HELSINKI UNIVERSITY OF TECHNOLOGY

Faculty of Chemistry and Materials Sciences

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OPTIMIZATION OF ASA EMULSIFICATION IN INTERNAL SIZING OF PAPER AND BOARD

Thesis for the degree of Master of Science in Technology submitted for inspection, Espoo November 13, 2009.

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HELSINKI UNIVERSITY OF TECHNOLOGY **ABSTRACT OF MASTER’S THESIS**

Faculty of Chemistry and Materials Sciences

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Optimization of ASA emulsification in internal sizing of paper and board

Abstract

In paper- and boardmaking, internal sizing is used for making the end product more resistant to liquid penetration. Rosin, Alkyl Ketene Dimer (AKD) and Alkenyl Succinic Anhydride (ASA) internal sizing agents exist for this purpose. ASA is added to the papermaking process in the form of an emulsion. The dispersion of ASA oil, water, and a stabilizing agent (stabilizer) are mixed under shear forces to create the emulsion.

In this master’s thesis, different emulsions, emulsification techniques and stabilizers in the process industry were studied. Emulsions in food, medical, petroleum and papermaking processes had potential stabilizers to be used for hydrophobation of paper and board with ASA. The comparison between rosin, AKD and ASA internal sizing agents was also done. The goal was to find optimal emulsification methods and emulsion stabilizers for ASA emulsification.

The effect of different ASA compounds, one pure ASA and the other, easy emulsifying (EE-ASA), with surface active agents (surfactants) added, were examined with various emulsion stabilizers. Emulsification process of ASA was studied by choosing thirty four stabilizers based on earlier experiments and literature over various fields of emulsification. The chosen stabilizers were reference cationic potato starch, different charge densities and molecular weights having cationic and anionic polyacrylamides (C- and A-PAM's), caboxymethyl celluloses (cmc's) and amphoteric polymers, among other stabilizers which gave steric or electrostatic stabilization effect on emulsion droplets. For the nano- and microparticle stabilization effect, bentonite and colloidal silica were utilized. Particle size, pH and visual determinations were carried out and twenty stabilizers were selected for turbidity and zeta potential testing. A good ASA emulsion particle size was in between 0.5 µm – 5 µm in d(0.5) values. The most stable emulsions had no phase inversion, only little creaming and foaming during the 4 hour study.

Eleven stabilizers were selected for sheet tests with ASA dosages of 1 kg/t and 2 kg/t. Water absorption tests showed the highest hydrophobation with medium molecular weight and medium charge density having 6.C-PAM and pure ASA and with polyvinyl alcohol, PVA 3-96, with both ASA's. Generally, pure ASA produced higher hydrophobation with only little difference to EE-ASA. The best Cobb_{60} hydrophobation values were around 21-23 g/m² of absorbed water. The best dry tensile index, around 90 Nm/g, were seen with cationic starch and EE-ASA, and the best wet tensile index of 65 Nm/g with medium molecular weight, medium cationic polyamidoamine-epichlorohydrin (PAAE) and EE-ASA.

Finally, six stabilizers were selected for deposition tests where ASA emulsions were exposed to precipitated calcium carbonate (PCC), $CaCO_3$, which is known to forms sticky deposits with ASA's hydrolysis products in paper or board machines water circulation. ASA emulsions stabilized with reference cationic starch showed the lowest deposit amounts, 1.3 and 1.2 g/m², with pure ASA and with EE-ASA. With EE-ASA, medium molecular weight and medium charge density having 6.C-PAM gained value 5.4 g/m² but caused serious deposition problems with pure ASA. The deposit nature on sample steel plates varied. PAAE emulsion was easy to remove from the metal surface, whereas starch emulsion would have needed chemical treatment to be removed. PAAE with pure ASA, indicated below average deposition amounts, 11.5 g/m². Generally neither of the two ASA's was superior compared to the other, when considering fouling. Reference starch and PVA indicated smallest ASA amounts on the deposition test sample plates based on thermal gravimetric analysis.

Cost savings could be realized with 6.C-PAM and with PAAE stabilizers with both ASA's. For reference starch, there was practically no difference between the two ASA's and for the 6.C-PAM, EE-ASA was better, whereas for PAAE, pure ASA showed best total results. The PAAE positive effects to wet strength made the chemical commercially interesting.

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Alkenyyli meripihkahappoanhydridin emulgoinnin optimointi paperin ja kartongin massaliimauksessa

Tiivistelmä

Diplomityön tavoitteena oli löytää paperin ja kartonginvalmistukseen sopivia emulsiota stabiloivia kemikaaleja eri teollisuudenalojen kirjallisuudesta. Kiinnostavimmat stabilointiaineet valittiin käytettäväksi alkenyyli meripihkahappoanhydridin (ASA) massaliimaemulsion valmistamiseen. Massaliimareseptin optimoinnin tavoitteena oli tuottaa mahdollisimman stabiili massaliimaemulsio, joka liimaa hyvin paperia ja kartonkia, toimii paperi- ja kartonkikoneella likaamatta prosessia, sekä mahdollistaa kustannustehokkaan hinnan asiakkaalle matalan annostarpeen myötä, lisäten paperin- ja kartonginvalmistuksen taloudellista kannattavuutta.

Kirjallisuusosassa vertailtiin eri teollisuuden alojen emulsioita (esimerkiksi ruoka-, lääke-, öljy-, ja paperiteollisuuden kemikaalit) ja niissä käytettyjä emulsion stabilointiaineita ja -menetelmiä. Tarkemmin vertailtiin paperin ja kartongin massaliimauksessa yleisesti käytettyjä ASA, alkyyli keteeni dimeeri (AKD) ja hartsiliimoja. ASA:n emulgointikokeita varten tutkittiin erilaisia steerisesti ja elektrostaattisesti emulsiota stabiloivia stabilointiaineita. Referenssiaineeksi valittiin yleisesti käytetty kationinen perunatärkkelys. Lisäksi stabilointiaineina käytettiin muun muassa eri varaustiheydellä ja molekyylipainoilla olevia kationisia ja anionisia polyakryyliamideja (C- ja A-PAM), amfoteerisia polymeereja ja karboksyylimetyyliselluloosia (CMC). Emulsion stabilointiin nano- ja mikropartikkeleilla valittiin bentoniitti ja silika. Kokeissa käytettiin kahta erilaista ASA:a. Ensimmäinen oli puhdas ASA yhdiste ja jälkimmäisessä, EE-ASA:ssa, oli mukana pinta-aktiivisia aineita, tavoitteenaan helpottaa emulgointiprosessia.

Emulgoitiin 34 stabilointiainetta kummankin ASA:n kanssa ja määritettiin emulsioista pH, partikkelikoko sekä visuaaliset ominaisuudet. Kaksikymmentä kiinnostavinta stabilointiainetta jatkoivat zeta potentiaali ja turbiditeetti mittauksiin. Emulsiopisaroiden tavoitekoko oli välillä 0,5-5 µm d(0,5) arvoina. Lisäksi tavoitteena oli, ettei kermoittumista, sedimentoitumista tai vaahtoamista neljän tunnin seuranta-ajanjaksona juurikaan esiintyisi. Yksitoista stabilointiainetta valittiin arkkikokeisiin, joissa käytetyt ASA-annokset olivat 1 kg/t ja 2 kg/t. Korkeimmat paperin hydrofobisuusarvot saavutettiin keskimolekyylipainoisella ja keskivaraustiheyksisellä 6.C-PAM:illa ja puhtaalla ASA:lla, polyvinyyli alkoholilla (PVA), ja EE-ASA:lla, sekä referenssitärkkelyksellä kummallakin ASA-liimalla. Puhtaan ASA:n havaittiin tuottavan hieman korkeampaa hydrofobisuutta kuin EE-ASA. Parhaat paperin hydrofobointiarvot olivat 21-23 g/m² paperiin absorboitunutta vettä. Paras kuivavetoindeksi saavutettiin kationisella tärkkelyksellä, noin 90 Nm/g ja EE-ASA:lla, paras märkävetoindeksi saavutettiin keskimolekyylipainoisella, keskikationisella polyamidiamiini-epiklorohydriinillä (PAAE) ja EE-ASA:lla, noin 65 Nm/g

Kuusi stabilointiainetta valittiin likaantumiskokeisiin, joissa käytettiin ASA-emulsioiden ja saostetun kalsiumkarbonaatin $CaCO_3$ (PCC) seoksia. Stabiileimman emulsion, parhaan liimauksen ja vähiten likaavan emulsion tuottivat referenssitärkkelys kummallakin ASA:lla, 6.C-PAM EE-ASA:lla ja PAAE puhtaan ASA:n kanssa. Keskimäärin kumpikaan ASA ei tuottanut toistaan huomattavasti vähemmän likaavia emulsioita, vaan kummallakin saavutettiin sekä hyviä että huonoja arvoja. Pintojen lian luonteessa oli huomattavia eroja. PAAE emulsioiden lika lähti helposti näytemetallilevyjen pinnoilta. Sen sijaan referenssitärkkelys emulsioiden lian irrottaminen olisi vaatinut kemiallisen käsittelyn liatuille metallipinnoille.

Kustannussäästöjä voidaan saavuttaa 6.C-PAM:lla, ja PAAE:llä. Tärkkelyksellä ei ollut juurikaan eroa kahden ASA:n välillä, 6.C-PAM:lla EE-ASA toimi paremmin ja PAAE:llä puhdas ASA tuotti optimaalisia tuloksia. PAAE:n positiiviset vaikutukset paperin märkälujuusominaisuuksiin tekevät kemikaalista kaupallisessa mielessä kiinnostavan.

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In Espoo, November 24, 2009

Jarno-Petteri Merisalo

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LIST OF ABBREVIATIONS

A-PAM	Anionic polyacrylamide
A-VAM	Polyamide derivative
AB	Acid-base
AKD	Alkyl ketene dimer
ASA	Alkenyl succinic anhydride
C-PAM	Cationic polyacrylamide
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$CaSO_4$	Calcium sulphate
CMC	Carboxymethyl cellulose
cmc	Critical micelle concentration
CO_2	Carbon dioxide
-COOH	Carboxyl group
DELSA	Doppler electrophoretic light scattering analyzer
DS	Degree of substitution
EE-ASA	Easy emulsifying alkenyl succinic anhydride
G-PAM	Glyoxylated polyacrylamide
GCC	Ground calcium carbonate
GGM	Galactoglucomannan
HCD	High charge density
HLB	Hydrophile-lipophile balance
HMW	High molecular weight
LCD	Low charge density
LMW	Low molecular weight
LW	Lifshitz-van der Waals
MCD	Medium charge density
MMW	Medium molecular weight
NaOH	Sodium hydroxide
-OH	Hydroxyl group
P-VAM	Polyvinyl amine
PAC	Polyaluminun chloride
PAAE	Polyamidoamine-epichlorohydrin
P-DADMAC	Poly diallyl dimethyl ammonium chloride
PCC	Precipitated calcium carbonate
PIT	Phase inversion temperature
PVA	Polyvinyl alcohol
SR	Schopper-Riegler
TGA	Thermal gravimetric analysis
TiO_2	Titanium dioxide
TNT	Trinitrotoluene
vdW	van der Waals

1 INTRODUCTION

Emulsions are used in all fields of chemical industry, food, pharmacy, cosmetics, agricultural and paper- and boardmaking among others. The emulsion properties and emulsion preparation are affected by the choice of continuous and discontinuous phases of emulsion, stabilizing substances, and surface active agents. In typical emulsions, the discontinuous phase drops are covered with stabilizing agents, called stabilizers. Stabilizers are nonionic or ionic polymers and microparticles. Emulsions can be optimized for specified use by selection of stabilizers. Molecular weights, degrees of substitutions and charge densities of stabilizers can affect the generated emulsion.

By modification of emulsion particle size, affected by shear force, shear time and preparation amount, the emulsification event can be optimized. Other control variables in emulsion preparation are, for example, concentration, pH and temperature. In papermaking, notable cost savings can be gained by a correct sizing agent and right sizing properties /1, 2/. It is defined as addition of the sizing agent to the stock in the wet-end of the paper machine before the wire section, to make paper more hydrophobic /3, 4/.

In literature part, for example, stabilizers, surface active agents, emulsions and emulsification techniques are discussed. The related theories are studied in order to adopt the information from other emulsion fields into the field of paper and board internal sizing emulsions. The impact of different surface active substances on sizing emulsion properties and functionality are presented. The internal sizing emulsions of Alkenyl Succinic Anhydride (ASA) are more widely examined in order to optimize the adjustability and cost-efficiency of commercial ASA in paper and board internal sizing. Comparison with other internal sizing agents, such as Alkyl Ketene Dimer (AKD) and rosin sizing agents are presented to understand better the pros and cons of the internal sizing agents.

In experimental study, two types of ASA's were used in emulsification experiments with over thirty stabilizers, including ionic and nonionic stabilizers and microparticle systems. The effects of stabilizer molecular weight or degree of substitution, charge density, presence of surfactants and emulsion particle size to the end product properties were all studied. Selected ASA-stabilizer emulsions were used for paper hand sheet preparation and hydrophobation, and to deposition tests with a specific device used by Lindfors /5/. The goal was to use experimental results in proposing ASA internal sizing systems for customers which’s other process conditions are known.

LITERATURE PART

2 EMULSIONS

The International Union of Pure and Applied Chemistry (IUPAC) defines *emulsion* the following way: "An emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible. Emulsions of droplets of an organic liquid (an oil) in an aqueous solution are indicated by the symbol O/W and emulsions of aqueous droplets in an organic liquid as W/O. In emulsions the droplets often exceed the usual limits for colloids size." /6/.

Another definition by Becher is: "An emulsion is a heterogeneous system, consisting of at least one immiscible liquid fully dispersed in another in the form of droplets, whose diameters, in general, exceed 0.1 μm. Such systems possess a minimal stability, which may be amplified by additives for example surface active agents and finely-divided solids." /7/.

Microemulsions are defined as a thermodynamically stable emulsion, while macroemulsions are not thermodynamically stable /6/. The thing that makes a liquid-liquid dispersion an emulsion is the fact that one immiscible liquid is dispersed in another, stabilized by a third component, called emulsifying agent /8, 9/.

Emulsions can be divided in two categories, two-phase emulsions and three or more-phase emulsions, of which W/O, O/W, W/O/W and O/W/O are examples /10/. Further on, emulsions can be divided based on discontinuous phase particle size, nano or mini- (10-100 nm), micro- (100-1000 nm), and macro- (0.5-100 μm) emulsions. Other divisions are based on the emulsion preparation process, low shear, high shear, high energy and ultrasound emulsification, or on field of use, for example, cosmetic, medical, agricultural, petroleum, food or papermaking emulsions /11/.

2.1 Properties

Important emulsion properties are emulsion particle size, stability, charge, pH and temperature. Charge and temperature dependence are typical characteristics in macroemulsion. Stability is affected by controlling temperature, pH and by selection of component charges. The particle size is the most important single property of an emulsion. Particle sizes are expressed as particle size distribution that can be labeled as monodisperse, polydisperse, symmetrical or asymmetrical, unimodal or polymodal. With microemulsions the situation is somewhat different due to the very small particle size and the same division does not apply. While particle size is related to drop surface area, it has a major effect on reactivity and stability. In general, the smaller the drop, the higher viscosity exists in the emulsion. Particle size, or droplet diameter, of an emulsion is usually not completely uniform. This is why particle size distributions are used. The particle size of an emulsion is affected by the amount and time of shear during emulsification and by the choice of stabilizer. From Figure 1, typical emulsion particle sizes and appearance can be seen. /7, 12/

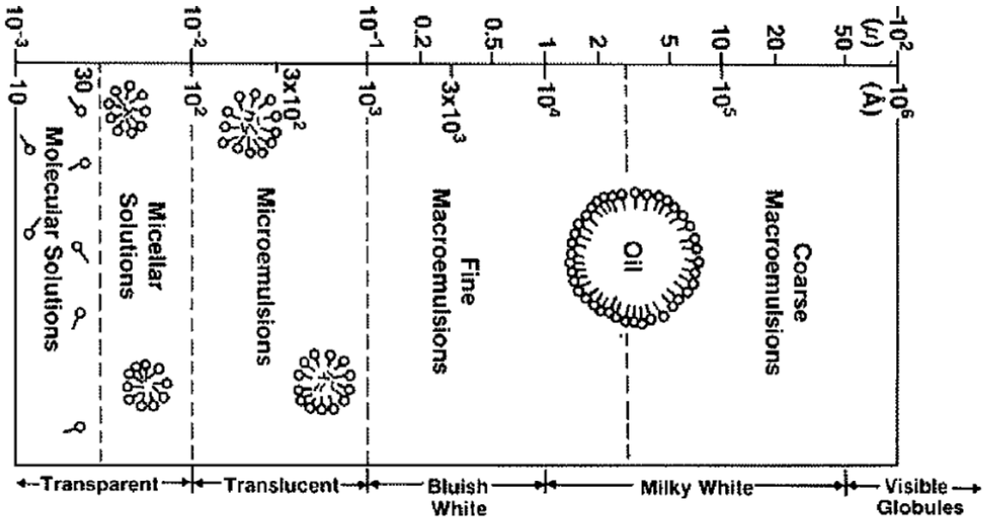

Figure 1. At the top, the dimensions of dispersed phase for liquid-liquid dispersions in µm, and at the bottom, the typical dispersion appearance in emulsions, can be seen. In the center are schematic drawings of stabilized emulsion oil drops in water /13/.

The particle size distribution is a result of emulsification and thus has important information about the emulsion properties. If 10 m^3 of oil is emulsified to the drop radius of 1 µm ($1x10^{-6}$ m), the total interfacial of area created is $3x10^7$ m^2, while the unemulsified oil surface area is 22.4 m^2. The increase of surface area is over million fold, adding the significance of the surface and interfacial properties /7/.

The particle size characterizes many properties of emulsion: viscosity, solubility, reactivity, and emulsification all depend on particle size. This is because emulsions are prepared by breaking drops and *coalescence*, i.e. the disappearance of the boundary between two particles, which can be droplets or bubbles in contact. This can also occur with the disappearance of boundary between a particle and a bulk phase followed by changes of shape. Coalescence leads to a reduction of the total surface area. The flocculation of an emulsion, the formation of aggregates, may be followed by coalescence /14/.

2.2 Interfaces and surface interactions

When two immiscible liquids are placed in contact, an *interface* is formed /15/. Since changes in emulsion appearance and properties occur in emulsion phase interfaces, the surfaces, forces, and charges between them are discussed. Surface tension is defined by the equation 1. A force F moving liquid surrounded by a plate CD at the length of Δd from point CD to C′D′, requires a work *w* done on the liquid for the movement. The force *F* is balanced by a counter-force operating along the length CD. If γ is defined as the force in Newtons per meter acting along this length, *Δd*, the force opposing the expansion of the film is $2\gamma l$. The surface tension γ can be defined as the work needed to generate a surface (Figure 2).

$$w = F\Delta d = 2\gamma l\Delta d = \gamma\Delta S \Leftrightarrow \gamma = \frac{w}{\Delta S} \tag{1}$$

Where,

w = is the work done for moving the plate [Nm].
F = is the force required for the moving work [N].
Δd = is the distance the plate moves [m].
γ = is the surface tension [N/m].
l = is the length of flank AB, CD and CD′ [m].
ΔS = is the surface area the plate movement outlines [m^2].

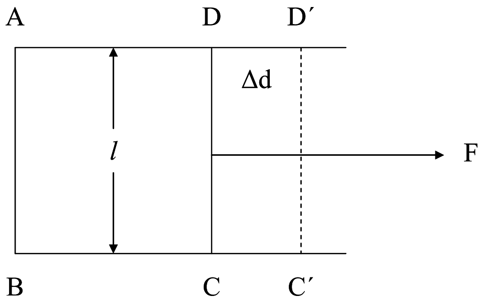

Figure 2. The physical definition of surface tension /7, 16/.

While surface tension only relates to surfaces between a liquid and a gas, the concept of *interfacial tension* describes also the boundary tensions existing between two liquids and between a liquid and a solid phase. Adhesion between two substances or particles is defined as the work that needs to be done to separate two surfaces from one another. The force resisting the separation work between two different material surfaces is called *adhesion*. Work of adhesion and free energy of adhesion are defined in equation 2. Illustration of adhesive forces is given in Figure 3. /17, 18/

$$
\begin{aligned}
W_A &= \gamma_1 + \gamma_2 - \gamma_{12} \\
\pi_L &= \gamma_l - \gamma_{lv} \\
W_A &= W_A^* = \pi_1 + \pi_2
\end{aligned}
\tag{2}
$$

Where,

W_A	is the work of adhesion [J/m^2].
γ1	is the interfacial tension of surface 1 [J/m^2].
γ2	is the interfacial tension of surface 2 [J/m^2].
γ12	is the interfacial tension shared between surfaces 1 and 2 [J/m^2].
πL	is the liquid pressure [Pa].
γl	is the interfacial tension in the liquid [J/m^2].
γlv	is the interfacial tension in liquid-vapor interface [J/m^2].
WA*	is the work of adhesion with vapor pressure [Pa].
π1	is the partial pressure of surface 1 [Pa].
π2	is the partial pressure of surface 2 [Pa].

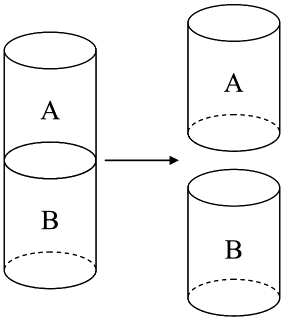

Figure 3. When cylinders A and B of pure liquids are pulled apart from their mutual interface, work equal to the work of adhesion W_A is required.

When a drop of liquid is dropped onto a smooth surface, adhesive forces affect between the solid and the liquid phase. If these forces are greater than the internal adhesion keeping the liquid together, the drop will spontaneously spread and perfectly wet the surface. In a balance between the adhesion of liquid and solid and the liquids internal adhesion, the drop forms a contact angle at the phase interface (Figure 5) /4, 5, 17, 19/. In solid-liquid interfaces the liquid can spread in three different ways on top of a surface. These are: forming a contact angle with the surface, spreading completely on the surface, or adsorbing onto the surface and then forming a contact angle (Figure 5). *Adsorption* is an accumulation of a substance onto a surface /3, 15/. A contact angle is formed if the spreading of a liquid on a solid is not complete. The more hydrophobic (i.e. water resistant) the surface is, the bigger contact angle water drop forms with the surface.

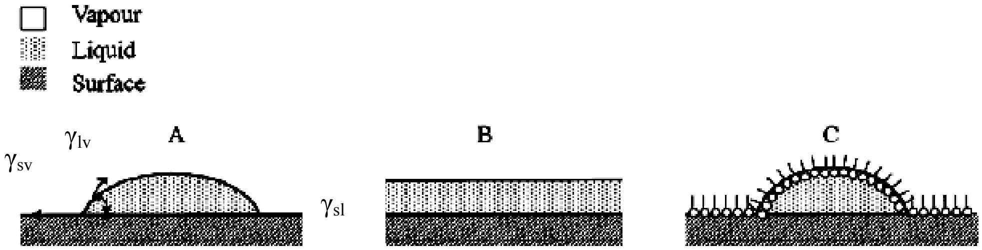

Figure 4. The three spreading ways of a liquid on a solid surface: A; the liquid does not wet the solid surface but forms a finite contact angle on the surface, B; the liquid wets the solid surface completely forming a separate layer with the surface, C; some of the liquid molecules adsorb onto the solid surface but others form a contact angle./20/.

