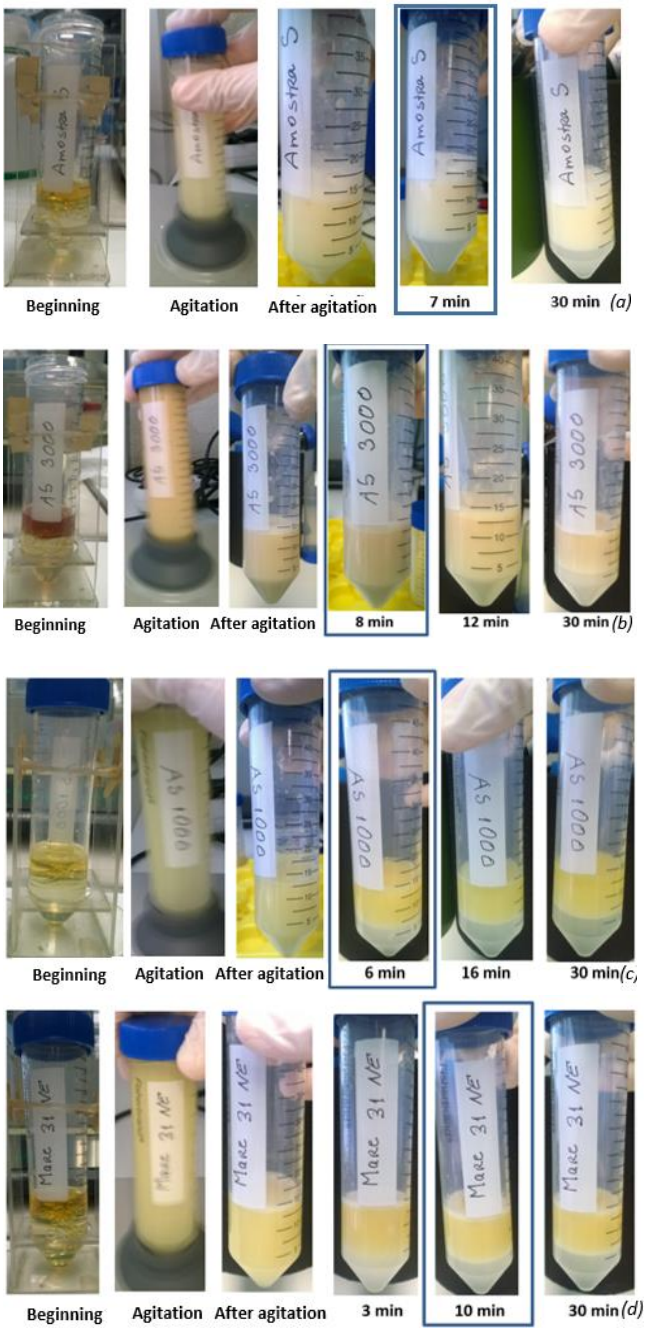


Figure 3 - ASA emulsions: (a) S sample, (b) Fennosize AS 3000, (c) Fennosize AS 1000, and (d) Mare 31 NE. The blue outline shows the separation of the phases.