In a case that a finite contact angle is formed, the equilibrium balance between the interfacial tension of the solid surface, liquid drop, and the vapor phase is expressed with Young's equation (equation 3) /21/.

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{3}$$

Where,

θ	is the definite contact angle between liquid and solid phase [°].
γ_{sv}	is the interfacial tension between solid-vapor interface [N/m].
γ_{sl}	is the interfacial tension between solid-liquid interface [N/m].
γ_{lv}	is the interfacial tension between liquid-vapor interface [N/m].

Between the different particle systems and interfaces in emulsions, attractive and repulsive forces are seen. These forces are electrostatic, or van der Waals (vdW) forces. The vdW forces are interactions between absorbed molecules and hydrodynamic forces /15/. The net attractive forces operating on a molecule in the interface are a combined effect of vdW interactions and the individual surface tensions of the two liquids. This is expressed in the theory of diffuse layer, which states that the layer forms from free ions in the fluid under the influence of electric attraction and thermal motion. In emulsions, intermolecular interactions can be divided into three groups, short-range repulsion between electron orbitals (Dorn repulsion), Lifshitz-van der Waals (LW) interactions, and Lewis acid-base (AB) interactions.

Dorn repulsion indicates itself in the incompressibility of liquids and solids. LW forces occur between all atoms and molecules and are due to the permanent and transient dipole moments created by the distribution and movements of electrons in the molecules. They are attractive and decrease with distance. AB forces interact between electron donor groups in one molecule and electron accepting groups in another. The influence of different functional groups on the adhesive properties of surfaces can be explained with AB interactions. /16/

Two surfaces in contact attract each other due to the LW forces. Because work is required to separate the surfaces, the aggregated state is thermodynamically more stable than the dispersed state. If the surfaces are separated in a liquid, the situation is different. If the liquid wets the surface completely, the particles can emulsify spontaneously. However, the fluid between the surfaces tends to reduce the attraction of the surfaces, being unable to generate colloidal stability. Stable colloids (i.e. 0.01-1 μm size material) can be prepared in many liquids which do not reduce attraction to zero. The repulsive and attractive interactions are additive properties. Depending on the range and strength of the interactions, different situations occur.

The vdW interactions are very strong at short distances and quite significant at distances of relevance to colloidal stability. An important property of the vdW forces is their universality. If the particles are set in a medium, the interactions distance dependence does not change, but the magnitude of the forces are reduced due to the vdW interaction between the liquid and the particles. vdW forces can be divided into three specific types: Keesom forces, acting between two dipoles, Debye forces, acting between a dipole and an induced dipole, and London forces, acting between two induced dipoles. /15/

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability assumes that the van der Waals forces between surfaces are independent of electrolyte concentration and particle charge, and that the electrostatic interactions are solely due to diffuse double layer interactions in a solution /16/. Due to the charge neutrality in an electrostatic double layer system, the charge balance develops between the charges on the surface and the free ions in the solution. Equilibrium is developed between the attraction of the counter ions to the surface and the diffusion away from the surface. The result is a potential difference between the particle surface and the neighboring liquid /15/. The potential differences at the given distances from the particle surface are called layers (round the particle).

When fine particles are dispersed in water, an electric charge is developed on the particle surface. The origin of this charge can be one of the three following; ionizable groups on the particle surface (for example -COOH), isomorphous substitution in the crystal lattice (faults and lattice disturbances), or adsorption of ions at the interface. The electrostatic attraction is a consequence of the surface charges whereas the vdW forces depend on the chemical nature of the solid phase. The counter ions at the charged surface are affected by three forces: electrostatic attraction, vdW forces and thermal movement. The interactions that influence colloidal stability are long-range compared to the interactions that govern the adhesion between surfaces in molecular contact. Typical distances range from 1 nm to 100 nm /15/.

In emulsions, their viscous properties change during time. In aggregated emulsions, the aggregate size increases over time because of the thermodynamical instability. These aggregates immobilize liquid from the continuous phase within the voids between the drops. Macroemulsions are practically never monodispersed, so that one phase would be perfectly mixed into another /13, 22/. Non-uniform drop size (i.e. particle size distribution) influences rheological properties. Hydration of the stabilizer and/or surface-active substance layer adsorbed around the oil drops in an emulsion will also influence the rheological properties. If the stabilizer is hydrated on the emulsion oil drop, the stabilizing effect can be lost. The high electric field strength at the particle surface leads to adsorption of water molecules and to an apparent increase in drop radius. The addition of electrolyte alters the degree of hydration. Then the effective thickness of the hydrated adsorbed stabilizer layer decreases, as the electrolyte concentration increases. /22/

2.3 Surfactants

Surfactants are surface active substances with various tasks in surface chemistry. In literature, the word emulsifier is commonly used in referring to any substance giving stability on emulsion discontinuous phase droplets or making the emulsification easier by lowering surface energies /6, 8, 9/. The problem arises when more than one chemical is used for the purpose at the same time. To avoid confusion in this study, the word *surfactant* is used when referred to surface active agents and word *stabilizer* is used when referred to those stabilizing agents used on the emulsion oil drop alone. Another categorization in literature is presented by Chen /2/.

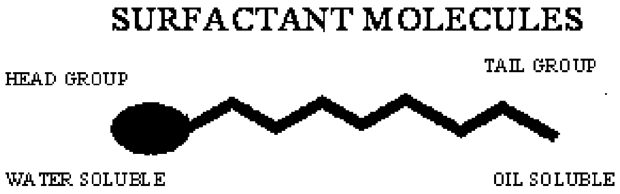

Figure 5. Schematic picture of a surfactant with hydrophilic head group and hydrophobic tail groups /23/.

Surfactants have dualistic amphiphilic character, which means one end is hydrophilic and the other hydrophobic (Figure 5). Surfactants adsorb at the interface between two phases of emulsion due to their amphiphilic molecular structure. They reduce the surface free energy required to increase any interfacial area by lowering the interfacial tension and allowing the finely dispersed media to easily be created /24, 25/.The phase diagram of a surfactant in emulsion is presented in Figure 6.

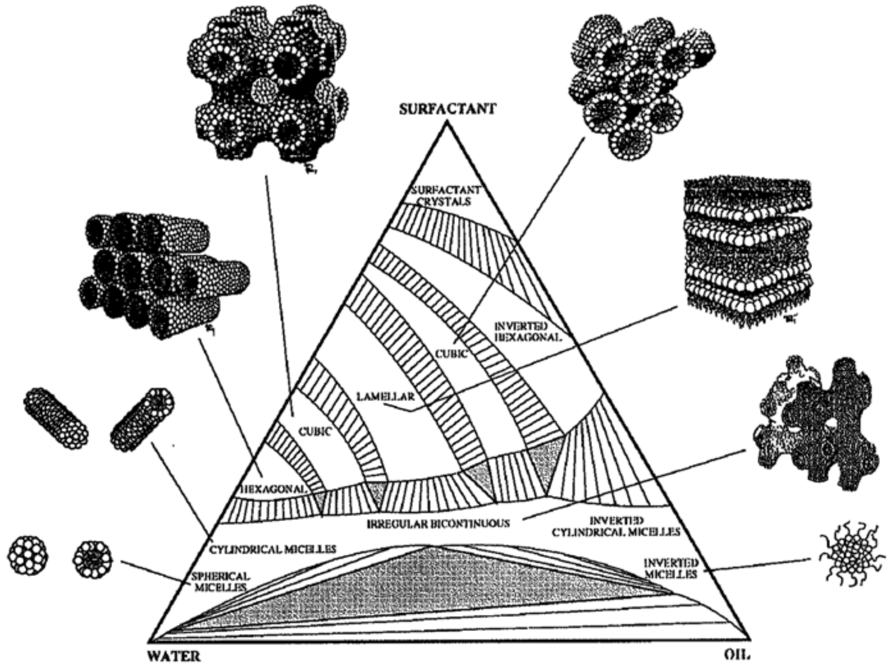

Figure 6. Schematic phase diagram of surfactant, oil and water systems. Outside the composition triangle, surfactant nano and microstructures in various phases are indicated /23/.

The surfactant degree of hydrophilicity or hydrophobicity is expressed by the hydrophile-lipophile balance (HBL), lipophile meaning hydrophobic. Emulsion surfactants can be characterized by their HBL value. The scale goes from 0 to 20. In general, values above 7 refer to hydrophilic surfactants and those below 7 to hydrophobic ones. The difference of surfactants is generally expressed by the HLB number, with the more oil soluble surfactants having low value and the more water soluble ones having high value of HLB /26/. This index is used to describe emulsion stability with many types of surfactants in all kinds of emulsions. /13, 27, 28/

For nonionic surfactants in general, a ratio between the hydrophilic saponification number and hydrophobic (lipophilic) acid number is in use to determine the HLB number. Specific equations exist, for example for, fatty acids and surfactant mixtures based on emulsion droplet coalescence. A logarithmic HLB scale for mole fractions of surfactants with many other group-specific methods, have been developed because the HLB number is an empirically defined quantity. A summarizing table of the HLB number effect on different surfactants is presented (Table 1). /7, 13, 15, 17/

Table 1. HLB number ranges and their application /7/

HLB number range	Application
3-6	W/O Emulsifier
7-9	Wetting Agent
8-18	O/W Emulsifier
13-15	Detergent
15-18	Solubilizer

- The size of emulsion droplets depend on the temperature and the HLB number of surfactants.
- The droplets are less stable toward destabilization close to the PIT.
- Relatively stable O/W emulsions are obtained when the PIT of the system is some 20 °C to 65°C higher than the storage temperature.
- A stable emulsion is obtained by rapid cooling after formation at the PIT.
- Optimum stability of an emulsion is relatively insensitive to changes of HLB value or PIT of the surfactant.
- Instability is very sensitive close to the PIT of the system.

Phase inversion temperature (PIT) is the temperature where a nonionic or ionic surfactant changes its appearance (Figure 7). The PIT of surfactants is influenced by the corresponding HLB value. The phase difference in emulsions exists mainly because of the difference in isotropic characteristics between the phases. The following conclusions can be made about the PIT /29/:

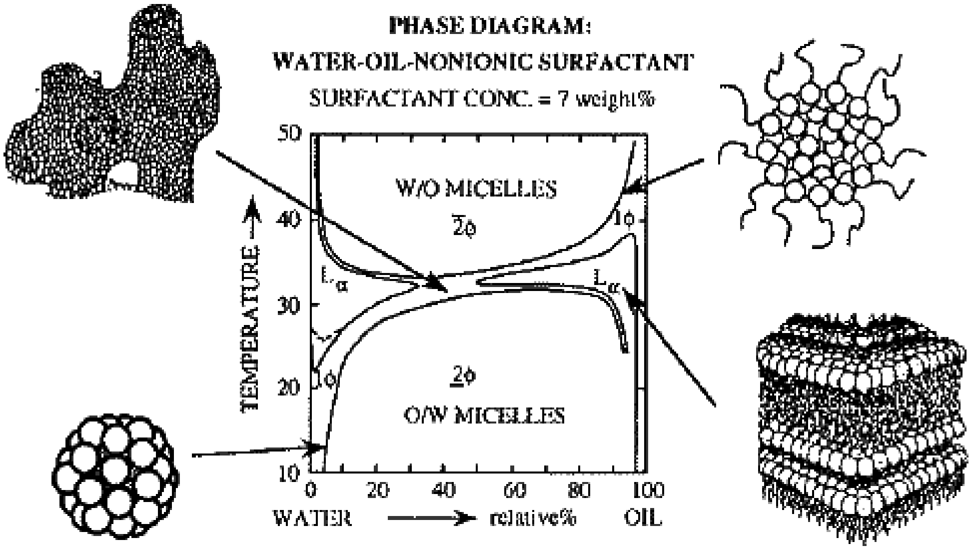

Figure 7. Phase diagram of $CH_3(CH_2)11O(CH_2CH_2O)5H$ (or$C_{12}E_5$), n-octane and water. Schematic drawings of different surfactant aggregates shape development in various points and phase transition can be seen /23/.

At the temperatures near the PIT, high solubilization of surfactant particles occur and the emulsion particle size may become very small if much surfactant is present, even with just a gentle stirring. The dependence of HLB and PIT leads to the conclusion that the addition of salts reduces the PIT and thus a surfactant with a high PIT value is needed in the presence of electrolytes (i.e. substance containing free ions) in order to obtain a more stable emulsion /29, 30/. An example on the presence of electrolytes can be taken from papermaking. ASA compound and Ca^{2+} ions can both be seen in paper and board machine water system. Hydrolyzed state ASA compound has lost its stability brought by a stabilizer and/or surfactant on its surface. In this state, ASA easily forms ASA-Ca^{2+} salt, affecting the process cleanliness and runnability. ASA-Ca^{2+} complexes are seen in deposit tests with various emulsions.

Surfactant head group surface area divided with the surfactant tail group surface area has significant effect on the stabilization efficiency of a surfactant /31/. This ratio defines the surfactant hydrophilicity or hydrophobicity. The relative size or the surface area of the head group (Figure 5) and the surface area of the tail group turns the overall nature of the surfactant roughly to either hydrophilic or lipophilic and the outcome can be determined by HBL number.

Surfactants in emulsions can form spontaneously larger ordered structures. This results because in an aqueous surfactant solution, the properties change quickly around a relatively small concentration range. Stable aggregates are formed if large enough monomers come together forming a *micelle* of 15-100 surfactant monomers /16/. Micelles form above a certain concentration limit called the critical micelle concentration (cmc) (Figures 6 and 7). While the thermodynamic properties such as surface tension and continuous phase activity change slowly above this concentration, a rapid increase in turbidity, (i.e. the light scattering properties of an emulsion), is seen. Turbidity increases with decreasing emulsion particle size /2/.

Above cmc large aggregates of micelles are formed and the aggregation process is cooperative. Most of the surfactant added in excess of cmc is incorporated into the micelles. The monomer concentration increases very slowly, and the chemical potential of the surfactant is almost constant above the cmc. When the concentration of cations increases, micelle formation is promoted and any addition of electrolyte also lowers the cmc. /16/

When an emulsion of a nonionic surfactant, or stabilizer, and hydrocarbon in water is heated, the emulsion becomes visibly turbid at a temperature known as the cloud point. At this temperature or slightly higher, the emulsion separates into a surfactant and/or stabilizer rich phase and to a water rich phase. Conversely, if the emulsion is cooled, a temperature called the haze point exists. Below the haze point, an oil-rich phase and a surfactant rich phase form. In the case of O/W emulsions, shorter surfactant chains enhance solubilizing power for a given length of surfactant hydrocarbon chain. In the case of W/O emulsions, inverse micellar phenomenon is seen (Figures 6 and 7). If the temperature of O/W emulsions is increased after reaching the cloud point, the surfactant phase coalesces with the hydrocarbon phase to form a W/O emulsion and the PIT is reached. /32/

2.4 Stabilization

Macroemulsions are thermodynamically unstable systems and thus aggregation occurs. For this reason, emulsion oil droplets must be stabilized using stabilizers and/or surfactants. Reasons for stability are related to emulsion droplet collision frequency and to emulsion energy barrier. In collision frequency, the colloidal particles (i.e. stabilizer and emulsion oil drops) can collide so rarely that the rate of aggregation becomes negligible. This cause is valid only in very dilute emulsions. The second case is relevant if there is an energy barrier which prevents particles from transferring to the thermodynamically more stable (aggregated) state. Then aggregation will not occur. Energy barrier can cause stability if repulsive interactions in emulsion are weaker than attraction at short distances, but stronger than attraction at intermediate distances /15, 16/. According to Abismail, emulsion stability depends on /24/:

1. Emulsion droplet size.
2. Density difference between emulsion dispersed and continuous phases.
3. Viscosity of the emulsion continuous phase.
4. Electrostatic and or steric repulsion between emulsion droplets. Stabilizers and surfactants have significant effect on these repulsions.

In macroemulsions, emulsion droplets can be stabilized against coalescence by polymers, surfactants or by nano- and microparticles. Stabilizers are non-surface active macromolecules added to increase the viscosity of the continuous phase and to reduce the mobility of droplets in order to prevent them from breaking up the emulsion – a phenomenon called *demulsification* /7/. After a viscosity increase, the droplets become cylinder-like and eventually lamellar (Figure 7). Stabilizers make emulsion stable sterically, electrostatically or by small particle stabilization which is one type of steric stabilization. Surfactants can be used solely or with stabilizers. The effect of surfactants is usually dualistic, they can have the stabilizing effect on the emulsion oil droplets, but at the same time, they ease the emulsification process itself /25/. Copolymers are another option to use with the actual stabilizer. Copolymers as well as other stabilizers and surfactants are not always but often synthetic. /16/

Steric stabilization, also called protective colloidal effect, is the general term for the stabilization of colloidal particles with non-ionic, soluble, polymers. If a particle or droplet surface is covered with a polymer which extends into the emulsion continuous phase, the polymer segments prevent the adhesion of the particle to other particles. The polymeric layer functions as a steric barrier against aggregation. When charged stabilizers are used for stabilization, the electrosteric stabilization is in question.

Polymers used as steric stabilizers should adsorb so strongly to the emulsion discontinuous phase surfaces that they do not desorb even when subjected to the shear forces occurring when particles collide (Figure 8). Other extensively used steric stabilizers than polymers are hydrophobically modified polysaccharides /33/. With this stabilization mechanism, the solubility of the adsorbed polymer chains is significant for the stability of the emulsion. The stabilization changes the behavior of the contact surface. /16/

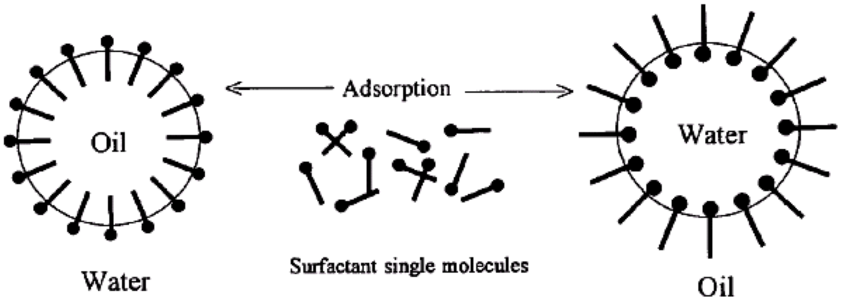

Figure 8. At left, oil-in-water emulsion (O/W), surfactant tails form the core of an aggregate; at right water-in-oil emulsions (W/O) the heads of the surfactants are in the core /34/.

A *Pickering emulsion* is an emulsion stabilized by nano or micro scale solid particles which adsorb onto the interface between the water and oil phases (Figure 9) /35/. When oil and water are mixed, small oil droplets are formed and dispersed throughout the water. Eventually the droplets will coalesce to decrease the amount of energy in the system. However, if solid particles are added to the mixture, they will bind to the surface of the interface and prevent the droplets from coalescing, causing the emulsion to be more stable. Hydrophobicity, shape, and the size of the particles can all have an effect on the stability of the Pickering emulsion. It is thought that the presence of solid particles at the liquid/liquid interface plays an important role in preventing the thinning of the liquid film between the droplets. Solid particles should form a continuous one-particle-thick film onto emulsion discontinuous phase droplet. This is why rough, asymmetric particles like bentonite are more efficient than smooth spherical silica particles in this task. /29, 36, 37/

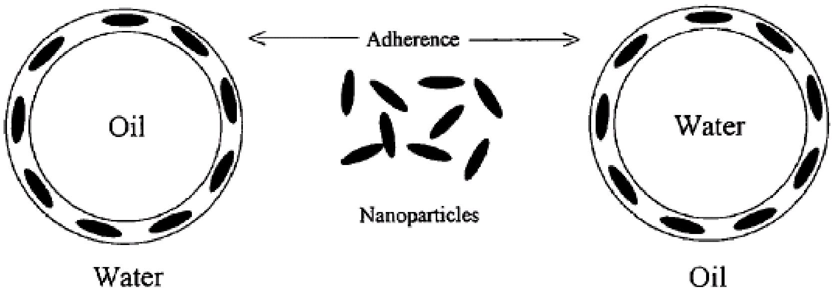

Figure 9. If nano- and microparticles with diameters ranging from 8 nm to 500 nm are used, instead of adsorption the particles adhere in the phase interface. At left, oil-in-water (O/W) emulsions, at right water-in-oil (W/O) emulsion /34/.

Surfactants may stabilize the emulsion discontinuous phase droplets in four ways /16, 25/. In the first case, the surfactant may be nearly insoluble and remain crystalline without swelling much with water. This is usually at a temperature well below the melting point of the surfactant. In the second case, the surfactant may dissolve readily in water. Dissolution is accompanied by surfactant spontaneous forming of micelles.

The third case is that the hydrophobic chains are oriented inward and the polar end groups form a hydrophilic shell (Figure 8). Surfactant micelles have the capacity to dissolve water-insoluble compounds inside of them. At concentration exceeding solubility, lyotropic liquid crystals, called mesophases are formed. These consist of rod-like or lamellar surfactant aggregates that are organized into defined structures (Figure 6). Although the aggregates show long-range ordering, they are flexible, and the surfactants are still mobile within the aggregates.

The fourth case is with very hydrophobic surfactants, which do not dissolve in water at all. However, when contacted with water at temperatures above their melting point, they may form aggregates in which an aqueous core is surrounded by a surfactant layer. These aggregates are called inverted, or *reverse micelles* (Figures 6 and 7). They also form a reverse hexagonal liquid crystalline phase in which the micelles have grown to infinite rods arranged in a hexagonal shape forming a lattice (Figure 6).

The stability is a balance of attractive and repulsive interactions at interfaces. The same interactions stabilize thin liquid films in foams between emulsion droplets and on solids. They are affected by adsorption of stabilizers and/or surfactants, ionic strength, dissolution and temperature. The stability of macroemulsions is independent of the nature, size, and shape of the particles in emulsion and dependent only on the interaction of the stabilizer with continuous phase temperature. /15/

Stabilizers and/or surfactants on emulsion discontinuous phase droplets can be differently saturated. This means that the surface coverage of the droplet by the stabilizer can be incomplete, complete, or over-filled. The surface coverage has an influence on the operations of the stabilizer and the behavior of the flock formed. The charge of the stabilizer polyelectrolyte also has an effect, whether it is high, medium or low charged, cationic or anionic.

2.5 Destabilization

Aggregation, in which terms *flocculation* and *coagulation* are also used, takes place in emulsions. Particles of discontinuous phase form larger complexes called aggregates /38/. Depending on the formulation process of an aggregate, it is given the more specific name of floc or coagulant. Coagulation is an aggregation phenomenon occurring due to the loss of stability in emulsion. The complete distinction between flocculation and coagulation is impossible because of many causative mechanisms, thus the general term aggregation is used. Regarding the distinction between aggregation and *coalescence*, one can roughly say that coalesced emulsion can be returned in the mixed emulsion state by applying shear (manual shaking), in it but to aggregated emulsions this makes no difference. Aggregation mechanisms are charge neutralization, electrical double-layer compression, patch model, bridging and complex flocculation /39/.

Figure 10 shows the destabilization events in emulsion /29/. Flocculation and creaming, for example, can occur simultaneously /40/.The deformation and flow of an emulsion depends on continuous and discontinuous phase rheological properties, meaning the viscosity of water and oil phase. The reason oil phase is used in the form of an emulsion rather than in its original state is the much wider range of flow characteristics and consistencies that can be achieved in an emulsion.

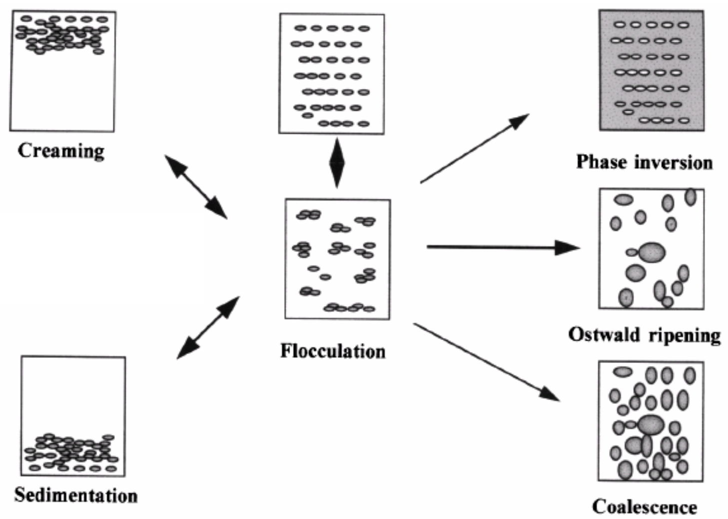

Figure 10. The destabilization phenomena in an emulsion. In the center up, stable O/W macroemulsion which flocculates due to the thermal instability during time causing one or many of the five changes in emulsion /24/.

According to DLVO theory, vdW attraction forces are the driving forces for coalescence and destabilization of an emulsion. For sterically stabilized emulsions the vdW interactions can be neglected if the whole oil droplet surface is completely saturated (i.e. covered with stabilizer), and if the molecular weight of the separate stabilizing chain segments is high /15/. Table 2 summarizes the effect of different parameters on colloidal interactions in emulsions according to the DLVO theory.

Table 2. Factors affecting colloidal stability in emulsion according to DLVO theory /16/

Parameter	The effect of parameter value increase on colloidal stability
Surface charge density increase	Increases
Electrolyte concentration increase	Decreases
Counter-ion valence difference	Decreases
Hamaker constant increase (vdW particle interactions)	Decreases
Temperature increase	Decreases or Increases
Dielectric constant of the solvent increase	Increases

Sedimentation and *creaming* is seen in phases with density differences. Aggregation occurs when droplets stay very close to one another for a far longer time than they would in the case with no attractive forces acting between them. Coalescence is seen when a thin film of continuous phase between two closely approaching droplets break. Laplace pressure, the pressure difference between inside and outside of the emulsion oil droplets, then causes the droplets to rapidly fuse into one droplet. If the droplets contain solid particles because part of the liquid in the droplets has frozen, full coalescence may not occur. In this case the terms clumping or partial coalescence are used. /27/

Particles forming an emulsion undergo irregular thermal back and forth movement called *Brownian motion*. It is caused by the molecules of the discontinuous phase that are bombing the emulsion particles. This phenomenon is seen with small particles in emulsion. Brownian motion increases the inter-particle collision probability, i.e. coagulation risk and destabilization of nano- and microemulsions and also small droplet sized macroemulsions. /7/

Five interactions play important roles in instability over time, leading to emulsion destabilization – a phenomenon called *coarsening* process /41/. These interactions are:

1. vdW forces between neighboring particles or droplets. Such interactions cause film instability during the late film drainage state.
2. Random mechanical forces exerted on dispersed particles by Brownian motion.
3. Capillary forces causing the further relaxation of a dumbbell-like particle to a sphere.
4. Buoyancy, resulting from the different gravities of two components that can be neglected for systems with little difference in density. Buoyancy makes the particles move directionally and causes the formation of a gradient of particle size distribution.
5. Friction resulting from viscous flow that is induced by the vdW, Brownian, capillary, and buoyancy forces.

When the repulsive energy is low, particle collisions will lead to aggregation, or more specifically coagulation. If there is no repulsive barrier (i.e. stabilizer) at all, coagulation can take place within seconds. In most cases the barrier is not high-energetic enough to completely prevent the aggregation. These types of emulsions coagulate slowly. The change in repulsive energy depends on the temperature, nature of the adsorbent on the surface, ionic strength, solvent, and stabilizer particle charge. These offer the possibility to control aggregation and stability by appropriate choice of parameters.

When coagulated gas bubbles (liquid droplets or foams in the emulsion) join together to coalesce forming larger bubbles or droplets, the total surface area of particles decreases. The surface energy of the system decreases, establishing an important driving force for the removal of particles. An indication of the driving force of the particle removal is called *Ostwald ripening* (Figure 10). Few emulsion droplets grow in size, at the cost of majority shrinking and disappearing /42/. It involves diffusion of discontinuous phase material from smaller to larger droplets due to the chemical potential of the material being higher for a smaller radius of curvature. Ostwald ripening does not occur if the solubility of the continuous phase droplets is insignificant. /16, 27/

A sterically stabilized emulsion cannot be destabilized by adding electrolyte, unless the stabilizer is desorbed from the emulsion oil droplet surface at the same time. Aggregation can be done by reducing the solubility of the polymer in the continuous phase. In this case, a collapse of the polymer conformation is achieved and the stabilizing effect is lost. The simplest way to aggregate macroemulsion droplets is to change the temperature of the solvent. When the solubility is reduced, there is a sharp transition from long-term stability to instability in the emulsion. Depending on the types of interaction which exist between the liquid state and the adsorbed stabilizer, instability can arise either through cooling or heating of the emulsion. The strong temperature dependence is characteristic for sterically stabilized emulsions and it separates them from the electrostatically stabilized ones, which are relatively insensitive to the temperature conditions. /15/

The mean emulsion droplet size of a stabilized system is determined by the balance between droplet breakup and the coalescence. Under shear forces, the interfacial forces are insufficient to balance the viscous forces leading to the droplets bursting. This can be compensated by the adsorption of surfactant if it is used. The surfactant adsorption lowers the interfacial tension between emulsion oil droplets and stabilizer. This reduction leads to decreasing of the stress needed to deform or break emulsion droplets. Changes in emulsion rheology, in interfacial elasticity, caused by transport of surfactant between bulk solution and interface, will influence the kinetics of the break-up process. /31/

In a mixture of microparticles as stabilizers and surfactants in an emulsion, surfactants can cause flocculation. This phenomenon is called surfactant induced flocculation. Synergistic stabilization of an O/W emulsion occurs when cationicized nanoparticles are mixed with the anionic surfactants in water. At conditions of maximum particle flocculation in the water phase, for which particles have zero charge, emulsion is most stable against both creaming and coalescence. Particle flocs are shown to adsorb onto emulsion oil droplet interfaces. /43/

2.6 Emulsification process

To create an emulsion, an oil phase, a water phase and a stabilizing ingredient are needed. Stabilizing ingredient can be stabilizer polymer, stabilizer microparticle, surfactant, or both stabilizer and surfactant. Usually shear forces are also needed. After a period of time in which the mixture of the continuous and discontinuous phases has been subjected to a shear, the immiscible discontinuous phase is scattered to small droplets into the continuous phase. This is how a two-phase, O/W or W/O, emulsion is formed. The formulation process is called emulsification /25/. Emulsification methods are divided between those with mechanical and non-mechanical processes. The need of shear amount and time as well as the need of additional surfactant varies between emulsion systems. The processes involved in emulsification can be seen in Figure 11.

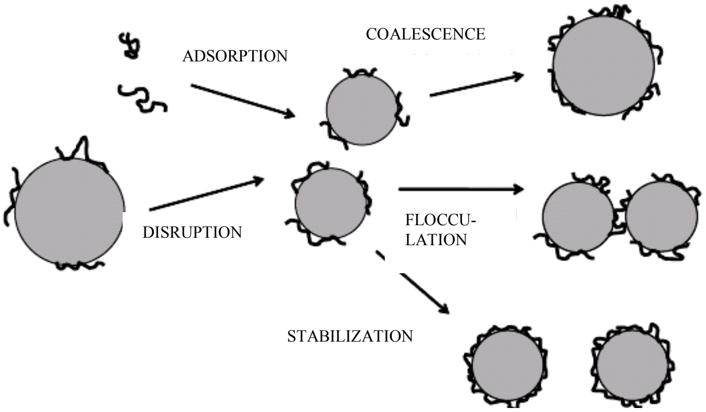

Figure 11. Physico-chemical processes involved in emulsification of oil droplets in water phase with stabilizer /44/.

Stabilization of fine droplets requires mechanical deformation of coarse droplets accompanied by rapid effective adsorption of stabilizer and/or surfactant at the new oil-water interface. Collision of droplets with insufficient coverage of stabilizer and/or surfactant leads to flocculation and coalescence or one of these events /44/. The emulsification process of macroemulsions include two steps: first, shear stress leads to droplet deformation which increases their specific surface area up to disruption. Second, the new interface is stabilized by stabilizer and/or surfactant /45/. Three droplet deformation mechanisms can be distinguished. These include shear forces in laminar flow, shear forces in turbulent flow and inertial forces in turbulent flow /46/. In the mechanical emulsification process devices are used to create the desired shear, whereas in non-mechanical processes no devices are needed.

Spontaneous emulsification can be seen with some substances when a proper amount of oil phase is diluted in water with little or no mechanical agitation used. There are three common mechanisms for spontaneous emulsification and they occur only one at a time. The first mechanism for spontaneous emulsification is due to interfacial turbulence and includes surfactants. Local variations in interfacial tension are caused by random statistical variations in the diffusion of the stabilizers and surfactants to the interface. These variations cause effective spreading and turbulence at the interface by a process similar to the *Marangoni effect*, that is, the mass transfer along an interface due to the surface tension gradient /47/. Spreading and turbulence result in droplets of one phase being trapped in the other layer.

The second and most common spontaneous mechanism is called diffusion and stranding. It is an example of a system with no surfactants. In this process a material that dissolves in one phase but is more soluble in the other, diffuses into the second phase. As it does, it carries along some of the components of the first phase which are insoluble in the second phase and are therefore stranded there in the form of drops.

The third mechanism postulates the existence of negative interfacial tensions. If the interfacial tension between two phases becomes negative, the surface area between them must increase because of thermodynamics. A system with a negative interfacial tension at equilibrium would be a solution rather than an emulsion. An emulsion, however, could still result if the negative interfacial tension is transient or becomes positive as the surface area increases. /48/

Few other non-mechanical processes in emulsification exist. One is based on the precipitation of the dispersed phase previously dissolved in the external phase. Changes in the phase behavior of the substances to be emulsified prompted by variation of temperature of composition are used to achieve the desirable dispersed state of the system. Another process is PIT method, which relies on the temperature effect on macroemulsions.

When heated up, a macroemulsions inverts its phases from O/W to W/O (Figure 7) /49/. The formation of nano- and microemulsions can also occur spontaneously. In this case, the discontinuous phase itself acts as a stabilizer and the result is nano- or microemulsion. The inner state disperses into nano-size droplets within the outer phase. Nano-sized droplets form and emulsify within the water /48, 50/.

2.7 Emulsification equipment

Introducing shear forces into macroemulsions and causing the discontinuous phase to break into small droplets can be done with various equipments. Different fields of emulsion uses have very different preferences on emulsions stability, emulsion amounts produced, and on the preferred properties. Some emulsions need to be hygienic; some can be toxic or even explosive. Some are meant to destabilize in a right moment and others should remain stable for years. Traditional and novel apparatuses according to paper and board internal sizing emulsions are here presented.

2.7.1 Rotor-stator homogenizator

One of the most common pieces of emulsification equipment in most fields is a rotor-stator homogenizator with small power/volume ratio (Figure 12) /45, 46/. Homogenization is a process where two immiscible phases are forced through a narrow aperture under relatively high pressure, causing sufficiently high shear to create small droplets. Stabilizers and/or surfactants in solution then form an interfacial layer, preventing emulsion coalescence /51/.

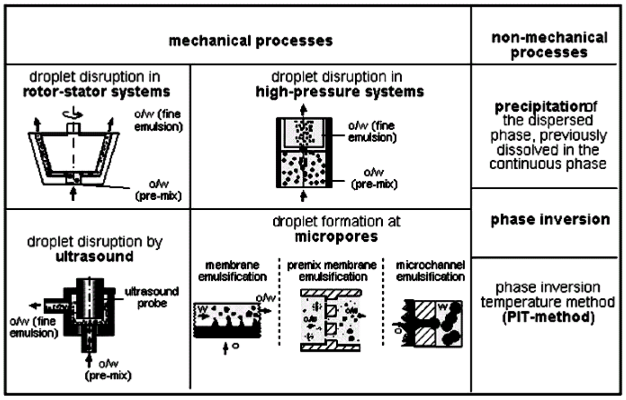

Figure 12. Four common ways to produce fine emulsions from pre-emulsified material. The division is made into mechanical and non-mechanical processes /49/.

2.7.2 Colloid mill

In colloid mills, the fluid mixture streams through a gap between a rapidly revolving disk and a static disk. Colloid mills, on the whole, are less power-efficient and produce more heat than rotor-stator homogenizers. Heat can often be damaging to emulsion products, so most instances, colloid mills require cooling during their operation. /46, 52, 53/. The high-pressure process of the colloid mill gives a smaller particle size but does not give as monodisperse particle size as does the rotor-stator homogenizer. The way the energy is brought to the system plays a significant role in colloid mills /45/.

2.7.3 Ultrasonic homogenizer

Ultrasonic homogenizers, sonicators, are used to supplement mixing and to reduce particle sizes of emulsions. Similar to high-pressure homogenizers, the wide particle size distribution, has hindered the use of the equipment in the continuous operations at industrial processes /49/. The fluid mixture streams between blades that vibrate at ultrasonic frequencies. The liquid cavitates and breaks up into small droplets. Cavitation is the formation and collapse of vapor cavities in a flowing liquid. A vapor cavity forms when the local pressure is reduced to the temperature of the flowing liquid. This happens because of local velocity changes. The collapse of the cavities causes powerful shock waves to radiate throughout the solution in proximity to the radiating face of the tip, thereby breaking the dispersed liquid.

The use of ultrasound gives the possibility to use less or no surfactant. Emulsion stability can also last longer /24/. On the other hand, ultrasound can produce too small particle size with too big variations for paper and board emulsions. Because the formation of droplets is a consequence of unstable oscillations of the liquid-liquid interface, capillary waves may occur and contributes only to dispersion, if the diameter of droplets to be disrupted is sufficiently larger than the wavelength of the capillary waves /25/. By first using ultrasound and then membrane emulsification –a novel method where emulsion is squeezed through porous membrane of a given material, an even particle size distribution would result /54/. The problematic small production amounts are still more suitable for medical vaccines than to paper machine internal sizing emulsions. Unlike colloid mills, ultrasonic homogenizers generate very little heat and do not require cooling. Another advantage of an ultrasonic homogenizer is its ability to be completely closed in, allowing formulations containing volatile liquids to be processed. /46, 52/

2.7.4 High shear machinery

Blending, stirring, and cutting all produce high shear by forcing a stirrer or blade through a mixture of two phases. This type of machinery is called a high-pressure homogenizers /49/. They are typically used to drive the premixed emulsion products through fine orifices at very high flow rates and bring about drastic reductions in the particle sizes of emulsions /46, 52/. The resulting small droplets must be quickly stabilized to prevent coalescence. The high-pressure homogenizers themselves do not provide very much smaller particle size than more traditional homogenizers.

2.7.5 Produced particle sizes

Emulsion particle size and particle size distribution are the driving elements of emulsification. Cost-efficiency should also be taken to account in the energy efficiency of the device. Equipment producing finer emulsion particle sizes usually has wider particle size distribution, that is, more polydisperse emulsion. Roughly emulsion particle sizes increases in following order: ultrasound < rotor-stator homogenizer < manual blending /11, 55, 56/.

In paper and board industrial emulsions, high shear agitation is typical. In laboratory scale low shear is usually enough, meaning that the use of homogenizer usually results to particle size of 1 µm or larger if no surfactant is used /11/. With added surfactant one can produce particle sizes of about 0.5 µm with relatively low-shear equipment such as colloid mill or kitchen blender. Ultrasound has also been applied successfully in laboratory scale for paper and board emulsions. Regardless, minimum particle size is never desired but an optimum is to be sought /57, 58/. The need for online control of particle size hinders the implementing of ultrasound devices as well as does the expensive technology of the continuous operating systems. Table 3 summarizes the typical equipments in different fields of emulsification.

Table 3. Emulsification equipment examples on different fields of use. Stabilizers and equipment vary with the different preferences of emulsions /10 ,13, ,26, 32 ,50 ,52, 59/. TNT in the table stands for trinitrotoluene

Emulsion field of industry	Example emulsion	Type	Emulsifying equipment
Food	ice cream	O/W	low shear stirrer
	butter	W/O	colloid mill
Medical/pharmaseutical	intravenous vaccine	O/W	ultrasonic homogenizer
	skin lotion	W/O	colloid mill
Agricultural	insecticide	O/W	manual blending
	pesticide	W/O	microencapsulation
Cosmetics	mascara	O/W	medium shear agitator
	hand lotion	W/O	low shear stirrer
Printing, graphics & paints	ball point ink	O/W	colloid mill
	inkjet ink	W/O	colloid mill
Petroleum	crude oil	W/O	homogenizer
Bitumen	asphaltene	W/O	process equipment
Explosives	TNT	W/O	rotary emulsifier or ultrasonic
Micro emulsions	Ouzo drink	O/W	no
	tertiary oil recovery	W/O	no
Paper and board	ASA	O/W	High turbine pump
	AKD	O/W	Homogenizator

2.8 Examples of different emulsions

The advantages for using emulsions compared to normal solutions in paper- and boardmaking have been listed by Vaurio /37/:

1. Emulsions permit the use of higher solids content at lower viscosity. This is valuable as paper is less distorted when lower mounts of water is used. More chemicals can be added.
2. Drying is faster and more cost-efficient.
3. Faster tack development allows better adhesives (e.g. sizing agents)
4. The use of otherwise insoluble polymers as stabilizers is possible.
5. In emulsions, materials that cannot be applied from a single solution can be mixed.
6. Water can be used in place of inflammable solvents.
7. Higher machine speeds can be used for applications.
8. The use of toxic solvents is unnecessary; this also eliminates obnoxious odors.
9. Most of the costly solvents can be eliminated.
10. The application may be less sensitive to temperature changes.
11. Emulsions can be applied successfully to porous absorbent paper.
12. Migration due to fluid movement in the drying process can be controlled.

Number five serves as the common reason for emulsion usage in internal sizing. Through the following examples, the scope is to locate specific advances alike in the list from other emulsion industries. Paper and board internal sizing emulsions are O/W emulsions and the emulsification of those can be improved by adjusting novel stabilizers, right emulsification techniques, and proper equipment from other fields of use. In paper and boardmaking the use of surfactants is many times unnecessary. Emulsions must be properly mixed and reasonable amount of shear is needed /60/.

2.8.1 Food industry

O/W food emulsions, creams, salad dressings and mayonnaise are mainly fluids having partly crystalline oil phases. These emulsions are stabilized by using small molecule surfactants like monoglycerides, diglycerides, sorbitan esters of fatty acids and phospholipids. They contain long-chain fatty acid residues, providing the hydrophobic group attaching to the lipid phase of the O/W interface and causing adsorption. Protein molecules or aggregates of protein molecules and mixtures of those can also work as stabilizers. Examples are casein micelle and egg yolk lecithin granules /26, 61/.

In food emulsification, most emulsion are not thermodynamically stable and do not form spontaneously. Shear is needed to apply to mix the phases together and colloid mills or high-pressure homogenizers are used (Figure 12). Colloid mills are used to produce mayonnaise and other products whose particle size is not very critical. To promote smaller droplets, high-pressure homogenization, stirring and cutting are applied. /7, 26, 51/

2.8.2 Medical industry

Medical emulsions used through external surfaces of the human body and body cavities are in the form of O/W or W/O-type creams containing medical substances. Typical surfactants with these creams are alkali salts of fatty acids, such as sodium stearyl sulphate. The nonionic stabilizers applied are stearyl alcohols in W/O emulsions and glycol ethers in O/W emulsions due to the higher emulsifying capacity needed for the task. /9, 62/

In medical vaccines, O/W emulsions are for intravenous route drug carriers or medical agents of their own /9/. There are only few stabilizers used in vaccine emulsions. Purified paraffin oils are desired for intramuscular use and phosphatides of egg or soya with vegetable oils. The phosphatide surfactants are nonionic materials such as Span (sorbitan compounds) and Tween (polysorbates) for intravenous applications. In intravenous vaccines there are strict requirements for particle size. Large oil drops could give rise to blockages in the body and droplets bigger than 5 μm are excluded in O/W emulsions. Other properties such as surface charge and stability are also controlled. /9/

Oral pharmaceutical emulsions are mainly of the O/W-type. Stabilizers with these are, for example, acasia, traganth gums and methyl cellulose. Many nonionic surfactants are also used instead of stabilizers. Emulsification in medical applications varies. In general the particle size is very small and special equipments are needed. In medical creams emulsions membrane emulsification and stirrers are used. In vaccines ultrasonication or homogenization are used to produce sufficiently fine particles. /9/

2.8.3 Cosmetic industry

Requirements for cosmetic emulsions include economy and ease of application, increase in rate and extent of penetration into the skin, possibility of applying both water and oil soluble ingredients simultaneously, and efficient cleansing action /7/. The hydrophilic nature of human skin permits greater penetration by an O/W emulsions than by straight oil or fat. Cold creams have high oil content and are typically O/W emulsions consisting of 20-40 % oil, a few percents stabilizer, some surfactants dissolved in the oil or water phases, dyes with perfumes, and deionized water. /52/

In cosmetic emulsions generally, turbulent flow is needed to break one of the liquids into small droplets and to disperse the droplets within the other, to continuous liquid phase. Minimum air present is required to decrease the foaming. Propeller and turbine agitators are used for preparing low and medium viscosity emulsions. For high viscosity creams, agitators capable of scraping the walls of the mixing container are preferred. For very high shear rates, for creams and lotions with very small particle size, ultrasonic mixers, colloid mills, or homogenizers are used /52/.