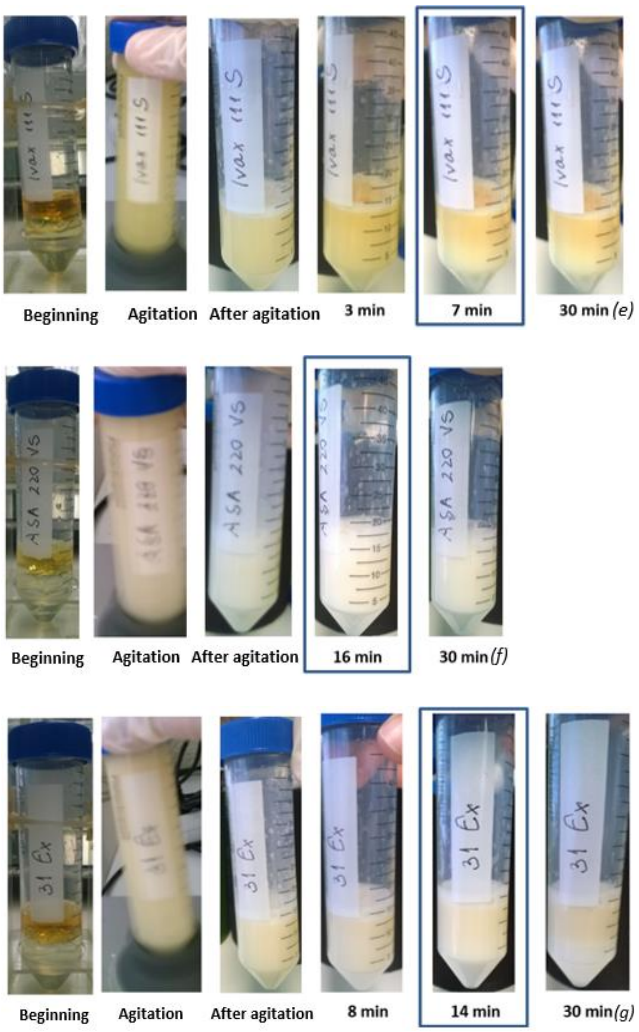


Figure 4 - ASA emulsions: (e) IVAX 111 S, (f) Mare ASA 220 VS, and (g) Mare ASA 31 EX sample. The blue outline shows the separation of the phases.

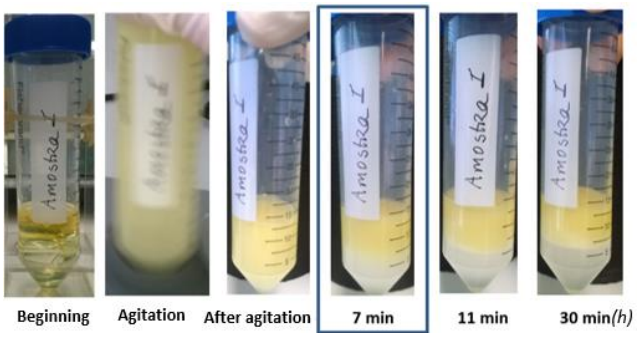


Figure 5 - ASA emulsion from (h) I sample. The blue outline shows the separation of the phases.

The Fennosize AS 3000, the Mare ASA 220 VS and the 31 EX samples present a relatively stable ASA phase after emulsification. In fact, the Mare ASA 31 EX sample is the one with the most stable ASA phase over time. The greater the stability of ASA, the better the spread onto the cellulose fibers.

With regard of foam formation, the Fennosize AS 3000, 31 NE, IVAX and 31 EX samples show only surface residue, while the Mare ASA 220 VS and S samples have a lot of foam, which highlights the surfactant existence. Stabilizers and surfactants have significant impact on emulsion particle size and stability. They exist to reduce cost of continuous on-site emulsification and to reduce hydrophobation losses through hydrolysis of ASA. The Fennosize AS 1000, the 31 NE and the I sample presented a clear aqueous phase at 30 minutes, and I sample solidified over time.

3.4.2. Emulsion particle size

The particle size distribution results of ASA emulsions with deionized water (ratio of 1.8) over 80 seconds are seen in Table 9. The desired particle size lies between 0.5-2 μm where the reaction rate is high enough to provide good sizing but not yet too reactive to increase the hydrolyses reaction as unbearably high. In fact, small droplets have a higher surface area, making the anhydride more susceptible to the undesired reaction with water, before ASA can be retained in the paper web and cured in the dryer section of the paper machine.

The most successful emulsions were those of the Mare ASA 31 EX and the Fennozise AS 3000 samples. They had emulsion particle sizes values between 0.5 – 2 μm with 54.1% and 35.3% of the particles with this interval size, respectively. Meanwhile, most of the emulsions prepared had the particle size d(0.5) values ranging in between 4-6 μm , which might suggest that the ASA ratio must be optimized. The most unstable ones, the Ivax, Fennosize AS 1000 and 31 NE, showed 0%, 6% and 9% values, respectively, in between 0.5–2 μm.