2.8.4 Agricultural emulsions

Agricultural O/W sprays are usually in the form called emulsifiable concentrate or soluble oil. They contain a solution of the toxicant in an organic solvent. To the solvent is added an oil-soluble surfactant. In use, water is added to the concentrate and the desired emulsion is prepared by manual mixing. Self emulsifying in agricultural emulsions is common. Since all degrees of water hardness need to be applicable, a calcium-insensitive agent is required. Cationic surfactants, like alkyl amine acetates, ethoxylated amines and some alkyl ammonium chlorides, unaffected by hard water, are used. The majority of emulsions have nonionic surfactants involved. Mixtures of anionic and nonionic surfactants are also used. Types of anionic surfactant are oil soluble and low-cost ones, for example calcium dodecylbenzene sulfonate. The advantage of nonionic hydrophilic surfactants like aromatic hydrocarbons with low cost and good availability, are the solubility to non-aqueous solvents. In addition to surfactants, numerous minor ingredients such as dyes, thickeners, stabilizers and defoamers are also used. /7, 48/

The agricultural emulsions should remain intact in the spray tank but should break instantly on contact with the surface, for example, plant leaf when sprayed. The toxic agent forms a thin film on a leaf surface and is not easily removed. If the emulsion does not break properly, much of the material drips off the surface with no use. This is why the particle size of these emulsions is important. If the emulsion droplets are too fine, breaking on contact with the surface tends to be incomplete; while if the droplets are large, creaming will take place, causing uneven distribution of the material on the sprayed surface. /7/

2.8.5. Inks

O/W ball point inks are compounded as emulsions to secure the rheology needed for static thickness in bulk and for thixotropic breakdown flow on dynamic filming through the ball holder interspaces. Thick inks exemplify the common method of using emulsification to secure viscosity and structure for the milling flow that is dominant in image transfer by printing and duplicating presses. Pigments are used as surfactants for emulsifying inks. Examples of O/W emulsion stabilizers are hydrocarbons, saponified resins, alkylated naphthalenesulfonic acids and their alkali salts. A colloid mill is typically used in emulsification. /37/

2.8.6. Asphaltic bitumen

Similar to paper and board emulsions, the main idea in asphaltic bitumen emulsions is the production of water repellent surfaces. They are used in road construction, roofs, floors, paper and fabric impregnation, electrical and heat insulation, and as binders for coal briquettes, carbon electrodes, and binders for other insulating materials. The most significant advantage of applying asphalt to road surfaces in the form of emulsion can be found from the ease of application. /63/

The fluidity of the emulsion is much higher than that of molten asphalt. It allows quicker application, and results in smoother coating than direct application would. It is also possible to use the emulsion on moist surfaces, but a problem in stability exists. In the first place, a reasonably stable mixture is desired so that it can be transported from the manufacturing point to the place of application and in some cases stored for a period of time without destabilization. On the other hand it is required that the emulsion breaks soon after application so that the film of asphalt forms and sets quickly. The breaking of bitumen emulsions occurs in two stages. First the stabilizer and/or surfactant is adsorbed and then the changes in interfacial tension and interfacial electrical conditions take place. Nonionic surfactants are used to a limited extent in some applications. Bitumen emulsions are usually prepared with homogenizers or colloid mills. /7, 63/

2.8.7 Nano- and microemulsions

Nano- and microemulsions are prepared from water and oil phases together with amphiphilic molecules in both phases. Typical drop size is 10 nm to 100 nm, while macroemulsions particle size exceeds 0.1 μm. In contrast to those, nano- and microemulsion systems can form spontaneously at a contact between the dispersion components with no special equipment needed. Microemulsions are transparent to the eye, have low viscosity, and are thermodynamically stable /32/. The small particle size of nanoemulsions leads to high surface area, being advantageous to those reactions whose reaction rate is dependent on interfacial area. These emulsions also show higher penetration into porous materials than macroemulsions allowing a more uniform dispersion of active substances. They are typically only soluble in disperse phase and yield high gloss and film integrity as in the case of waxes and paint vehicles. /64/

An example of spontaneous emulsification, the ouzo-effect, occurs when water is poured in a strong alcoholic anise-based drink. The anisolic compounds which are soluble in ethanol form nano droplets and emulsify in water. During water addition the color of the solution turns from transparent to opaque and milky. Microemulsions exist in food, medical, agricultural, cosmetics and petroleum industries. Ouzo drink, vaccines, pesticides, fuels for diesel engines, leather waxes, and floor polishes are all examples of those. More extraordinary applications of microemulsions are the use in tertiary oil recovery, drilling fluids, marine fuels, microlatex coatings on textiles, cleaning detergents, reaction media, extraction media, and the use in microparticles production /22, 32, 64/

2.8.8 Paper and board industry

In paper- and boardmaking, the most common emulsions are the sizing emulsions of ASA, AKD and rosin. ASA's and rosins are typically liquid in room temperature while AKD is waxy. A special requirement of paper and board emulsions is the ability to stabilize the sizing agents against water. The problem is that both water and cellulose fibers are hydrophilic and the sizing agent needs to be attached on the fibers only and should not react with water. Sizing agents form the oily discontinuous phase of emulsion and act in contact with anionic, hydrophilic cellulose fibers while water forms the continuous phase.

The mission of sizing emulsions is to bind small particles into a fiber surface and to modify the water repellency properties of the end product for different requirements. In addition to internal sizing, emulsions in papermaking are used in foam control, surface sizing, to make copy paper electro conductive, in encapsulated coating, in laminating, where emulsion act as adhesives, and in flame proofing of paper and board. /37/

Paper and board emulsions are produced on site due to their high reactivity or delivered as ready-to-use. Stability is often poor because of a necessary compromise; whether the sizing agent is reactive against fibers and also against water, not being very stable in aqueous system due to *hydrolysis*, or the stability is better at the cost of lower reactivity. The requirements for equipment and emulsion particle size vary depending on the desired end-product properties. Low shear, high shear and high energy devices are all used. By the correct stabilization of an internal sizing agent, emulsification can be done efficiently. Proper stabilizers are cationic starch, polymers or microparticles such as polyacrylamides or colloidal silica /65/. Surfactants can be used for emulsion stabilizing but are usually used together with actual stabilizer to make the emulsification easier and more user-friendly. Some emulsions can even stabilize themselves without any stabilizer being used /57, 58, 66/. A summary of examples in the fields of emulsion technology equipments and requirements can be seen in Tables 3 and 4.

Table 4. Emulsion examples from different fields of use with various stabilizers and special requirements /10,26 ,13,32 ,50 ,52, 59/. TNT in the table stands for trinitrotoluene

Emulsion field of industry	Example emulsion	Type	Special requirement
Food	ice cream	O/W	to destabilize just before use
	butter	W/O	to stay stable when spread
Medical/pharmaseutical	intravenous vaccine	O/W	drug release point in the human body
	skin lotion	W/O	moisturizing and curing effect
Agricultural	insecticide	O/W	small amount of spray should kill the insects
	pesticide	W/O	stay on a leaf when raining
Cosmetics	mascara	O/W	uniform pastell color and opaque, hygienic
	hand lotion	W/O	instant absorption
Printing, graphics & paints	ball point ink	O/W	good flow, no smearing
	inkjet ink	W/O	rapid drying on paper, no smearing
Petroleum	crude oil	W/O	destabilization of unwanted emulsions
Bitumen	asphaltene	W/O	solidification
Explosives	TNT	W/O	to stay stable and detonate safely
Micro emulsions	Ouzo drink	O/W	oil supersaturation upon sudden dilution with water
	tertiary oil recovery	W/O	changes in interfacial tension when temperature is changed
Paper and board	ASA	O/W	hydrophobicity & interaction with hydrophilic
	AKD	O/W	hydrophobicity & interaction with hydrophilic

Through examples from emulsions, requirements, emulsifiers, stabilizers, surfactants and equipment from the significant fields of emulsion technology, the goal was to gather any useful information for adaptation in the use of paper- and boardmaking emulsions. A special interest has been on O/W emulsions, those being the only important ones in the field of paper- and boardmaking since water always acts as the continuous phase. The use of stabilizers and equipment has been the main focus of the emulsion examples. Devices that are already in use in paper and board industry are constantly developed, but completely new implementations, suitable for the task in internal sizing emulsions, were not indicated /66/. Rotor-stator homogenizer and high-shear equipment were generally used in all fields studied as well as in paper industry. In the case of rotor-stator homogenizer, surfactant is used and in the case of high-shear machinery, no surfactant, in general, is needed. The ultrasonic emulsification techniques were most commonly used in medical emulsion applications but also applied in paper and board emulsions in laboratory scale. The use of microparticles and some synthetic polymers as stabilizers have shown to be interesting.

As a procedure, papermaking is not the most trivial one. First water is added to the process and then it is taken away. The cellulose fibers are first swollen with water and then dehydrated and shrunk by drying. Fibers are needed to make flexible to make the paper stiff. The most significant paradox concerning emulsions is the dispersion: every substance in papermaking needs to be carefully dispersed but the fine material still needs to be retained on the end product. In addition to that, fibers are chemically flocculated and then dispersed. Waterborne treatments are needed to make the end-product water resistant. These facts make the emulsification in the field of papermaking unique. /67/

3 INTERNAL SIZING OF PAPER AND BOARD

The word sizing is used when talking about paper and board hydrophobation. Two kinds of sizing; *internal sizing* and surface sizing exist. In internal sizing the sizing agent is added in the wet-end of paper and board machine. The liquid penetration into the paper and board body is limited by modification of the product inner structure. In surface sizing, the sizing agent is applied on dry paper web in the dry end of paper machine. Surface sizing modifies the liquid penetration properties of paper and board surface. /3, 4/

When planning a sizing system, the wet-end chemistry and chemicals need to be systematically considered and selected due to the individual chemistry of every paper and board machine. In internal sizing, the most important chemicals under consideration excluding sizing emulsion are: filler, retention aid, pulp starch, use of alum, biocide system and surfactant. The charge, molecular weight and dosage of each of these must be determined. /4/

3.1 The purpose of sizing

In internal sizing (hereafter sizing) the intention is to modify the paper and board inner liquid absorbing properties. This means altering the surface energy of the fibers /68/. Improved hydrophobicity can be gained due to the formation of low-energy regions on fiber surfaces. They inhibit spreading and penetration of water into paper and board body. The fiber surface is transformed from relatively high-energy state, rich in groups and capable of hydrogen bonding, to modified state, where the free energy of the surface is reduced. The development of hydrophobicity depends on interactions between the sizing agent and other papermaking components involved in the machine-specific papermaking process. Sizing agent is added into the papermaking process as an emulsion. /4, 69/. The desired amount of hydrophobicity is somewhat dependent on the end product preferences. Between sized paper and board grades, highest hydrophobicity is needed with liquid packaging boards and the lowest in writing papers. With packaging boards, liquid needs to stay in its package and must not wet the material, whereas in writing papers, the hydrophilic inks must somewhat penetrate and absorb to the paper.

Requirements for efficient sizing are good anchorage and fiber surface coverage by the sizing agent. Internal sizing process takes place in three somewhat distinct stages. These are; the retention of the amphiphilic sizing agent molecules by the fibers during web formation process in wire section, the spreading of sizing agent molecules over the fiber surfaces and the orientation of the sizing agent molecules at the fiber surface in order to create hydrophobic low energy surface and to anchorage sizing agents on the surface groups of fibers and fillers. Sizing agent amphiphilic structure means that they have hydrophilic part and hydrocarbon part. The introduction of hydrophobic groups onto the fiber surface in internal sizing is essential. /3, 4, 68, 69, 70, 71/

Paper and board fibers include cellulose and hemicellulose containing hydroxyl groups (-OH). These groups react strongly with water, creating the desired hydrophobic nature in paper and board. Water removal from fiber surfaces is done using chemical treatment /33, 72/. Polar hydroxyl groups of cellulose are shielded by the absorbing parts of the sizing agent, reducing paper wettability. Successful sizing hinders the rate of water penetration within and between the fibers and is controlled by the degree of sizing. Paper and board web porosity and structure have a major effect on water penetration control, while penetrating liquid surface tension, including chemical properties affect only somewhat. Penetration occurs in many simultaneous ways: through fiber pores and cavities, uneven paper and board surface, capillary structure, by migration through the fiber surface, by absorption to the fiber and by the diffusion inside the fiber. The processes cannot be functionally separated from each other. The dominating type of penetration is determined by the properties of the liquid phase, structure of the paper and board, pressure, temperature, penetration time and the hydrophobicity of the paper and board components.

The contact angle between water and paper or board sheet is sensitive to three effects at the fiber-liquid interface. These include molecular packing, surface morphology and chemical constitution. During sizing the chemical constitution is affected /4/. The hydrophobic nature of the sizing agent increases the contact angle. So the rate of water penetration to the fibers, i.e. liquid flow inside the wood fibers because of pressure difference and capillary forces, decreases /21/. Figure 13 illustrates schematically the development of paper and board hydrophobicity when the amount of internal sizing is increased. With no sizing, the contact angle, θ, is close to zero. The penetration of water into the sheet is fast and the drop spreads completely to the wetted surface. When the contact angle is under 90° but greater than zero, the solid surface usually tends to be partly wetted by the liquid. When the contact angle is equal or greater than 90°, no penetration occurs and the surface is not wetted. Only external pressure added to the system, would force the liquid inside the porous fibers. Pores are made smaller and more closed by sizing, the liquid transfer inside the fibers is restricted /33, 73/. The more hydrophobic the product is, the stronger are the fibers anchored by sizing /4, 21, 33, 74/.

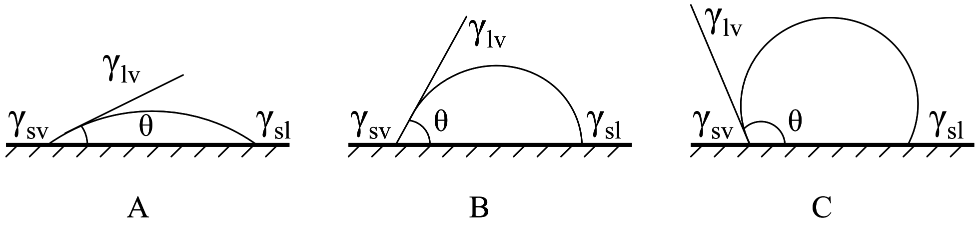

Figure 13. The changes in contact angle, θ, during hydrophobation. A: no hydrophobation, B: Bigger contact angle because of hydrophobation, C: Hydrophobic contact angle. The surface is anionic and the liquid drop is cationic. sl stands for solid-liquid interface, lv for liquid-vapor interface and sv for solid-vapor interface. γ is the interfacial tension for each interface /75/.

3.2 Sizing chemicals

To classify sizing agents, two approaches are given: division by application pH, to acidic, neutral and alkaline sizing, and division by functionality, meaning cellulose reactive ones and non-cellulose reactive sizing agents /76/. Sizing in neutral pH with one of the cellulose reactive sizes, Alkyl Ketene Dimer (AKD) or ASA most recently, is the most common practice. Reasons for this are the reactivity and sizing efficiency of ASA and AKD, good availability of suitable $CaCO_3$ precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) fillers and the increase of recycled fiber usage. Polymeric sizing agents are also available but due to their lower sizing efficiency and especially lower cost-efficiency they are not discussed here /70/.

The transition from acidic pH paper- and boardmaking systems to neutral and alkaline pH systems is mainly due to $CaCO_3$. Growing amount of PCC as filler can be use to replace the high cost cellulosic fibers. $CaCO_3$ can't be used in very acidic pH due to the crowding of carbonate in the water system. The most common sizing compounds are presented by Roberts /4/ (Figure 14). Important components in internal sizing emulsion are the sizing agent and the stabilizer. The sizing agent may or may not contain surfactant. From unreactive sizes, rosin is used at acidic condition with alum. Rosin sizing is the traditional sizing method used in acidic pH excluding maleic anhydride esterified rosins, whereas reactive sizes AKD and ASA work mainly in neutral or alkaline pH range.

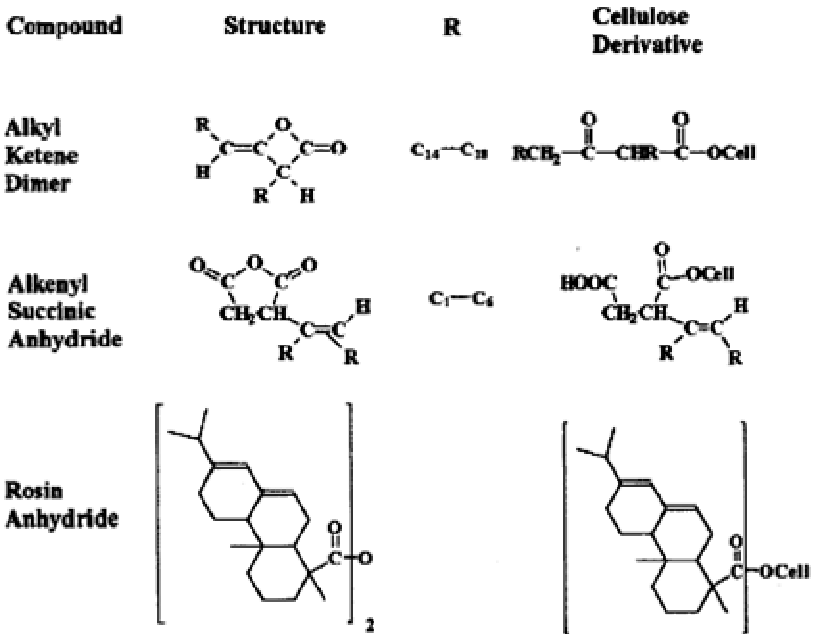

Figure 14. The common internal sizing compounds, traditionally considered to work with direct covalent reaction of the sizing agent and cellulose /4/.

3.2.1 Reactive sizing agents

The most common reactive sizes are AKD and ASA. The detailed description of ASA is presented in the following chapters. AKD is water insoluble waxy material commercially prepared from fatty acids, typically palmitin and stearic acids, with a long hydrocarbon chain. The acids are dimerized in the form of acid chlorides into ketene dimers, forming the body of AKD. The yielding compound has central lactone ring with two hydrocarbon chains attached (Figure 14). The carbon chain length of the hydrocarbon is between 14 and 20, usually between 14 and 18. Linear saturated AKD is solid under 50 °C and AKD's prepared from unsaturated or branched acids are liquids at room temperature. As a stabilizer, cationic starch and other cationic polymers like polyacrylamides are typical for AKD. AKD is used with ink-jet printing papers, but is more common in supercalandered papers and especially in liquid packaging boards. /3, 4, 77/.

3.2.2 Rosin sizing agents

Rosins used in paper and board sizing are prepared from a mixture of resinous acids and small amounts of fatty acids /3/. Rosin consists of tricyclic diterpene monocarboxylic acids (Figure 14) and can be produced by saponification, resulting water soluble sodium or kalium salt called soap size, or it can be emulsified as free acid with casein stabilizer. Both compounds are anionic. Because of aluminum hydrolysis, the rosin-alum sizing pH is between 4 and 5. Due to the anionic nature of rosin, cationic additives are needed to attach rosin on the anionic cellulose fiber surfaces. Alum is cationic when added to the paper or boardmaking system, and its moiety can react with water or with rosin. In higher pH, meaning neutral or alkaline conditions, the potential of alums moiety to react with water rather than with fiber and the sizing agent overlaps.

Rosin structure can be fortified in the reaction of diene and maleic anhydride or fumaric acid by introducing additional carboxyl groups into the rosin. The reaction increases the number of carboxylic acid groups per molecule. Carboxylic acids are active in attachment and anchoring on cellulose fibers, so the fortification improves the sizing performance. Rosin can be used in neutral pH via esterification, cationic stabilization, or by using polyaluminum chloride (PAC). In esterification, rosin is modified with ethylene glycol before fortification. After this, saponified rosin acids together with aluminum sulfate prove an efficient sizing at pH 6-7. PAC is used with dispersed rosin sizes. It is able to bind rosin size and act as a retention aid and coagulant for anionic substances but it does not decrease pH like alum due to the fact that it is pre-hydrolyzed aluminum salt. Rosin is used with fine papers, sack papers and board. /4, 78, 79, 80, 81/

3.3 Effect of fillers on internal sizing

Fillers in papermaking are used to gain cost savings in raw materials by replacing the high cost fiber material, cellulose, with low cost material. Most common fillers are calcium carbonate ($CaCO_3$), clay, talc, titanium oxide (TiO_2) and calcium sulphate ($CaSO_4$) /82/. Calcium carbonate is the main filler used in alkaline sizing conditions. It can be used in the form of precipitated $CaCO_3$ (PCC), ground calcium carbonate (GCC) or ultra-fine limestone /81/.

PCC is used with ASA due to its relatively low price and fair availability. It has a small particle size and high surface area, causing bigger ASA consumption, though it has a positive zeta potential and therefore it shouldn't react with ASA or fibers. This is why PCC can be added to the stock before sizing emulsion. PCC any way can disturb the ASA emulsion reacting with fibers due to its high interfacial area. On the other hand, while an ASA compound does not in its original state react with PCC, its hydrolyzed state forms deposits with calcium. ASA sizing enables high filler usage in the furnish but high filler level requires also larger amounts of ASA due to the high specific surface are of small particle size having PCC.

When PCC is used a chemical additive is added into the process to affect brightness, color, retention and sizing. Additives are electrolytes, polyelectrolytes, charged polymers or colloidal microparticles /16/. The specific surface area of calcium carbonate particles is roughly equivalent to that of the wet pulp fibers. Fine material has much higher surface area. Assuming that sizing particle adsorption is in direct proportion to specific surface area, it would be expected that the fines fraction would rinse an uneven amount of sizing compound. To the extent that they remain in the sheet, however, they will contribute to the sizing effect. /81/

Clay is known to need bigger amount of sizing agent than PCC /81/. This is due to the higher filler surface area and the smaller filler particle size. A higher surface area consumes more ASA. This and the price are the downsides of clay, whereas the downside of PCC is the size reversion it can cause with ASA. With clay no reversion is reported, at least at alkaline pH range /83/. The type and amount of filler and other additives used can have significant effects on later occurring reversion. The loss of sizing occurs with PCC but not with clay /84/.

3.4 Effect of retention on internal sizing

In paper- and boardmaking it is crucial to attach and retain the small particles, such as additives, fillers, pigments and nano- and microparticles to the fiber network. By doing this the small particles are prevented from ending down through the wire to the white water circulation of the paper machine. Succeeding in this is problematic because of the vast size difference of papermaking compounds (Figure 15). The challenge is also the binding of the small particles into the fibers and fiber network that needs to be carried out without flocculating the fibers themselves. /85/

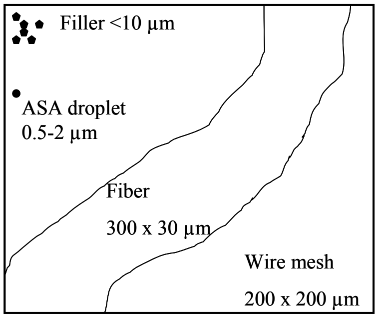

Figure 15. The comparative sizes of the components in papermaking. Due to their small size compared to cellulose fibers, the fillers and others additives are needed to flock onto the fibers by internal sizing or they will end up in process water through the wire.

Retention is defined as the amount of material retained from overall material passing a certain measurement point /82/. First-pass, or wire retention in paper- and boardmaking, is most used in retention measurements. It can be said to be the retained fraction of a given material on wire, passing through the headbox of a paper machine. Poor retention will lead to a carry over of the water system and thereby sizing agent deposits and poor sizing. High first-pass retention depends on /82/:

1. The size of the particles to be retained.
2. The size of pores in the web and geometry of forming fabric (wire).
3. The forming rate of paper or board web.
4. Basis weight of paper or board.
5. The dewatering method.

A retention aid is a chemical additive that increases the retention of cellulose fibers, fiber fines, fillers or pigment additives to the paper web via coagulation or flocculation mechanism, which in emulsification are undesired phenomena but are wanted here. Retention aid is charged and has typically a high molecular weight /86/. Retention aids can be divided by their mechanism into coagulants, macro flocculants and micro flocculants. /87/

Retention is achieved by electrostatic interactions between sizing agent droplets and the fiber surfaces. In this stage, the sizing agent molecules are not to spread over the fiber surfaces and become oriented. This would disturb the interfiber hydrogen bonding and development of strength between the surfaces of cellulose fibers during consolidation and drying of the wet paper or board web. During the spreading of retained size over fiber surfaces, the physical properties of the sizing agent molecules play a major role. The droplets must be stable enough against hydrolysis and still mobile enough to cover the fiber surfaces during drying. To achieve decent orientation of the fiber network by covalent or electrostatic bonding, the formation of strong interaction between the polar end of the sizing molecule and the fiber surface is needed. /4/

4 ALKENYL SUCCINIC ANHYDRIDE SIZING

Alkenyl Succinic Anhydride (ASA) was patented for increasing the water resistance ability of cellulose in 1963 by Wurzburg and Mazzarella /88/. At first, ASA was applied only for neutral papermaking at the pH range of 7.5 - 8.5 because of the poor understanding of its chemistry and applicability /81/. Later the use has widened to pH range 4.5 - 9 /80/. Many paper processes in Europe and in North America have been converted from rosin and AKD sizing to ASA sizing, from acidic pH to alkaline or neutral pH due to cost-efficiency issues. ASA provides the possibility to use relatively large doses of low-cost PCC, decreasing the needed amount of expensive cellulose fibers in paper and board. Other reasons for conversion are the ability to use recycled fibers and the possibility to save in energy consumption as ASA curing needs no more than the natural heat of the paper or boardmaking process. Immediately achievable final properties make online converting, paper and board testing, packing and shipping possible directly off the machine line due to the rapid cure of ASA size /60, 66, 89/.

Some of the most common ASA internal sized paper and board grades are /81/:

- Coated wood containing papers.
- Uncoated wood free writing and printing papers.
- Coated recycled paper.
- Liner board.
- Office papers.
- Sack paper.
- Gypsum board.

ASA is added to the paper- and boardmaking process as an aqueous emulsion because it is insoluble in water itself /90/. Emulsion properties including stability, emulsifying method, and the use of stabilizer and/or surfactant need to be optimized. The most important property related to ASA emulsion stability is the particle size of the ASA droplets. Although many stabilizers are widely used, new applications are still needed and developed. Equipment in emulsification varies and the desire for a simple and cost-efficient system still exists /66, 70, 88, 90/. Wide adjustability of ASA guarantees the usage in many paper and board grades.

4.1 Chemistry and reactions

ASA is synthetically produced and can be made with carbon chains ranging from 8 to 24 carbon atoms. From C8 to C18 carbon numbers, ASA is liquid at room temperature.

In commercial compounds there are typically 18 isomerized linear carbons or a mixture of C16 to C18 partially branched and isomerized carbon chains. Carbon numbers under 14 tend to drive anhydrides thus making them effective in sizing, and carbon numbers more than 20 are solid in room temperature, not desired for emulsification /4, 80/. Cellulose-reactive ASA is derived from petrochemical feedstock, from l-alkenes and α-olefins by catalytic isomerization, followed by an addition reaction with maleic anhydride (Figure 16). The reactive anhydride ring 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. /4, 20, 81, 91/

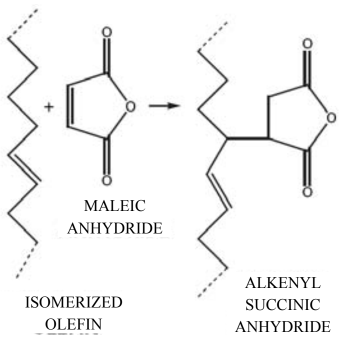

Figure 16. The preparation of Alkenyl Succinic Anhydride (ASA) by ene reaction between isomerized α olefin and maleic anhydride /80/.

From its physical properties, ASA is a yellowish, oily liquid and has extremely low water solubility (Table 5). It may also have faint oily odor /90/.

Table 5. Physical properties of ASA at C16-C18 chain length /92/

Appearance	Yellow to amber liquid	
Density	960	kg/m3
Viscosity	15-16	mPas
Melting point	-12,5	°C

The hydrophobicity of ASA is provided to the fiber surface of cellulose by a long chain hydrocarbon. The hydrophobic alkenyl group orientates away from the fiber which renders the fiber surface water repellent. Traditionally it is said that cellulose d AS rapidly by forming a covalent ester bond with one of the hydroxyl groups of component in cellulose (Figure 17). This is the reason why ASA sizing needs no external heat in the sizing process and can be used in relatively low temperatures /4, 81/. Today, no agreement on ASA-cellulose bonding amount, or ASA's hydrophobation efficiency, compared to the ASA total amount, exists. /20, 69, 70/

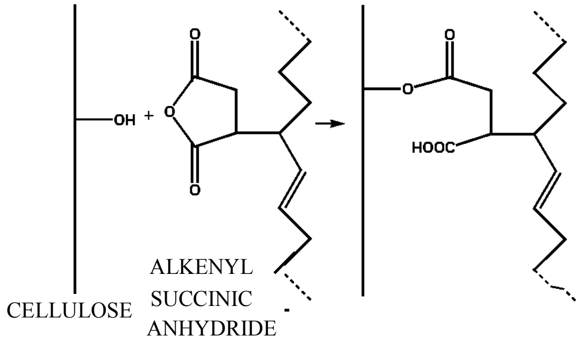

Figure 17. ASA internal sizing. The esterification reaction of ASA with cellulose /80/.

The functionality of the anhydride is the reason for ASA's high reactivity /81/. This makes ASA hydrolyze in water and quickly become unstable as sizing agent. After hydrolysis, ASA is traditionally said to no longer provide hydrophobation and to no longer retain onto the paper web. Instead, it would end up looping to the water circulation system. According to Bajpai and Farley, unreacted residual ASA in the sheet will hydrolyze to its dicarboxylic acid form (Figure 18). This compound no longer forms an ester bond with cellulose. Nishiyama, Isogai and Onabe have found indications of very little if any formation of covalent ester bonds between ASA and cellulose /93/. According to Hubbe, the complexity of bonding measurements and device sensitivity issues, or the hydrolysis conditions of ASA, may have been reason for these results /70/. Nishiyama also stated that unreacted ASA is needed in the sizing process due to the presumption that only the anhydride from of ASA can be efficiently distributed onto fiber surfaces /93/.

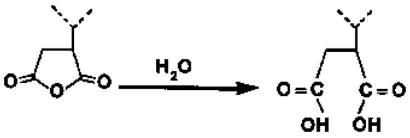

Figure 18. The hydrolysis of ASA to dicarboxylic acid with water. On the left side, the ASA sizing agent and on the right side the hydrolyzed state ASA /92/.

According to Gess and Bajpai, the hydrolysis product of ASA is readily dispersible in water but not very soluble, acting as a de-sizing agent /80, 81/. The more ASA emulsion contains hydrolyzed ASA, the more hydrolysis accelerates. Because of this auto catalyzed reaction, optimum sizing in the ASA system is said to be achieved by maximizing the level of reaction with cellulose and minimizing the degree of hydrolysis /1-3, 81/. It is agreed that hydrolysis should me minimized and avoided /20, 69, 70, 80, 81, 70, 94, 95/. Then again, the on harmfulness or the usefulness of the hydrolyze product of ASA and water is questioned: Hatanaka showed that it is possible to employ sizing with the hydrolyzed, diacid soap form of the ASA, and it worked the same way rosin soaps work in rosin sizing /96/. These results cannot be directly transported to neutral or alkaline ASA sizing, since they were carried out with pH below 5.5 and with 1 % or more alum present /70/.

The example of Neimo shows the effect of temperature and pH on ASA hydrolysis rate in Figure 19. Higher temperature and higher pH increase the hydrolysis reaction significantly /33/. This can be taken as an advantage since ASA sizing needs no additional heating for curing. Process pH above 10 and temperature above 60 °C are both said to cause problems /1, 4/. Although the rate of reaction with cellulose increases with pH, the best degree of sizing does not increase with pH but is reached at about neutral conditions /94/.

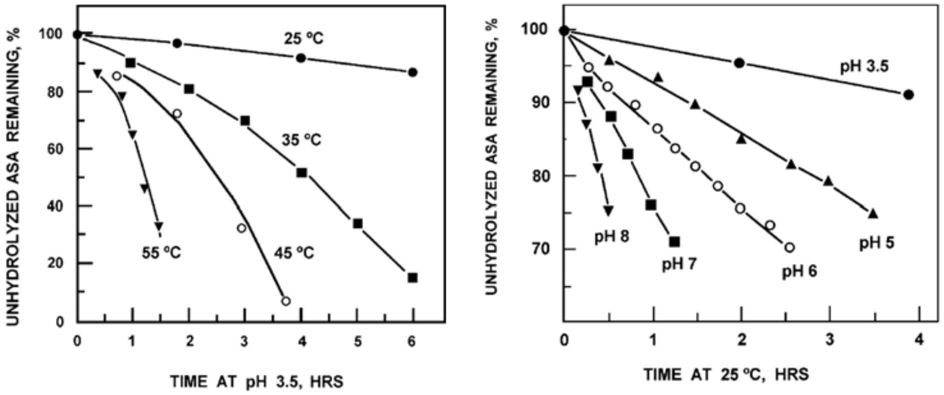

Figure 19. On the left, the ASA rate of hydrolysis as a function of temperature at pH 3.5. On the right, the ASA rate of hydrolysis as a function of pH at the temperature 25 °C /33/.

In hydrolysis, the shielding action of the stabilizer and/or surfactant at the ASA droplet surface is lost. ASA's stabilizer may act as a barrier of water to the ASA droplet surface. As water diffuses through the stabilizer barrier, hydrolysis occurs, the emulsion becomes destabilized and the rate of hydrolysis increases. The hydrolysis product of ASA combined with cations present in paper or board machine white water system forms insoluble succinates. Calcium, magnesium, sodium, copper and other metal salts form tacky deposits with hydrolyzed ASA and can impair the runnability, stuff paper- and boardmachine textiles like felts, make cylinders tacky and cause picking problems in the press section of the paper machine. Properties affecting the ASA hydrolysis rate on paper machine are gathered in the Table 6 by Martorana.

Table 6. Factors affecting to ASA hydrolysis. – decrease in hydrolysis, + increase in hydrolysis /1/

Parameter	Impact
Temperature rise from 20 °C to 70 °C	+++
pH rise ftom 4 to 9	++
Ca2+/Mg2+ concentration rise from 0 to 1000 ppm	++
Cationicity rise of starch/polymer	-
Rise of starch molecular weight	--
Rise of starch-ASA ratio from 0.2:1 to 1:1	--
Increase of emulsion particle size from 0.5 µm to 3 µm	++

4.2 ASA in paper- and boardmaking process

ASA is supplied as oily liquid, practically in 100 % active form having no charge or affinity for anionic cellulose fibers and is needed to be protected from moisture. Because of the fast reactivity of ASA, it is emulsified on-site. Storage time of prepared emulsion should be minimized. Emulsion should be kept at pH 3.5 or lower and the temperature slightly above freezing to minimize the hydrolysis reaction during storage /80, 81/. In the actual sizing process the hydrolysis is minimized by preparing the emulsion as late as possible, preferably only seconds before adding to the stock. This is a way to minimize the contact time of ASA oil drops and water. As well as in storage, the process pH needs to be stable and the temperature as low as possible for the paper- or boardmaking process. High pH, above 12, induces most of the sizing loss. The presence of basic material in the sheet likely enhances the breakage of the ester bond between ASA and cellulose. The way to lower the process pH is to add aluminum sulfate or PAC immediately after emulsification /81/.

ASA can evaporate during the drying of paper. In this case, vapor-phase transport of the ASA sizing agent is seen. Gess and Rende have found ASA and its byproducts from hoods of the paper machine drier section /80/. These deposits can be reduced by increasing ASA's molecular mass by using longer alkenyl chain ASA. ASA sizing is said to take place by various mechanisms, which are: flowing and spreading, diffusion and migration of the ASA oil droplets /20, 69, 70/. The migration through the paper web fibers occurs via vapor phase or via steam distillation on the droplets of water. ASA droplets can go into the vapor phase and after that re-deposit on another fiber surface after migration. The lower is the vapor pressure of ASA, the faster the migration through a paper web.

The rate of migration of ASA through a paper web depends on the vapor pressure of ASA, the bond energy between ASA and water, the distance ASA droplets would have to travel to achieve a uniform distribution through the cellulose fiber mat, and the energy available for this process to occur. To prove the migration phenomena, ASA was sprayed onto one side of a paperboard sheet by Gess. ASA showed the ability to migrate and develop hydrophobicity throughout the thickness of the board product. The ability to size the opposite side of the sheet increases with time and higher temperature. /81/

Many different forms of ASA are seen during the paper- and boardmaking process. The unbound ASA is usually in the hydrolyzed form, in Na-soap hydrolyzed form or in Ca-soap hydrolyzed form (Figure 20). It can also remain in the unreacted form. ASA is said to be in the bounded form when the desired fiber bond with cellulose exists /97/. Novak and Rende have stated that those ASA molecules that are adsorbed on calcium carbonate surfaces, can more easily revert to a non-sizing from during the storage of the paper /83/.

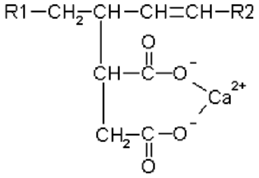

Figure 20. ASA hydrolyzed state dissociated with Ca^{2+} /20/.

Dosing of ASA is a result of process-specific calculations. On the other hand, higher amount gives better sizing response but is more expensive and may cause more deposit problems. For a carton board, typical ASA dose is said to be about 0.2 % to 0.35 % /80, 81/. The dosage for fine papers is stated to be typically from 0.1 % to 0.18 % by mass of oven dry fiber /1, 81/. With novel ASA products, the dosages can be some what smaller /98/. The difference between an ASA sizing agent dosage of chemical pulp and mechanical pulp is notable. The dosage with chemical pulps is much smaller due to the removal of lignin, as only the cellulose-based reactive substances remain in the pulp. In mechanical pulps all components, including lignin, remain in the fiber matrix increasing the consumption of ASA.

Factors affecting the needed amount of ASA are: the possible amount of surface size, filler amount, specific surface area of ASA oil drop, retention, stock type and the closure of water circulation. Closed systems have higher amount of charge and need more

ASA. Also, the configuration of the paper and board machine press-section has an effect on dosing. /81/

ASA addition can be done to thin stock or to thick stock depending on the paper- and boardmaking process. For example, the addition of ASA-cationic starch emulsion is done either to the thick stock at the stuffbox accepts or to thin stock, as close to the headbox as possible. In the latter case, the addition locations are the outlet of machine chest and the inlets of fan pump or screens. Addition to thick stock has its advantage on retention potential of ASA and fine material. Dilution water is a problem, though, because of the hydrolysis of ASA and water. Addition to thin stock is used to minimize the potential for hydrolysis; however the problem here is that the ASA association with fillers causes retention problems. Which option to take is mill-specific, but thin stock addition is favored when an immediate and proper mixing is available. /80, 81/

Common problems in ASA sizing are listed by Gess/80/:

1. Deposit control: non-ionic resin esters coming from the pulp mill along with bleaching, can reduce sizing efficiency and promote loss of sizing response. This is called size masking.
2. Retention: paper- or boardmaking in a neutral or alkaline pH system requires combination of cationic and anionic retention aids for optimum retention of the cellulose fines and any PCC filler. Too high amount of anionic charge will slow the drainage of the furnish and increase the costs of paper and board production due to the increased need of drying energy.
3. Control of micro organisms: potential reaction of anionic retention aids with chloride or sodium hypochlorite. Retention aids react with biocides causing the loss of retention and biological control because neither of the chemicals are doing their proper task.

4.3.1 Emulsification

When ASA is mixed with stabilizer and water under shear forces, the discontinuous ASA oil phase is scattered as small oil droplets into the continuous water phase. Stabilizer particles attach to the ASA oil droplet surfaces giving stabilizing effect against water hydrolysis reaction, if the right amount of stabilizer is applied to give complete saturation on oil droplets. The desired particle size lies between 0.5 -1.5 µm, where the reaction rate is high enough to provide good sizing but not yet too reactive to increase the hydrolysis reaction as unbearably high /1, 37, 60, 66, 99, 100/. A stable emulsion with no sizing response is not desired whereas a very reactive emulsion reacts so much with water that ASA is consumed in the hydrolysis reaction. Good sizing efficiency is achieved when as much ASA as possible is reacted with fibers. If reaction with water is dominant, bad sizing results. Typical surfactant is non-ionic alkyl phenyl ethoxylate and it can be used in addition to stabilizer or even by itself, providing the stabilization effect /77/. Its function is to enhance sizing agent spreading, facilitate emulsification and stabilize emulsion /91/.

Even distribution of ASA oil droplets onto a fiber web can be assisted by producing the desired size emulsion droplets. Stabilizers and surfactants have significant impact on emulsion particle size and stability. They exist to reduce costs of continuous on-site emulsification and to reduce hydrophobation losses through hydrolysis of ASA. Some commercial ASA sizes contain small amounts of surfactant to make emulsifying easier /80/. In general, ASA emulsification at an industrial scale requires high shear equipment (Figure 21). The basic equipments in industrial ASA emulsification are listed by Gess and Jenkins /66, 80, 100/:

1. A venturi system.
2. A turbine system.
3. A cavitron system.
4. Multi-stage centrifugal pump.

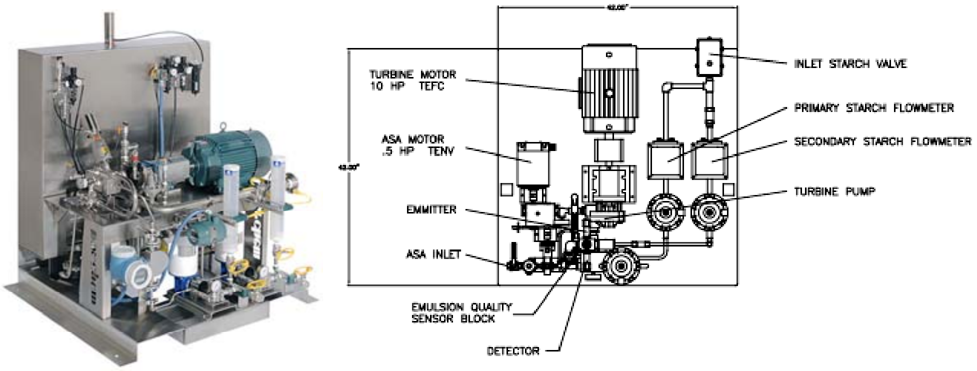

Figure 21. Norchem A3000 ASA turbine pump emulsifying unit /101/.

The high-shear turbine is the most used system /102/. With effective mixing the emulsion prepared tends to be more homogenic and last longer as stable. A low-shear venturi system is the simplest device. It has only a few moving parts, but its disadvantages are the necessity to use surfactant and the resulting large particle size. The particle size distribution produced is over 1 µm in minimum. A cavitron emulsifying pump, unlike the venturi system, may need continuous maintenance. Multi-stage centrifugal pumps are available but not in very common use. /4, 80, 99/

ASA emulsification with ultrasound can be used to produce smaller droplets with less energy in a cost-efficient way, contributing to better sizing due to the increase of the droplet surface area /58/. The industrial ASA ultrasound emulsification process is not seen and would require an online particle size measurement to operate /58/. While ultrasound emulsification requires no surfactant use, low-shear emulsification can require 0-5 % surfactant added. High shear equipment use typically 0-1 %. The desired situation is often to use the minimum amount of surfactant /81/.

4.3.2 Stabilization

ASA droplets are stabilized sterically (Figures 8 and 22), electrically and by particle stabilization. Stabilizers used are most commonly starches, polymers or microparticles. After stabilization, the properties of ASA no longer notably affect to the activity between different surfaces. By the right choice of stabilizer and the formulation of the protective layer, the properties of the ASA size and the paper or board sized can be controlled. In neutral and slightly alkaline conditions, the possibilities to affect ASA emulsion stability are to regulate stabilizer molecular weight and charge, affecting to the paper or board hydrophobicity /103/.

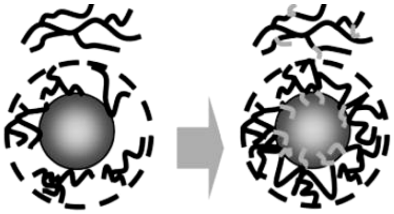

Figure 22. Starch on ASA droplet. The stabilizing effect of cationic starch (left) and an improved, esterified starch (right). The esterified form gives better colloidal stability in ASA emulsion towards water and other hydrophilic substances /84/.

Due to the surface coverage by steric stabilization, the internal sizing operations in water are enabled. Stability mainly depends on ASA emulsion particle size, pH, and temperature with water hardness. The size reversion is described to mean the loss of size response with time. The mechanism for sizing reversion of ASA and also AKD is the hydrolysis of the covalent ester bond between the size molecule and cellulose hydroxyl group /77/. A loss of the ester bond over time and the basic materials remaining in the finished paper or board accelerate the ester bond breakage, allowing sizing agent reorientation, and thus loss of liquid repellency. /84/

The most common ASA emulsion stabilizer, cationic starch has its concentrations usually around 1-2 % in emulsion, and the ratio of starch to ASA is generally about 1-6:1 /1, 4, 81/. The types of starches commonly used in ASA emulsion stabilization are potato, tapioca, corn, waxy maize and its *amphoteric* (i.e. anionic or cationic charge, based on pH) derivatives. Starches can be acidified with alum, citric or adipic acids. Several co-stabilizers of starch also exist, for example hydrophobically modified corn starch prepared by reacting Octenyl Succinic Anhydride (OSA) together with cationic corn starch. /84, 104/

Other common ASA stabilizers are cationic and anionic polyacrylamides (C-PAM's and A-PAM's). In addition to the typical stabilizing layer, these can have multiple layers on top of a sizing agent /105/. In ASA's case the interfacial multilayer on top of an anionic reagent consists of cationic, anionic and cationic stabilizers. The use of multiple protective layer systems on a sizing agent droplet is possible for example with differently charged polyacrylamides. These layers are: C-PAM, A-PAM and C-PAM with possibility to use different molecular weights and charge densities. The outmost layer determines the total charge /105/. PAM's are about one third of the usage of all different synthetic stabilizers commercially used with ASA. The ratio of polymer to ASA with PAM's is generally about 0.05-0.4:1.

Nonionic galactomannan, guar gum, polysaccharides have also been used for stabilizing emulsion with nonionic alkyl phenol ethoxylate as a surfactant. The combination of stabilizer and surfactant is said to decrease deposits and give better sizing response than with cationic starch /106/. The polymerization of new stabilizers and other stabilizing systems for ASA sizing are widely developed. A novel example which is stated to meets the requirements for a stabilizer system is poly dimethyl diallyl amine chloride acrylamide n-butyl methacrylate (P-DAVM) with surfactant /107/. Wide interest and research on stabilizers is on going due to deposit problems in many paper machines /5, 60, 70, 89/. Cost-efficient stabilizer systems which guarantee cleaner process conditions are in certainly in demand.