According to the manufactures, industrial ASA emulsifiers allow instant verification of emulsion quality, it is therefore also important to analyse the particle size distribution result 10 seconds after emulsification. In fact, Fennosize AS 1000 and 3000 emulsions stand out from the rest, with 93.7% and 100%, respectively.

Table 7 – Particle size distribution (μm) and its percentage of ASA emulsions with deionized water.

TIME (s)	Fennosize 3000	Fennosize 1000	Mare ASA 220 VS	Mare ASA 31 EX	Mare 31 NE	S sample	IVAX 111 S	I sample
10	**1.258 (27.7%)** **0.539 (72.3%)**	**1.161 (93.7%)** **0.046 (6.3%)**	5.560 (7.3%) 3.330 (45.8%) 0.183 (46.9%)	3.630 (59.5%) **0.485 (40.5%)**	6.000 (100%)	4.820 (100%)	5.960 (100%)	4.250 (100%)
20	6.000 (14%) **0.693 (86%)**	3.470 (68.7%) 2.950 (31.3%)	4.440 (79.9%) **0.576 (20.1%)**	2.982 (87%) **0.2741 (13%)**	6.000 (100%)	5.970 (14%) **0.864 (50%)** **0.723 (36%)**	5.070 (100%)	3.470 (100%)
30	3.240 (86.9%) **0.336 (13.1%)**	**0.296 (100%)**	1.856 (73.4%) **0.290 (26.6%)**	4.870 (73.7%) **0.353 (26.3%)**	6.000 (100%)	0.314 (100%)	6.000 (100%)	6.000 (100%)
40	5.870 (8.4%) **0.778 (91.6%)**	6.000 (100%)	2.185 (100%)	6.000 (1.5%) **0.660 (98.5%)**	6.000 (100%)	0.302 (100%)	5.250 (100%)	0.183 (100%)
50	**1.454 (88.2%)** 0.145 (11.8%)	4.980 (23.8%) 0.321 (76.2%)	2.563 (61.8%) **1.172 (38%)**	**1.575 (24.8%)** **0.546 (67.1%)**	6.000 (100%)	4.700 (78.7%) 0.243 (21.3%)	6.000 (100%)	6.000 (100%)
60	2.537 (100%)	5.110 (100%)	5.410 (33%) **0.1649 (67%)**	6.000 (1.5%) 0.678 (98.5%)	6.000 (100%)	2.488 (31.8%) 0.474 (68.2%)	6.000 (100%)	6.000 (100%)
70	4.190 (100%)	6.000 (100%)	6.000 (3%) **0.655 (41%)** **0.193 (56%)**	5.230 (64.2%) **0.567 (35.8%)**	6.000 (7.7%) **0.765 (76.5%)** **0.116 (15.8%)**	0.342 (100%)	6.000 (100%)	**1.011 (75.9%)** 0.201 (24.1%)
80	3.120 (100%)	4.400 (100%)	5.700 (41%) **1.188 (17%)** **0.187 (42%)**	4.510 (63.7%) **0.614 (36.3%)**	6.000 (100%)	**0.740 (76%)** 0.223 (24%)	4.150 (100%)	6.000 (100%)
AVERAGE	5.890 (4.4%) 3.410 (46%) **1.477 (14.6%)** **0.788 (20.7%)** 0.473 (14.6%)	5.180 (69.6%) **0.916 (6%)** 0.304 (24.4%)	4.940 (23.7%) 2.352 (29%) **1.196 (12%)** **0.570 (8%)** 0.184 (28%)	4.010 (45.9%) **0.576 (54.1%)**	6.000 (88.4%) **0.765 (9.6%)** 0.116 (2%)	4.830 (29.8%) 2.487 (3.3%) **0.813 (15.8%)** 0.321 (51.2%)	5.750 (100%)	5.960 (74.4%) **1.002 (10.1%)** 0.187 (15.5%)