4.3.3 Additives in ASA sizing

Poly aluminum chloride (PAC) can improve ASA retention at the wire section, runnability at press and drying sections of paper or board machine, and overall sizing efficiency. Aluminum salts also reduce the needed ASA dose due to the reaction between ASA and aluminum hydroxide. Reduction of web breaks due to the low size tackiness related to pH, retained metal and the amount of free acid can also be seen. The complex of hydrolyzed ASA and alum is not a sticky deposit. It is harmless and non-reactive substance in the process. /4, 81, 94, 108/.

Another aluminum compound, papermaker's alum, is used with the dosage of 0.2-0.5 % of the fiber dry weight. Improvements in fines and filler retention can be seen, especially when anionic retention aids are used /109, 110/. The contact time of alum and a water system must be kept short because alum works as a cationic donor. Normally alum is added to the thick stock to provide time for pH stabilization before the ASA emulsion is added. A small amount can still be added close to the headbox to increase drainage /81/.

4.3 ASA internal sizing compared to other sizing systems

Compared to any other size, ASA has the highest rate of cure. The reaction with cellulose hydroxyl groups takes place rapidly in the dryer section of the paper machine at less than 5 % web humidity. More than 90 % of the attainable sizing potential in most cases is achieved before the size press unit, and complete sizing develops immediately off the paper machine. The selection of ASA or AKD as a sizing agent depends on the individual mill and paper or board machine conditions as the requirements of both products are different /111/.

AKD is slower in reactions with fewer problems in unwanted hydrolysis reaction, has a cure time of days or weeks, and needs high temperature in the paper machine drier section to develop fully /80, 81/. With AKD the slower rate of reaction minimizes hydrolysis /77/. The paper or board properties are controllable and measurable straight away with ASA, while with AKD the measurements cannot be done immediately.

Traditionally, low reactivity has been thought to be the difference in cellulose reactive sizes and rosin, the anchorage to cellulose is said to be different. In rosin sizing anchoring is provided through the bonding interaction between aluminum in the size precipitate and surface hydroxyl and carboxyl groups of the cellulose. Alum reacts with rosin to form internal size precipitate at the wet-end. The particle size and cationic charge density are determined by this process, which effectively control retention and distribution of the sizing agent on the fiber. The chemical transformation of rosin and alum determines the sizing efficiency. Rosin sizing is practically free from microbiological content due to the amounts of alum used and the acidic environment. In some cases, like higher pH, they are used. With AKD and ASA, biocides need to be used. /112/.

AKD gives an advantage on emulsion stability by staying quite stable for several weeks, but therefore demands more conditioning in the papermaking process. AKD can be transported via tankers in ready-to-use formulations and stored, while ASA emulsion is prepared on-site. The emulsification system at the paper and board machine is required. Transportation of nearly 100 % ASA enables purchasing of a larger batch at one time, since active size amount in the delivery is higher. Dry 100 % ASA can be stored as long as desired, whereas ready-to-use AKD needs to be used during few months, depending on consistency. ASA dosage needed for efficient sizing is, a little higher than that required with AKD but relatively cheaper overall /3, 80, 92, 111, 110/. While AKD is very unreactive towards cellulose, its reacted form provides high level of sizing. This is why even using a high percentage of AKD is said to have somewhat lower sizing effect compared to ASA /4, 81/. Few wet-end conditions of common internal sizes are summarized in Table 7.

Table 7. Effect of wet-end conditions to ASA sizing. – negative effect, + positive effect, 0 no effect /113/

Property	**ASA**	**AKD**	**Rosin**
pH	5 - 8.5	7 - 8.5	4.2 - 6.5
Increase of electrolyte concentration	-	-	-
Increase of specific surface area fines/fillers	-	-	-
Dispersion of anionic substances	-	-	-
Inrease of fiber-COOH bonding	+	+	+
Increased amount of trash	-	-	- → +
Inreased amount of hydrolysis products	-	(+)	0
Use of papermaker's alum	+	-	+
Temperature	-	-	(-)

The excess unreacted AKD on a sheet is not a problem due to the low reactivity and difference in chemistry compared to ASA. A hydrolyzed AKD ketone has a small positive sizing effect but is not as effective as the covalent bound of the size. The hydrolysis product of ASA, however, is a problem. It has serious effects on sizing if not retained in the sheet. This limits the sizing achieved using ASA. Excess unreacted ASA is hydrolyzed by the equilibrium moisture in the sheet /4, 80/. Low first-pass retention is detrimental to the sizing efficiency with ASA compared to AKD /114/.

Paper sized with AKD tends to have a low friction coefficient against paper machine and converting machinery metal surfaces so it is very slippery. This can cause problems with registration in subsequent converting operations, like printing, along with other undesirable effects. Anti-slip agents can be added to the sheet to ease this problem but not totally erase it. Unlike AKD or rosin, ASA does not affect the friction coefficient of the paper or board. This is advantageous in recycled grades. /4, 81/

ASA is typically used with grades that need moderate liquid penetration resistance /115/. This is why many writing and printing papers are sized with ASA. One reason

ASA works well in this regime is that most of these grades also require surface sizing applied by a size press after the dryer section. It is required to have a very high liquid resistance before the size press to control the penetration of the surface sizing solution. It is often not possible to achieve enough sizing with AKD in this situation by the time the sheet reaches the size press. On the contrary, for heavily-sized products such as liquid packaging board, the goal is to obtain the maximum degree of liquid penetration resistance possible. Using ASA to achieve very high hydrophobicity can be useless due to the de-sizing effect of hydrolyzed ASA. Use of high amounts of ASA emulsion will always result in increased potential of hydrolysis and lower the sizing of the sheet. On the contrary, in the case of AKD, a large dosage generally produces higher levels of sizing /4, 77, 81/.

Wide available pH range makes ASA very compatible in recycled paper sizing /81, 99/. This enables the use of high amounts of recycled fiber and filler. In recycled grades more ASA is required if there are sources of contamination, such as oleic acid. Sizing with ASA appears to be less expensive than using AKD /100/. The differences in toner adhesion are also significant. AKD sized sheet are substantially less hydrophobic than sheets treated with conventional rosin-alum size. The same property is important in applications involving extrusion coating of paper or board with a polymer.

While AKD has the advantage over ASA in user-friendliness, the cost reduction on sizing and other chemicals was seen in both high quality liner mill and a writing paper mill /60, 89, 111/. A size which would be more reactive than AKD but whose hydrolysis product did not de-size like ASA's, would be optimal. For this, Isogai has proposed alkyl oleate succinic anhydride. The acid hydrolysis of starch produced smaller ASA particles and improved ASA retention, resulting increased sizing efficiency. Another compound, esterified octenyl succinic anhydride is also more hydrolysis resistant /114/. These finding have been hardly applied in papermaking due to the lack of experience. Many other components are also studied but general practice is still sought, confirming the position of ASA. Table 8 sums up the different end product properties of internally sized paper from the three main sizes used. /4, 60, 111, 112, 116/

Table 8. Comparison of common internal sizing agents /117/. Effects of sizing on various properties of sizing agents – means negative effect, + means positive effect, 0 is means no effect

Property	Rosin	AKD	ASA
Strength	0(-)	0	0
Brightness	0(-)	0	0
Optical brightness	-	-	0
Adding of $CaCo_3$	-	+	+
Acid resistance ability	-	+	-
Ageing resistance ability	-	+	+
Rate of reaction	+	-	+
Friction	+	-	0
PE adhesion	+	-	0
Color adhesion	+	-	0
Bacterial growth	+	-	-
Hydrolysis	+	-	-
Adjustability with wet-strengthening chemicals	+	-*	-*

*melaminformaldehyde and ureaformaldehyde can be used

EXPERIMENTAL PART

5 OBJECTIVES AND EXPERIMENTAL PLAN

The objectives of experiments were to find good emulsion stabilizers, prepare stable ASA emulsions, give paper proper hydrophobation and to keep the papermaking process surfaces clean. In the four-step experimental plan various possible stabilizers were tested based on the literature search. The goal was to select proper stabilizers for use in ASA internal sizing. The most important requirements for ASA sizing emulsion stabilizer are to:

1. Stabilize the ASA sizing emulsion properly.
2. Give high hydrophobicity in ASA internal sizing of hand sheets.
3. Show as little as possible fouling in deposit tests.

From Figure 23 the experimental plan procedure can be seen. Emulsification of each stabilizer with two different ASA's was done in each individual step. The selections of stabilizers during the experiments were based on stability, sizing efficiency and the diversity of the different stabilizers available.

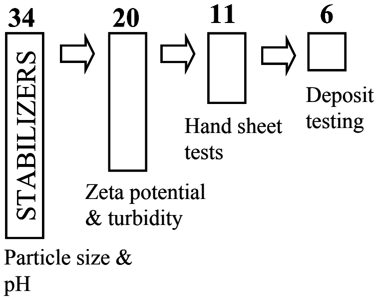

Figure 23. The proceeding of experiments. The size of the stabilizer bar depicts the amount of tested stabilizers and the exact number is seen above. In every step, ASA-stabilizer emulsification was done.

In the first step of the experimental plan, thirty four stabilizers were selected based on literature with potential in sizing emulsion stability and in internal sizing. Stabilizers were emulsified with two different ASA's. The twenty nine stabilizers out of thirty four were commercial chemicals already in use in the paper chemical industry, while the others were laboratory trial products. For most of the stabilizers, for example cationic starch, polyacrylamides and CMC's, the background information gave good guidance in making the selections for experiments /1, 2, 4, 71, 75, 80, 81, 105, 106, 114/. Having the particle size goal roughly in the range 0.5-5 µm, some stabilizers could be limited from the interest after the particle size tests of the ASA-stabilizer emulsions, simply based on the literature /1, 66/. The pH measurements were done in order to see the impact of ASA compared to stabilizer in emulsions and also to get some indication about the emulsion stability.

In the second step, after rough screening of stabilizer-candidates, the stability was studied in-depth. The zeta potential, mobility and turbidity of the twenty selected ASA emulsions were measured. Emulsification was done with both ASA's and with the twenty stabilizers. Results from this step clarified the stabilizer usability in ASA sizing emulsions, making the further selection possible.

In the third step, ASA emulsions were prepared with eleven selected stabilizers and these emulsions were used to make paper hand sheets with internal sizing including retention aid. Based mainly on Cobb_{60} sheet tests, stabilizers were selected for the deposit tests.

In the fourth step, six stabilizers were emulsified with ASA's and then mixed with PCC filler. The emulsion-PCC mixtures were circulated at a specific deposit tester /5/. The goal was to determine the fouling effect of ASA sizing emulsions. The sample plates at deposition tester simulated paper machine surfaces in drying cylinders. Emulsion-PCC condition simulated the water circulation system in paper- and boardmaking. Deposit amounts and visual characteristics were determined from the sample plates. Thermal gravimetric analysis (TGA) was then carried out for the deposited plates and the decomposition of stabilizers and ASA was seen.

During all the experimental steps, emulsion visual characteristics were observed and literal descriptions of each emulsion written. Light microscope pictures were also taken from selected emulsions in order to distinct the closer visual differences between stable and unstable emulsions.

6 MATERIALS AND METHODS

6.1 Materials

6.1.1 ASA sizing agents

Two types of ASA, produced by Kemira Ltd, Austria, were used as sizing agents. Pure ASA compound is referred as pure ASA. The second ASA compound includes surface active agents and is referred as easy emulsifying ASA (EE-ASA). /98/

6.1.2 Emulsion stabilizers

Table 9 shows the stabilizers used in every experimental step. Most of the stabilizers are commercially available and made by Kemira Ltd. The stabilizer selection procedure for the different steps of the experimental plan is handled with more depth in APPENDIX I. Most of the stabilizers of this work have been used in emulsification for decades /7/, but only some used in ASA sizing /2, 3, 66, 70/.

Table 9. Stabilizers used to give stabilizing effect on ASA oil droplets in each step of the experimental plan

Stabilizer description	Paricle size & pH	Zetapotential and turbidity	Sheets	Deposition
Cationic Starch - REFERENCE	X	X	X	X
1. C-PAM	X	X		
2. C-PAM	X			
3. C-PAM	X			
4. C-PAM	X	X	X	
5. C-PAM	X	X		
6. C-PAM	X	X	X	X
7. C-PAM+P-DADMAC	X			
1. A-PAM	X	X	X	
2. A-PAM	X	X	X	X
3. A-PAM	X			
4. A-PAM	X			
5. A-PAM	X			
5. A-PAM	X			
1. CMC	X	X	X	
2. CMC	X			
3. CMC	X			
4. CMC	X			
5. CMC	X			
1. Bentonite	X	X	X	X
1. Silica	X	X		
G-PAM	X	X		
A-VAM	X	X		
P-VAM	X	X		
P-DADMAC	X	X		
PVA	X	X	X	X
Pectin	X	X	X	
PAAE	X	X	X	X
1. Amphoteric polymer	X	X		
2. Amphoteric polymer	X			
3. Amphoteric polymer	X			
Dicyandiamide	X			
Bonding agent	X	X		
GGM	X	X	X	

Cationic potato starch was produced by Roquette Nordica Ltd, France. Cationic and anionic polyacrylamides (C-PAM's and A-PAM's), were produced by Kemira Ltd, Finland. Carboxymethyl celluloses (CMC), products, were produced by CPKelco Ltd, Finland. Microparticle bentonite was produced by Kemira Ltd, Germany, and microparticle colloidal silica, was produced by Kemira Ltd, Finland. Glyoxylated polyacrylamide (G-PAM), polyvinyl amine (P-VAM), poly diallyl dimethyl ammonium chloride (P-DADMAC), and polyamidoamine-epichlorohydrin (PAAE), were produced by Kemira Ltd, Finland. Pectin 76280 from citrus peel was produced by BioChemica Fluka Ltd, Germany and polyvinyl alcohol 3-96 (PVA) by Sigma-Aldrich Fluka Ltd, Germany. Polyamide derivative (A-VAM) and first and second amphoteric polymers were produced by Derypol, S.A., Spain. The third amphoteric polymer was produced by Kemira Ltd, Finland as well as dicyandiamide and bonding agent. Galactoglucomannan (GGM) was produced at Åbo Akademi University, Finland.

To characterize stabilizers, the charge densities were compared to reference starch, having a very low cationic charge. Its degree of substitution (DS) was medium, 30 %. Based on this, the scale from a low to high values was formulated, where a low DS value or as well low charge density (LCD) is 0.5 meqv/g and under, medium (MCD) 1-3 meqv/g and a high charge density (HCD) above 3 meqv/g. They were also compared inside the specific group. In addition to that, some stabilizer charges were pH dependent in a way that pH affects the charge density degree, while amphoteric stabilizers could change their charge completely from negative to positive or the other way around. The charge symbol, +, - and 0 are used with the charge density abbreviations. The scale for molecular weights was also formulated, based on starch, C-PAM's and A-PAM's molecular weights, Low molecular weight (LMW) is under 0.1 Mg/mol, medium (MMW) 0.1-3 Mg/mol and high (HMW) above 3 Mg/mol. Molecular weight is affected by substance structure, production manner and measurement method. /118/

Seven C-PAM's had molecular weights and charge densities from low to high (LMW to HMW). The mixture of 7.C-PAM and P-DADMAC had high total molecular weight and high total charge density. 3.C-PAM with LMW, had a pH dependent charge density and was highly cationic in acid pH and low cationic in neutral and alkaline pH range.

Six different A-PAM's had molecular weights from LMW to HMW, as well as charge densities from LCD- to very HCD-. Five different CMC's had charge density values, ranging from low to medium, low being near to DS 50 % and medium near to DS 70 %. Molecular weights varied from LMW to HMW according to the code number, increasing values having higher molecular weight. Carboxyl chain length had an impact on the stabilization effect.

Three amphoteric polymers, 1-3, had HMW, HMW and MMW. The charge density was slightly anionic with HMW products. Their charge densities were pH dependent, being highly anionic in acid pH and low anionic or cationic in neutral and alkaline pH, which were the conditions during all experiments. Amphoteric polymers have earlier been used as dispersion chemicals with pigments in paper chemistry.

Bentonite and silica stabilized the ASA emulsions with small particles, instead of steric or electrostatic stabilization based soluble nonionic, polymers, which were the case in C-PAM's, A-PAM's and CMC's /35/. Microparticles formed Pickering emulsions with pH dependent MCD- between 0.15-0.5 meqv/g in neutral conditions. Due to the characteristics, particle sizes and shapes are reported instead of molecular weights. The particle sizes were around 1 µm with lamellar bentonite and around 5 nm with silica which was spherical in shape. Silica consists of silicon oxide and bentonite of polyaluminum silicate. Bentonite is an unhomogenic natural product, containing silicon acid, sol silicates and very small amounts of some cations, on its surface, like iron.

The novel experimental laboratory products, G-PAM, A-VAM and P-VAM had LMW, HMW and HMW. G-PAM had branched structure and LCD+. A-VAM had branched structure and pH dependent charge density, being HCD+ in neutral and alkaline conditions. P-VAM had HCD+. Polyamide derivative P-VAM has been earlier used as water removal chemical in paper- and boardmaking.

GGM was taken to the test series with the intention of finding new applications to unmodified wood separated GGM. It would have good availability and a high cost-efficiency if the right application did exist. GGM is a polysaccharide and its molecular weight was very low, 0.04-0.05 Mg/mol, and it was nonionic or had very LCD-. GGM included 3 % of galacturonic carboxyl acids. GGM type of products has been used earlier by Koskela and Hormi /106/.

P-DADMAC had MMW and HCD-. PVA had an esterification rate of 30-40 %, hydrolysis rate of 96.8-97.6 Mol%, MMW of 0.5 Mg/mol and was nonionic with practically no charge density. Residue acetyl amount was 2.3-3.1 %. Pectin had LMW and DS value was 63-66 %, indicating MCD-. The ash content was stated to be under 7 %. P-DADMAC had been earlier used for pitch control, a promoter for anionic retention aids and charge neutralization. PVA has been used as paint thickener, adhesive and textile sizing agent before /119/. Pectin has been used in ASA stabilization previously /105, 120/.

PAAE had a very branched and cross-linked structure. It had MMW and MCD-. Dicyandiamide had LMW and MCD+. Bonding agent was a polyacrylamide derivative. It had a very branched and cross-linked structure. It was used in order to see the bonding ability of the chemical, among the stabilizing effect. It had MMW and LCD+. In addition to bonding agent, PAAE, GGM, PVA, and 1.A-PAM (LMW, LCD-), were used to study the strengthening effect of the paper structure. PAAE has been used earlier as wet-strength agent, and dicyandiamide has earlier been used as fixative. It bounds anionic trash from the paper and board machine water system and can be labeled as anionic trash catcher. Table 10 summarizes the charge density, degree of substitution and molecular weight details of the stabilizers.

Table 10. ASA emulsions stabilizer properties. Molecular weights, degrees of substitutions and charge densities are described as low, medium and high.

Stabilizer description	Mw [Mg/mol] or DS [%]	Charge compared to reference: cationic + anionic -	
Cationic starch	MEDIUM	VERY LOW	+
1. C-PAM	HIGH	HIGH	+
2. C-PAM	HIGH	MEDIUM	+
3. C-PAM	LOW	PH DEPENDENT, LOW	+
4. C-PAM	MEDIUM	MEDIUM	+
5. C-PAM	VERY LOW	MEDIUM	+
6. C-PAM	MEDIUM	MEDIUM	+
7. C-PAM+P-DADMAC	HIGH+MEDIUM	HIGH	+
1. A-PAM	LOW	LOW	-
2. A-PAM	HIGH	MEDIUM	-
3. A-PAM	HIGH	LOW	-
4. A-PAM	VERY HIGH	MEDIUM	-
5. A-PAM	MEDIUM	MEDIUM	-
6. A-PAM	VERY HIGH	MEDIUM	-
1. CMC	LOW	MEDIUM	-
2. CMC	LOW	LOW	-
3. CMC	MEDIUM	MEDIUM	-
4. CMC	HIGH	LOW	-
5. CMC	HIGH	LOW	-
Bentonite	PARTICLE	ANIONIC PH DEPENDEND	-
Silica	PARTICLE	ANIONIC PH DEPENDEND	-
G-PAM	LOW	LOW	+
A-VAM	HIGH	PH DEPENDENT, HIGH	+
P-VAM	HIGH	HIGH	+
P-DADMAC	MEDIUM	HIGH	+
PVA	LOW	NO CHARGE	**0**
Pectin	LOW	MEDIUM	-
PAAE	MEDIUM	MEDIUM	+
1. Amphoteric polymer	HIGH	PH DEPENDENT	+/-
2. Amphoteric polymer	HIGH	PH DEPENDENT	+/-
3. Amphoteric polymer	LOW	PH DEPENDENT	+/-
Dicyandiamide	LOW	MEDIUM	+
Bonding agent	MEDIUM	LOW	+
GGM	VERY LOW	VERY LOW OR NONE	**-/0**

The saturation of the stabilizer on ASA oil droplets with all stabilizers used was expected to be at least 100%. Information from earlier projects was used to determine the polymer-to-ASA ratio for the desired saturation. Too low a ratio would promote destabilization and too high ratio depletion flocculation. Based on earlier research, 0.1:1 was high enough ratio to fully cover the surface of an ASA oil droplet for all stabilizers /105/.

6.1.3 Pulp

The composition of stock used in sheet tests was 50 % chemical kraft pulp made from birch and 50 % chemical kraft pulp made from pine. Both pulps were beaten to Schopper-Riegler (SR) number 25 in a Valley beater according to ISO 5264/1, excluding the wet disintegration before beating. The pulp was cycled in the hollander without weights for 30 minutes. SR measurements were carried out according to ISO 5267-1. The pulp concentration was determined according to ISO 4119:1995 standard and dry matter content according to ISO 638:1978. As a pulp starch, reference starch stabilizer was dosed 5 kg/t. pH was kept between 8.0 and 8.5 with 10 % NaOH adjustment.

6.1.4 Other chemicals

Retention chemical by Kemira Ltd, Finland, was used as a retention aid of the paper hand sheets. It had very HMW compared to stabilizer C-PAM's, and MCD+. Albacar 5970 scalenohedral $CaCO_3$ PCC produced by Specialty Minerals Ltd, England, was used to simulate process filler in deposit testing. This PCC had particle size of 1-2 µm, lamellar shape and specific surface area of 6-12 g/m^2 /121/. The PCC's zeta potential was 11.5 mV ± 9.8 mV. 10% NaOH was used for pulp pH stabilization in hand sheet tests and in deposit testing, and 5 % NaOH was used in sample plate cleaning.

6.2 Methods and equipment

ASA emulsion preparation, stability measurements, hand sheet tests and deposit tests were done at Kemira and at Helsinki University of Technology, Finland. ISO standard procedures were followed and standard equipments were used with few exceptions that are mentioned in the specific procedure descriptions. Those procedures with no standard are explained more in-depth or references to extensive procedure descriptions are given.

6.2.1 Emulsion preparation

Cationic potato starch stabilizer solution was prepared containing 2.5 % of starch and deionized water. The solution was cooked for 30 minutes at temperature between 94-98 °C under good mixing. After cooking, the solution was cooled to room temperature and used within a day. The starch for the fourth step of experimental plan, the deposit tests, was cooked as 3.5 % solution. Other stabilizer solutions were prepared as 0.1 % consistency into deionized water in the first, second, and third steps of the experimental plan. In the fourth step the stabilizer solution consistency for stabilizers other than starch was 0.15 %. Stabilizers in solid form were assumed as absolute dry, and liquid ones were prepared according to their dry matter content. Solid stabilizers were mixed one day with magnetic stirrers and liquid ones for two hours before emulsification. ASA consistency was 1 % /2/.

A Braun 500W Powerblend MX 2000 blender was used for emulsification (Figure 24). A kitchen blender has been used also earlier in laboratory scale by Chen /2/. It emulsified the stabilizer solution and ASA sizing agent with continuous mixing of 2 minutes at the position 1 on the scale of 1 to 5. The single emulsion preparation amount was 0.3 liters in first, second and third steps of the experimental plan. In the fourth step 0.6 liter amounts were emulsified and it was the maximum possible amount for the device.

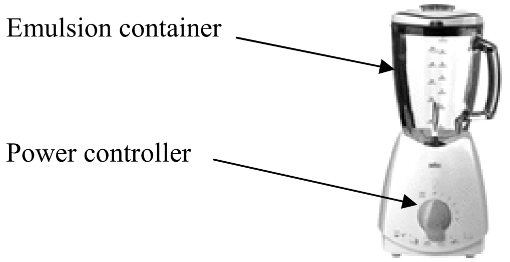

Figure 24. Braun Powerblend MX 2000 500W kitchen blender was used for emulsification of ASA-stabilizer emulsions. The power scale of the controller goes from 0 to 5. Emulsion container size is 1.75 liters.

Starch-to-ASA ratio was 2:1 during all experiments, the cationic starch functions as an emulsion stabilizer, a retention promoter and also the same way surfactants work (i.e. ease the emulsification event), in sizing emulsions /2/. In the first step of the experimental plan the stabilizer-to-ASA-ratio of 02:1 was used for all the other stabilizers. In the second, third and fourth steps the ratio was 0.1:1.

6.2.2 Emulsion measurements

Emulsion particle size measurements were done with Master sizer 2000 device by Malvern Instruments, UK. This technology relies on static light scattering, using the Mie theory to determine the particle-size distribution. The intensity of the scattered light is measured by multiple photosensitive detectors /57/. The refractive index of both ASA's was chosen to be 1.500 for all the measured emulsions. For the continuous phase, water, refractive index of 1.330 was used. Emulsion was diluted before measurement. The particle size results were reported as d(0.5) values meaning that over 50 % of the particles are the same size or below the value reported. The measurements were done straight after emulsification, 30 minutes after emulsification and four hours after emulsification, to see the changes in emulsion stability.

pH values of each ASA emulsion were measured with Mettler Toledo MP 120 pH meter by Mettler Toledo, UK. The measurements were done in the experimental plan first step, straight after emulsification, after 30 minutes and after four hours, to see possible changes in pH values Selected ASA-stabilizer emulsions were also scanned with Leica DMLM optical microscope by Leica Ltd, Germany at the 0 and 30 minutes from the emulsification. Fit 1 and magnification of 50 were used.

Emulsion turbidity measurements were executed with Turbiscan MA 2000 device by Sci-Tec Inc, USA, which is depicted in detail by Mengual and Lemarchand. /122, 123, 124/. The optical method uses light transmission and backscattering to analyze the sedimentation, creaming, flocculation and coalescence phenomena in emulsions. Multiple light scattering theory is applied in Turbiscan computer program calculations /125/. Four hour measuring time was chosen at the measuring interval of five minutes during the whole operation.

Turbiscan data for analyses was selected according to Figure 25. The data point locations from test tube bottom were; values between 3-10 mm for the minimum backscattering, values between 30-32 mm for average backscattering and maximum backscattering values from the whole tube length, meaning in practice, the 45-50 mm location. Searched backscattering data were calculated with Microsoft Excel linear regression function, which gave trend line slopes and their standard errors in matrix form. The trend line slope numerical values describe the emulsion stability.

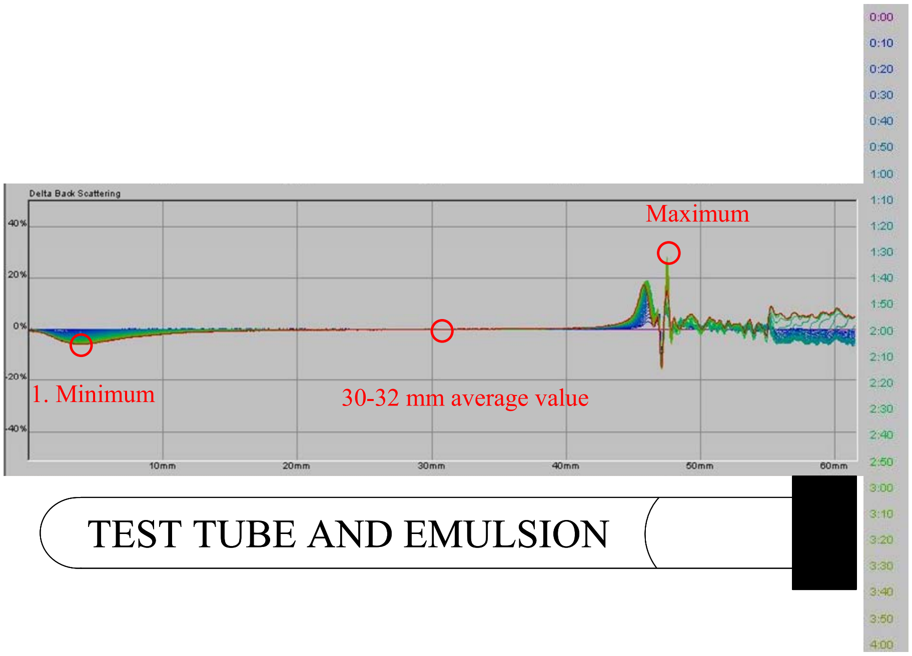

Figure 25. Selecting data from Turbiscan device graph. Under the graph the test tube is seen. The graph x-axis values are distances from the test tube bottom in millimeters. At the left side y-axis shows the change of backscattering in percentage and at the right side y-axis, the sampling time with color changing during time can be seen.

For zeta potential measurements and emulsion droplet mobility results in electric field, Coulter DELSA SX 440 by Langley Ford Instruments, USA, was used. DELSA is an abbreviation of Doppler electrophoretic light scattering analyzer. It is an analytical instrument that measures distribution of electrophoretic mobility and zeta potentials of particles and colloids (0.02-30 µm in diameter, sedimentation limited) in liquid suspension using laser Doppler velocimetry /126/. Emulsions prepared were diluted to 1:50 into deionized water from emulsification consistency and run straight away, after 30 minutes and after four hours from emulsification.

6.2.3 Paper hand sheet preparation

For the paper hand sheets, 1 kg/t and 2 kg/t ASA dosages were used, based on emulsion stability and sizing agent consumption literature /15, 99, 116/. The retention aid dosage was 0.2 kg/t. It was used in all emulsions, excluding those that where stabilized by using 2.A-PAM (HMW, MCD-). In these cases, the same 2.A-PAM was used as a retention aid with the dosage of 0.2 kg/t. First, ASA emulsion, diluted to 10% from emulsification concentration, was added to the one sheet pulp amount under good mixing and after 10 seconds time, retention aid was added. After 10 seconds more time, the stock was added to the sheet preparation mould and it was used according to standard ISO 3688.

Paper hand sheets were formed according to ISO 5269-2 with exceptions in wet pressing and drying. The sheets were filtrated for 10 seconds and pressed straight after forming, first for 20 seconds with one clean and two used blotters and then for 2 minutes with 4 bar pressure with sheet press by Lorentzen & Wettre, Sweden, and after that dried in vacuum pressure drier by Ernst-Haage, supplied by Lorentzen & Wettre, Sweden, for 3 minutes time with negative pressure of 0.9 bar. The sheet was vacuum pressed with one blotter on the other side, the sheet wire side facing to the vacuum drier with no blotter. Twenty used blotters were used during wet pressing instead of pressing plates. Sheets were conditioned according to ISO 187 before testing. Sheet preparation procedure phases are presented in a table in APPENDIX II.

6.2.4 Paper hand sheet testing

Cobb_{60}, dry and wet tensile indices, grammage, air permeability and thickness of the sheets were measured. Grammage goal was 80 g/m² ± 2 g/m² typical in laboratory trials /2/. It was determined according to ISO 536 and thickness according to ISO 534 with micrometer 250 by Lorentzen & Wettre Ltd, Sweden. Tensile properties were measured according to ISO 1942-2 with SE062 apparatus by Lorentzen & Wettre Ltd, Sweden. In wet tensile index determinations, 2 minutes wetting time and light drying was used for the test pieces before testing. Air permeance was done according to ISO 5636-3 with air permeance tester 166 by Lorentzen & Wettre Ltd, Sweden, and Cobb_{60} measurement according to standard ISO 535:1991(E) with standard Cobb W2 apparatus by Lorentzen & Wettre Ltd, Sweden.

6.2.5 Deposition testing

Deposition tester described by Lindfors /5/ was used to contaminate 0.5 mm thick stainless steel AISL 316 model plates with surface quality 2B (figure 26). The size of the curved steel plates was 61 mm x 134 mm and 7 mm (Figure 27). The contamination was done with 4 liters of 0.9 % ASA emulsion including stabilizer and 1.5 % of PCC. The PCC product was first diluted from solid form to 20 % solution and mixed one day. The flow of the deposition device was adjusted to 1.5 l/min. The electrical engine by ABB Ltd, Finland was working on 13 rpm, corresponding about 28 m/min. At the beginning of each 30 minutes test run, the pH was adjusted in between 8.0 and 8.5 with 10% NaOH. After that, pH was not further controlled. The test plates were attached to the cylinder drum according to the Figure 26 by four screws each. An air fan was used to heat the deposition tester and the emulsion container was placed in hot water bath. The temperature was between 35 °C and 55 °C during the 30 minute runs.

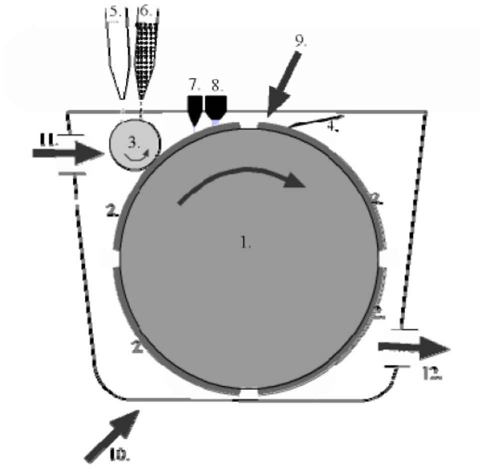

Figure 26. Schematic drawing of the deposition tester. 1: sample holders cylinder (diameter 150 mm); 2: sample surfaces; 3: press roll; 4. doctor blade; 5: chemical addition 1; 6: chemical addition 2, 7: high pressures shower; 8: low pressure shower; 9: air fan (heating); 10 heating; 11: circulation flow inlet; 12: circulation flow outlet /5/.

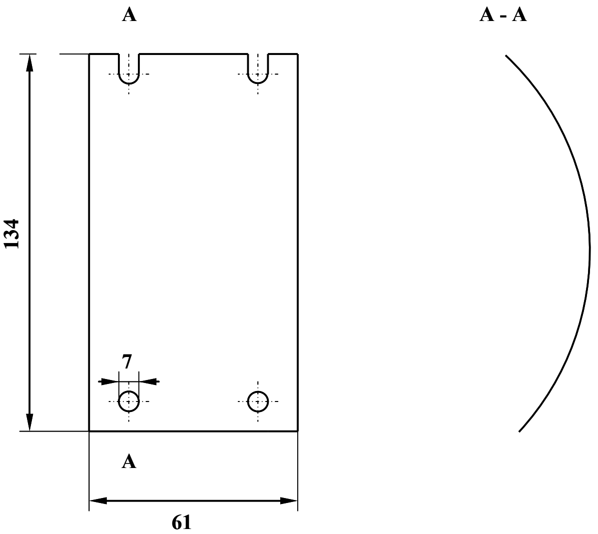

Figure 27. Mechanical drawing of a stainless steel sample plate used in deposition tester. Width 61 mm, height 134 mm and hole diameter 7mm.

After 30 minutes of circulation, the device was stopped and test surfaces removed from the cylinder drum. The sample plates were dried in 105 °C oven for 10 minutes to remove additional water and then weighed. Plates were weighted before and after the contamination to determine the deposit amounts. The results could be presented in the form of g/m² due to the plate treatment: a standard method for plate wiping after deposit test was formulated, i.e. surface area of the deposit on the plate was known and the g/m² value could be calculated. The surface area was (0.134 m - 0.017 m) x (0.061 m - 2 x 0.002 m) = 0.0057 m².

Steel sample plates were washed and coded before deposition tests. Branson B1200 E3 ultrasonic cleaner by GWB, USA, was used. The operation frequency was reported to be 47 kHz ± 6 % by manufacturer. Four plates were placed in 800 ml decanter at a time and the decanter was placed in ultrasonic cleaner containing deionized water as a medium for ultrasonic waves. Each stage of the cleaning session was 10 minutes and the cleaning substances in different stages were: acetone, 5 % NaOH, two times deionized water and finally ethanol in this order. Between acetone, NaOH and ethanol stages the plates were dried with Nitrogen gas.

Thermal gravimetric analysis (TGA) used for deposited sample plate testing is an analytical method to measure the weight loss (or weight gain) of a material as a function of temperature. TGA has been used before in internal sizing evaluations /120/. In the test procedure, the material is heated and it can loose weight via drying or from chemical reactions that liberate gasses. The material can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and weight gain are disturbing processes to the sample material, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods /127/. For this reason reference samples were run with pure ASA and EE-ASA and starch individually first. The reference graphs helped the interpretation of the actual ASA-stabilizer graph peaks.

The TGA device was Mettler TGA/SDTA851 by Mettler, UK. The thermal ramps were set to heat increase from 30 °C in 10°C/min to 900 °C. From selected contaminated sample plates, a solid 2-30 mg sample was scratched to TGA microbalance. The goal of TGA was to get information about the content and separation of organic and inorganic matter, i.e. ASA-stabilizer components and PCC. TGA peaks were interpreted to deposition amounts by using the information about Calcium carbonate, $CaCO_3$, breakage during heating process, seen in equation 4:

$$CaCO_3 \rightarrow CaO\ (s) + CO_2\ (g) \qquad (4)$$

Breakdown that is seen is the evaporation of CO_2 carbon dioxide. Inorganic solid CaO calcium oxide remains as in the form of ash after thermal treatment. Carbon dioxide, CO_2, molecular weight is (12,01+2 x 16,00) g/mol = 44,01 g/mol. The amount of remaining CaO can be calculated by assuming that $CaCO_3$ is pure and the breakdown is complete. The remaining amount of $CaCO_3$ is divided by the molecular weight proportion of CO_2, 0,441, and the desired remaining CaO amount is evaluated.

7 RESULTS AND DISCUSSION

7.1 Emulsion stability

The particle size results of pure ASA and all stabilizers are seen in Figure 28. Very successful emulsions were those of PVA (LMW, 0), pectin (LMW, MCD-), 1.amphoteric polymer (HMW, LCD-), 2.amphoteric polymer (HMW, LCD-) and dicyandiamide (LMW, MCD+). They had emulsion particle size values in between 1 -3 µm d(0.5), which means that 50 % of the particles in measured emulsion are the size or smaller of the given value. Most of the emulsions prepared had the particle size d(0.5) values ranging in between 4-5 µm. The most unstable ones, the emulsions of 3.amphoteric polymer (LMW), 7.C-PAM-P-DADMAC mixture (HMW, HCD+) and 5.C-PAM (very LMW, MCD+), aggregated in emulsification and showed d(0.5) values over 10 µm. Reference starch (MMW, very LCD+), with pure ASA had emulsion particle size d(0.5) values 4-5 µm.

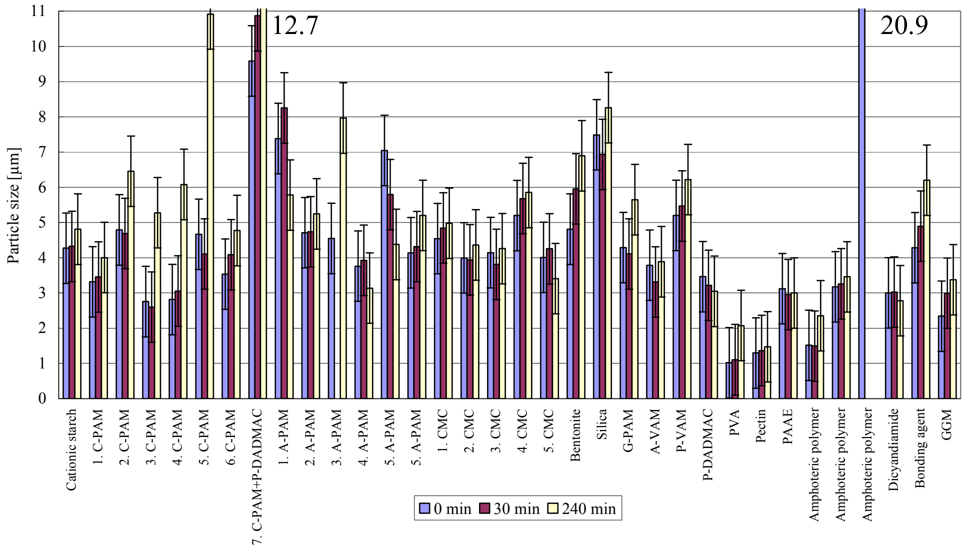

Figure 28. Particle size d(0.5) values of emulsions with pure ASA. d(0.5) means that 50 % of the particles in measured emulsion are the size or smaller of the given value. Standard deviation values are presented.

When EE-ASA was used, the average droplet diameter was radically smaller than that of ASA emulsions (Figure 29). On average, the particle size d(0.5) values were near 2 µm. The best emulsions had particle sizes from 0.5 to 1.5 µm stated optimal in literature, based on balance between reactivity and stability /60, 66/. Those values were gained with starch (MMW, very LCD+), 5.C-PAM (very LMW, MCD+), 6.C-PAM

(MMW, MCD+), P-DADMAC (MMW, HCD+), 1.amphoteric polymer (HMW, LCD+), bonding agent (MMW, LCD+) and GGM (LMW, LCD-/0).

The 4.C-PAM (MMW, MCD+), 1.A-PAM (LMW, LCD-), P-VAM (HMW, HCD+), PVA (LMW, 0) and all CMC's tended to have even too small particle size with EE-ASA for optimal emulsion, thought having great reactivity, they would cause too high rate of hydrolysis /1, 2, 75/. The 3.amphoteric polymer (LMW LCD-), 3.C-PAM (LMW, LCD+), dicyandiamide (LMW, MCD+), and G-PAM (LMW, LCD+) aggregated straight after emulsification and had emulsion particle size d(0.5) values over 10 µm.

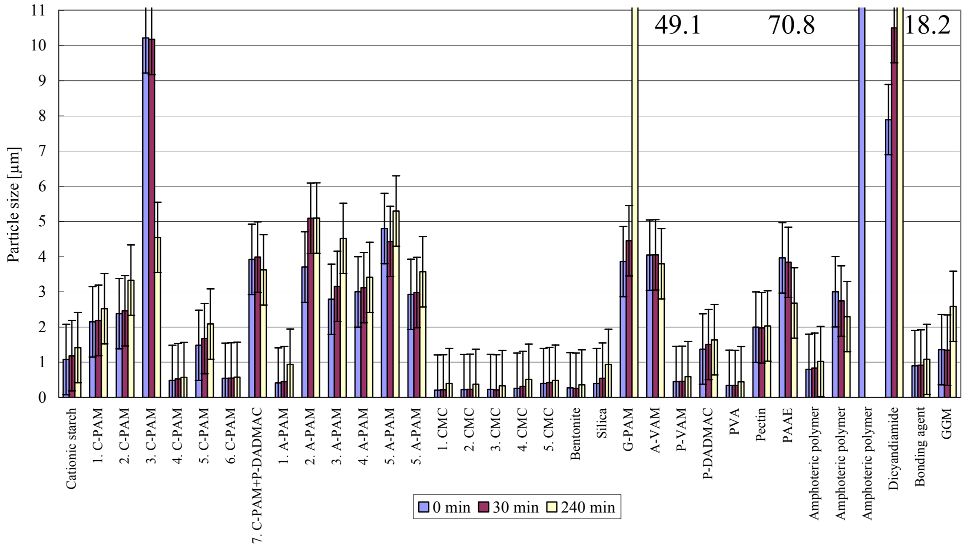

Figure 29. Particle size d(0.5) values of emulsions with EE-ASA. d(0.5) means that 50 % of the particles in measured emulsion are the size or smaller of the given value. Standard deviation values are presented.

With pure ASA, low molecular weight stabilizers gave optimal particle sizes. Unsuccessful emulsion stabilizers had all medium charge density. With EE-ASA, aggregates seemed to form with emulsions stabilized by low molecular weight stabilizers. Successful stabilizers had low to medium charge densities. The difference in industrial emulsification and laboratory scale operation has to be taken in notice, since industrial emulsification often produces smaller particle sizes than laboratory devices. This means that some of the emulsions stated medium or high, based on literature, in these experiments, would give stable and smaller sized emulsion droplets in industrial environment.

With four stabilizers the differences between two ASA's were significant. The 3.C-PAM (LMW, LCD+) and dicyandiamide (LMW, MCD+) showed near optimal values with pure ASA but high aggregation with EE-ASA. In the case of dicyandiamide it might have been the stabilizer chloride reacting with ASA's surfactant. The mixture of 7.C-PAM-P-DADMAC (HMW, HCD+) and silica (LCD-) showed average and even too small values with EE-ASA but high aggregation of particles with pure ASA. This indicates that for the first two mentioned stabilizers, the surfactants were detrimental. For the last two, they were needed to create optimal emulsion.

Average emulsion pH with pure ASA, was slightly over 4.5 and with EE-ASA, around four. The 4.A-PAM (very HMW, MCD-), and CMC's indicated highest emulsion pH's over six. C-PAM's with the rest of the stabilizers had pH values in between four to five. Pure ASA had slightly higher pH's than EE-ASA. pH values of each emulsion are presented, in APPENDIX III.

ASA's themselves had pH value around three to four. High pH values were caused by stabilizers. High pH was not desired since lower pH gives lower level of ASA hydrolysis and is thus desired /95/. It has been shown that already in pH 8, ASA hydrolysis is fast, whereas only little hydrolysis can be seen in pH 6 /105/. If the pH value of an emulsion decreases fast during time, the emulsion stability is typically poorer than with those emulsions with stable pH values during time. The rate of stabilizer adsorption on ASA oil droplet surface is dependent on the degree of hydrolysis, which was greater in sheet preparation and deposit test, because the pH was fixed to resemble process conditions, to 8-8.5.