Based on the previous conclusions, for each sample the optimal ASA ratio was analysed, which leads to a better fiber wetting and operable concentrations range. In fact, dosing of ASA is a result of process-specific calculations. A higher amount gives better sizing response but it is more expensive and may cause more deposit problems. Tables 10 and 11 show the particle size distribution results of ASA emulsions with cationic starch for the optimal ratio. The particle size of all emulsion decreased, except in case of the Mare ASA 220 VS sample, probably due to the large amount of surfactant. The presence of stabilizer in the Fennosize AS 1000 sample had a significant impact on emulsion particle size, 85.3%, with a ratio of 1.6, giving complete saturation on the ASA droplet. As shown in Table 9, the Mare ASA 31 EX emulsion has a particle size from 0.5-2 μm of 71.7%, this being the only sample whose industrial ratio (1.8) corresponds to the optimal ratio.

Table 8 – Particle size distribution results of Mare ASA 31 EX, Fennosize AS 1000 and 3000 emulsions with cationic starch.

Mare ASA 31 EX		Fennosize AS 1000		Fennosize AS 3000	
1.0	1.8	1.0	1.6	1.8	3.0
5.500 (44.2%)	4.840 (28.9%)	3.540 (5.1%)	3.900 (7.6%)	5.810 (45.7)	5.730 (30.2%)
1.473 (55.8%)	0.550 (71.1%)	2.509 (32.5%)	1.989 (18.8%)	2.107 (2.4%)	1.485 (2.8%)
		1.711 (45.1%)	0.954 (66.5%)	0.522 (51.9%)	0.577 (67%)
		1.034 (17.3%)	0.304 (7.1%)		

Table 9 - Particle size distribution results of Mare ASA 31 NE, IVAX 111 S, S and I samples and Mare 220 VS emulsions with cationic starch.

Mare 31 NE	Ivax 111 S	S sample	I sample		Mare 220 VS
1.6	2.6	2.0	1.4	2.4	1.4
5.550 (26.6%)	5.920 (24.9%)	3.310 (22.2%)	5.830 (8.9%)	5.140 (43.8%)	5.620 (66%)
1.162 (73.4%)	4.340 (22.1%)	1.011 (77.8%)	1.788 (45.2%)	1.582 (8.3%)	1.387 (32%)
	1.088 (31.9%)		0.638 (30.8%)	0.501 (47.9%)	0.277 (1.3%)
	0.504 (10.6%)		0.1431 (15.1%)		
	0.1645 (10.4%)				

There is a correlation between these results (Tables 10 and 11) and the findings obtained from the methods described previously, specifically that samples with a branched structure are less hydrophobic and lead to a better fiber wetting. Fennosize AS 3000 sample showed good particle size values with a ratio of 3.0, which is less expensive.

The difference in industrial emulsification and laboratory scale operation has to be taken into consideration, since industrial emulsification often produces smaller particle sizes than laboratory devices. This means that some of the emulsions which stated medium or high, based on literature, would in these experiments give stable and smaller sized emulsion droplets in industrial environment.

3.5. Accelerated ageing test

The ageing of cellulose sheet was undertaken under two different ageing conditions. The ultraviolet light below 340 nm simulates a high temperature environment such as a desert, and the condensation cycle which alternates with UV cycle contributes to acceleration of the exposure conditions and to mimic a storage environment. Figures 6 and 7 present the experimental results.

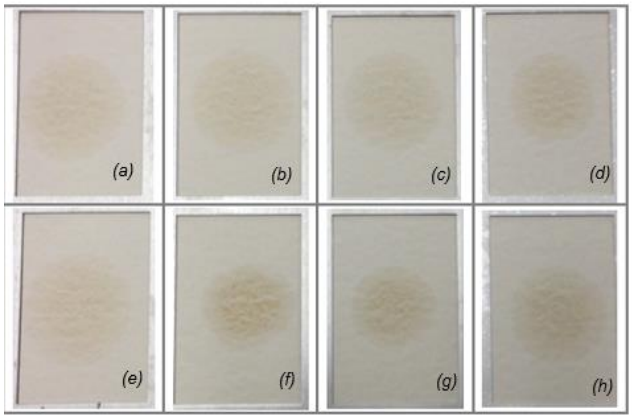


Figure 5 – Accelerating aging tests using UV light: (a) Mare ASA 31 EX; (b) Mare ASA 220 VS; (c) S sample; (d) Fennosize AS 1000; (e) Mare 31 NE; (f) IVAX 111 S; (g) I sample; (h) Fennosize AS 3000.

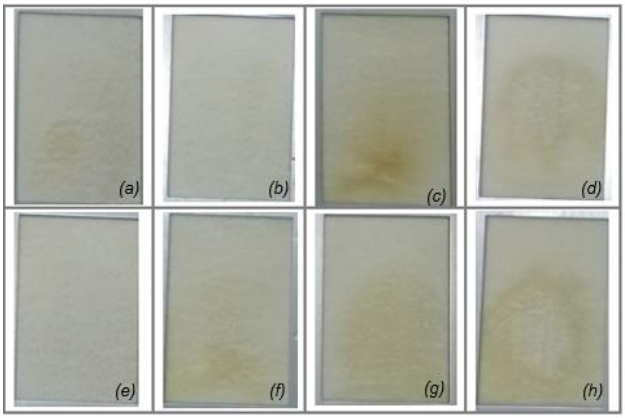


Figure 6 - Accelerating aging tests using UV/condensation cycle: (a) Mare ASA 31 EX; (b) Mare ASA 220 VS; (c) S sample; (d) Fennosize AS 1000; (e) Mare 31 NE; (f) IVAX 111 S; (g) I sample; (h) Fennosize AS 3000.

As might be expect, single sheets aged at humid conditions (Figure 7) age faster than those aged at UV conditions (Figure 6). Through ASA impregnation in the cellulose sheets, it was verified that most of the commercial samples did not changed the sheets color, with the exception of *(c)* the S sample, *(d)* the Fennosize AS 1000*; (f)* the IVAX 111 S*; (g)* the I sample; *(h)* the Fennosize AS 3000. In particular, the S sample impregnation results in a brown spot on the sheet surface due to photochemical degradation with the formation of coloured compounds. It should also be noted that the best performing commercial samples are *(a)* the Mare ASA 31 EX, *(b)* the 220 VS and *(e)* the 31 NE, because they preserve the whiteness of the sheets. This study shows the impact of ASA (even small amounts) in the yellowing of paper.

4. Conclusions

The results show that the quality and purity of ASA depend fundamentally on the type of olefin used in its production which influences the kinetics of paper yellowing. The accelerated ageing test displayed the impact of ASA (even small amounts) in the yellowing of paper, being the S sample with the worst performance, while the Mare ASA 220 VS and the Mare ASA 31 NE samples preserve the whiteness of the sheets.

The eight samples were characterized comprehensively with FT-MIR, NMR and HPLC. The composition data retrieved from the spectrum and chromatographic analysis are in agreement with the results from the rancimat method and emulsification tests. Another of the main objectives of this study was the optimization of ASA emulsions, i.e. improving the stability and sizing efficiency of emulsions. The Fennosize AS 3000 sample is the most resistant sample to hydrolysis and the emulsions prepared with this sample are expected to be more stable on the paper machine, which will result in a less intense formation of foaming and aggregation, but also to an increase in the hydrophobization effect.

Additionally, simple methods for assessing the quality of ASA in the process were developed and tested, as for example the freezing test and the rancimat method, so that critical points of emulsification process were identified. This increases the company knowledge concerning ASA specifications strengthening the advantages when negotiating with suppliers. Moreover, these tests can be easily transposed to the company's Quality Control operation.

5. Acknowledgements

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