In Figure 30 the zeta potential values for pure ASA emulsions can be seen. C-PAM's had zeta potentials in between 0-60 mV. The zeta potential values of 4.C-PAM (MMW, MCD+) and 5.C-PAM (very LMW, MCD+) turned to negative after four hours, implicating instability. A-PAM's had negative zeta potentials in between -30 and -80 mV. G-PAM (LMW, LCD+), A-VAM (HMW, HCD+), and P-VAM (HMW, HCD+), all had medium positive zeta potentials. P-DADMAC (MMW, HCD+) had the highest positive value of zeta potential, over 60 mV. Pectin (LMW, MCD-), GGM (very LMW, LCD-/0) and PVA (LMW, 0) had average negative zeta potentials. The 1.amphoteric polymer (HMW, LCD-), had negative, near to zero zeta potential, 6.C-PAM (MMW, MCD+), and bonding agent (MMW, LCD+), had slightly positive zeta potentials.

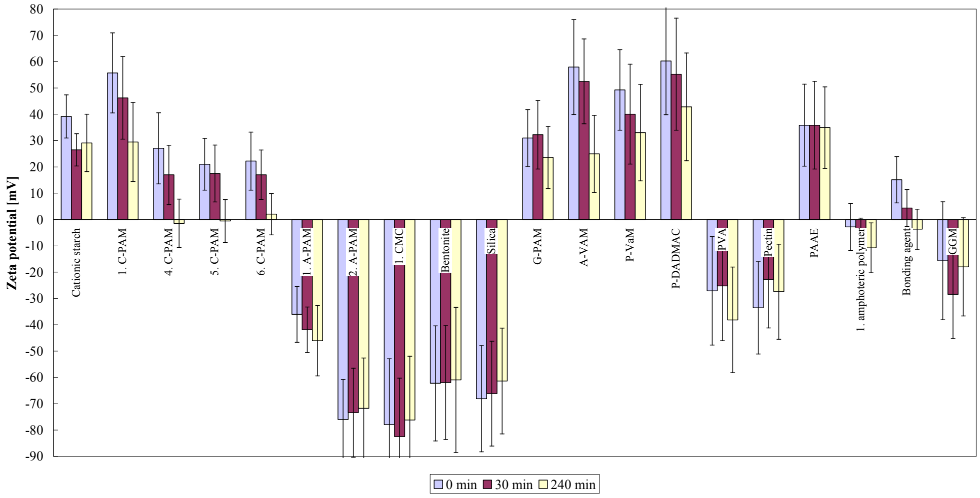

Figure 30. Zeta potential values for emulsions with pure ASA and stabilizer. Standard deviation values are presented.

Those emulsions indicating only small changes in zeta potential values during 4 hours measurements were the most stable ones. With pure ASA, these had typically medium charge density, like PAAE (MMW, MCD+), and bentonite (MCD-). The most unstable ones were: 4.C-PAM (MMW, MCD-), 5.C-PAM (very LMW, MCD-), 6.C-PAM (MMW, MCD+), and bonding agent (MMW, very LCD-/0) had low to medium molecular weights.

In Figure 31, zeta potential values of EE-ASA are presented. 1.C-PAM (HMW, HCD+), A-VAM (HMW, HCD+) and PAAE (MMW, MCD+) had average cationic zeta potential values. Most of the anionic zeta potential values were quite high, near to -80 mV. Only PVA (LMW, 0) and GGM (LMW, very LCD-/0) had medium negative zeta potentials, around -50 mV. The difference in zeta potentials between two ASA's was not as significant as it was in the case of particle sizes.

Those stabilizers indicating good emulsion stability based on zeta potential were reference starch (MMW, very LCD+), 1.A-PAM (LMW, LCD-), 2.A-PAM (HMW, MCD-), 1.CMC (LMW, MCD-), bentonite (MCD-), silica (MCD-), PVA (LMW, 0) and P-DADMAC (MMW, HCD+). Poor stability were seen with 4.C-PAM (LMW, MCD+), 5.C-PAM (very LMW, MCD+), 6.C-PAM (MMW, MCD+) and with bonding agent (MMW, LCD+) stabilizers.

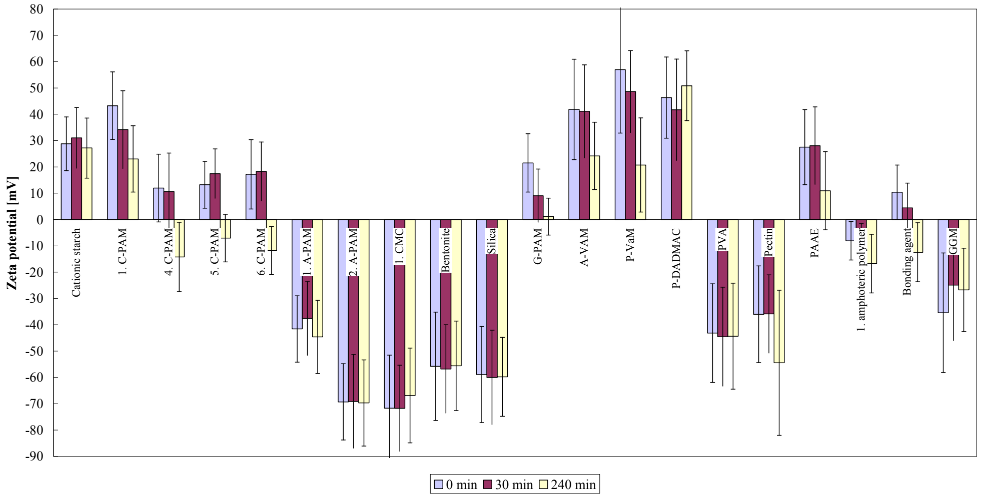

Figure 31. Zeta potential values for emulsions with EE-ASA and stabilizer. Standard deviation values are presented.

Most of the best working stabilizers had low molecular weights and also high charge densities. The best results were all gained with highly anionic stabilizers, and with P-DADMAC (MMW, HCD+), with EE-ASA, and PAAE (MMW, MCD+), with pure ASA. Both microparticle systems seemed to work well. Poor stabilizers had on average medium molecular weights and medium charge densities, especially medium cationic stabilizers showed poor emulsion stability, excluding PAAE. It is stated that high charges can some times be advantageous in stabilization /105, 128/. While poorer in stability, stabilizers with lower zeta potential are said to enable the use of higher ASA dosages, higher hydrophobation and even the use in higher hydrophobicity -needing paper and board grades /129/.

Emulsion stabilities based on Turbiscan measurements with both ASA's are seen in Figure 32. The best stability values are near zero and most unstable emulsions had values over 0.4 to over 1. The most unstable stabilizers were P-DADMAC (MMW, HCD+), and P-VAM (HMW, HCD+). Surprisingly, pectin (LMW, MCD-), also showed poor stability with EE-ASA based on turbidity, while showing high stability with other experiments. Pectin stability with pure ASA was high based on all stability tests. Otherwise the results from Turbiscan showed good correlation with the rest of the stability analyses. The best stability was seen with 4.C-PAM (MMW, MCD+), and 5.C-PAM (very LMW, MCD+), starch (MMW, very LCD+), PVA (LMW, 0) and 6.C-PAM (MMW, MCD+). Their values were way below 0.05 on the relative stability scale, formulated based on turbidity experiments. On average, EE-ASA emulsions showed little worse stability compared to pure ASA emulsions.

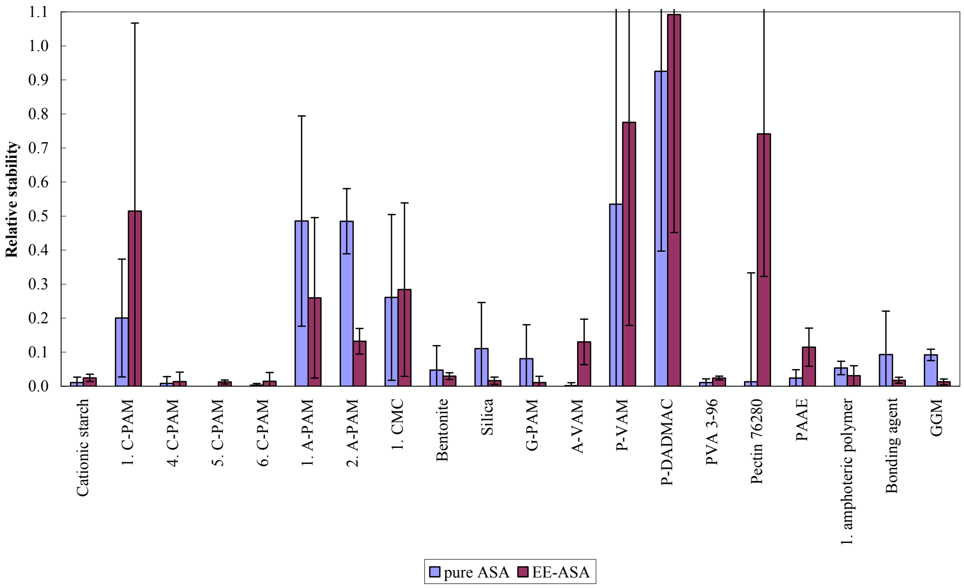

Figure 32. Turbiscan relative stability graph based on linear regression trend line slopes of minimum and maximum backscattering values and average values from original emulsion backscattering data. Small bar indicates good stability and big bar unstable emulsion. Averages for both ASA's with stabilizers are presented. Standard errors and standard deviations were used in calculating presented error bars.

Emulsion particle size determinations by microscope are used for stability determinations earlier /7, 130/. ASA stability by microscopy have been inspected by Lindström and Savolainen, among others /129, 131/. Emulsion droplet aggregation and particle sizes can be seen in these pictures (Figures 33 and 34). In the case of pectin (LMW, MCD-), the emulsions with both ASA's were stable and the particle size was fixed with only little variations. The size difference of emulsion droplets is very notable compared to 3.amphoteric polymer (LMW) emulsions, which indicated poor stability and too big emulsion particle size, unwanted in ASA sizing (Figure 34) /129/.

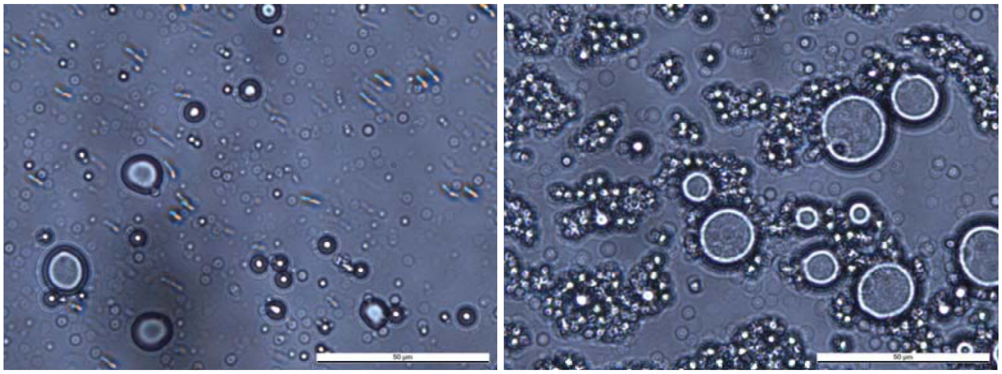

Figure 33. Two pectin (low molecular weight, medium anionic charge density) stabilized ASA emulsions 30 minutes after emulsification. At the left, pectin with pure ASA, and at the right, pectin with EE-ASA. 50 times magnification was used.

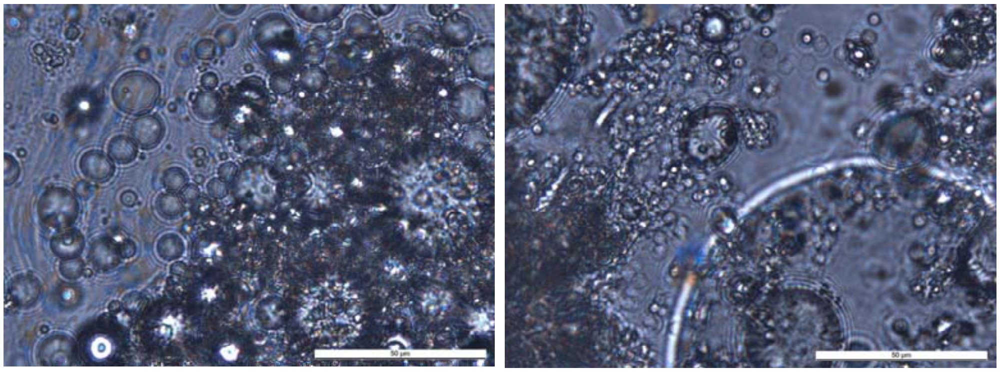

Figure 34. Two 3.amphoteric polymer (low molecular weight), stabilized ASA emulsions 30 minutes after emulsification. At the left, chemical with pure ASA, and at the right, chemical with EE-ASA. 50 times magnification was used.

In Figure 34, all emulsion particle sizes are seen, indicating wide particle size distribution and unwanted amounts of aggregation. Emulsification with this stabilizer could hardly be done. The result was very uneven and phase interfaces could be seen by naked eye during and after the emulsification, not typical for successful emulsification process. Black shadows in the pictures resemble foaming and aggregation. These phenomena could be seen from the sample droplet best by naked eye. More microscopic pictures are found from APPENDIX IV for comparison of the stability.

Surfactants are said to predominate the adsorbed layer (i.e. phase interface) when present. Walstra /30/ has studied the effects extensively but suggests further investigations on surfactants related to emulsion stability. In elsewhere, the surfactants are told to boost emulsion stability, for example in the case of PVA stabilizer with surfactant /132/. To understand the impact of surfactant in EE-ASA an in-depth study would be required. In their article, Goswani and Bahadur /133/ stated that an emulsions, stabilized by a mixture of stabilizer and surfactant, would be less stable compared to only stabilizer stabilized, or only the surfactant stabilized emulsion. The surfactant activity in EE-ASA emulsions might have also affected negatively to the stability in these tests, compared to those emulsions of pure ASA. Surfactant and stabilizer interactions at W/O emulsion interfaces have been extensively studied by Stenius and Miller /134, 135, 136/.

7.2 Properties of the hand sheets

Most important values in hand sheet testing were those of Cobb_{60} and tensile indices. Cobb_{60} values are presented in Figure 35 with hand sheet grammage values. For sheets, good sizing was indicated around Cobb_{60} values of 20-30 g/m² which is the desired range for many paper grades /1, 4, 21, 66, 68, 71, 99, 107, 111, 112, 137, 138/.

Most of the Cobb$_{60}$ water absorption values were under 30 g/m² for both ASA's used. Exceptions from this were EE-ASA emulsions of 2.A-PAM (very HMW, MCD-), with smaller 1 kg/t ASA dosage, bentonite (MCD-), with both ASA's, and also the emulsions of 1.CMC (LMW, MCD-). The results with 2.A-PAM can be explained by the different retention system. The 2.A-PAM itself was used instead of normal retention system causing poor retention. Poor sizing emulsions had on average a high or a medium anionic charge density.

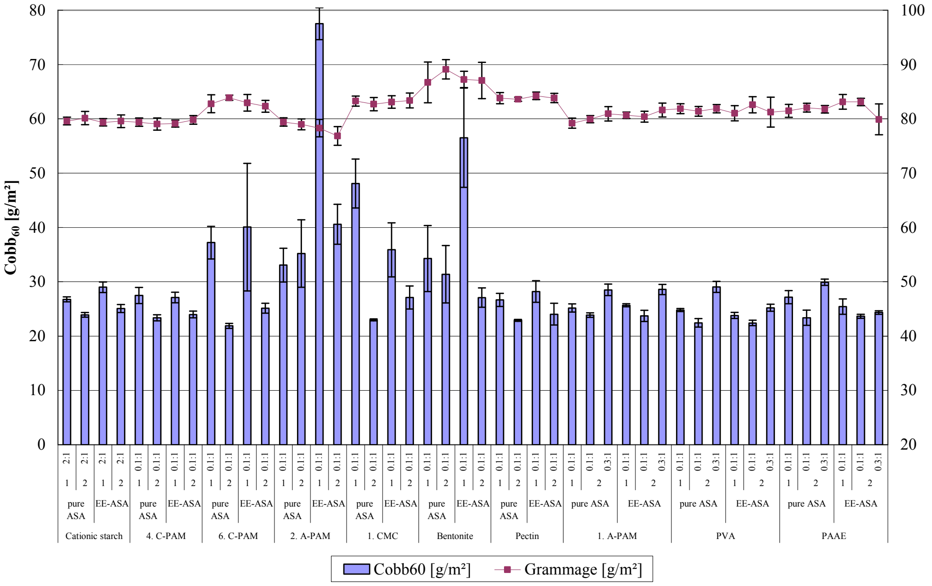

Figure 35. Cobb$_{60}$ water absorption and grammage values of the paper hand sheets. ASA dosages can be seen at the x-axis. Cobb$_{60}$ values on the left y-axis and grammage values on the right y-axis. Standard deviation values are presented.

The best stabilizer-ASA combinations were seen with higher ASA dosages with only little differences in between. The 6.C-PAM (MMW, MCD+), with both ASA's and showing values of 22 and 25 g/m², PVA (LMW, 0) with both ASA's and with polymer-to-ASA ratio of 0.1:1, 1.CMC (LMW, MCD-), with pure ASA, and pectin (LMW, MCD-). Starch (MMW, very LCD+), gained 25-28 g/m² water absorption values with all ASA emulsions and both dosages, showing the average level of hydrophobation suitable for example for writing papers /4, 107/. The lower overall hydrophobation values with higher ASA dosage and higher stabilizer-to-ASA ratio can be explained with disturbing effect of excess stabilizer in the system.

The highest hydrophobation was gained with pure ASA, and mainly with medium stabilizer charge density. Most of the poor sized sheets were prepared with EE-ASA, excluding 1.CMC (LMW, MCD-), with lower pure ASA dosage.

The grammage goal was reached with most of the ASA emulsions but too high values were indicated with the sheets of 6.C-PAM (MMW, MCD+), 1.CMC (LMW, MCD-) and with pectin (LMW, MCD-). These had grammage values of 85 g/m² and above. After pectin sheets, the pulps were changed and the problem solved (Figure 35). After the pulps change, only little variation in grammage was seen. The internal sizing agents or stabilizers had no effect on grammage. The value is dependent more likely on sheet preparation procedure and retention system. The effect that was seen with grammage did not have notable effect on hydrophobation or tensile strength values.

In Figure 36 dry and wet tensile indices for selected stabilizers are presented. Wet tensile indices for measured sheets, ranged from 3 to 7 Nm/g. The values of dry tensile strength ranged from 45 to 88 Nm/g. The differences on average were quite small, the distinction between lower and higher ASA dosage, 1 kg/t and 2 kg/t, could still be seen. Most of the different emulsions had their dry tensile indices around 70-80 Nm/g, only few showing values above 80 Nm/g.

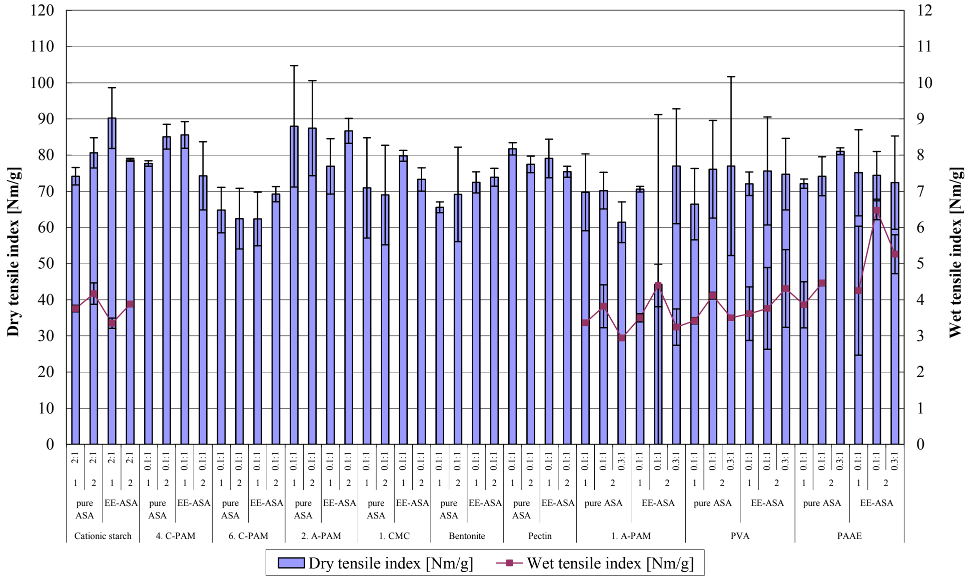

Figure 36. Dry and wet tensile indices of the paper hand sheets. Dry tensile indices on the left y-axis and wet tensile indices on the right y-axis. Standard deviations are presented.

The highest dry tensile indices were seen with starch (MMW, very LCD+), with higher pure ASA dosage, with 2.A-PAM (HMW, MCD-), with both dosages, 1 kg/t and 2 kg/t, of pure ASA, GGM (LMW, very LCD-/0), with higher pure ASA dosage with 0.3:1 stabilizer-to-ASA ratio and with lower EE-ASA dosage.

Poor dry tensile indices were seen with 1.A-PAM (LMW, LCD-), with higher pure ASA, dosage with stabilizer-to-ASA ratio 0.3:1 and with EE-ASA, with stabilizer-to-ASA ratio 0.1:1, with 6.C-PAM (MMW, MCD+), with both pure ASA dosages and with lower EE-ASA dosage.

The best wet tensile indices were seen with PAAE (MMW, MCD+), with higher EE-ASA, dosage, with both stabilizer-to-ASA ratios, the higher causing poorer result. Another successful value was gained with GGM (LMW, very LCD-/0) with EE-ASA, having the lower stabilizer-to-ASA 0.1:1 ratio.

Poor wet tensile indices were seen with 1.A-PAM (LMW, LCD-) both ASA's with higher stabilizer-to-ASA ratio 0.3:1 and also with lower pure ASA 1 kg/t dosage. GGM (LMW, very LCD-/0) also showed poor wet tensile index with higher pure ASA dosage with higher stabilizer-to-ASA ratio 0.3:1. Numerical table of hand sheet tests is presented in APPENDIX V.

Best dry tensile index values were gained with low charge density having stabilizers and the superior value of PAAE with EE-ASA in wet tensile indices was possibly due to its ability to form ester bond with carboxyl groups. Good hydrophobation was also seen due to this tendency of PAAE. The good dry strength values of PAAE can be explained by the fact that heating promotes its working as a strengthening agent. Differences between the two ASA's could clearly be seen with starch (MMW, very LCD+) in the case of dry tensile indices. EE-ASA, showed higher strength values with starch, as well as with bentonite (MCD-), and with 1.CMC (LMW, MCD-).

Also in the case of wet tensile indices the EE-ASA showed slightly better tensile strength properties. Higher stabilizer-to-ASA ratio, 0.3:1, in general caused lower tensile indices, excluding PVA (LMW, 0) with EE-ASA, which had clearly higher tensile index with higher ratio 0.3:1. It seems that that generally surfactants boost ASA sizing emulsion wet tensile properties but somewhat hinders the dry tensile properties.

7.3 Deposition tendency of the emulsions

In Figure 37, the fouling amounts of the deposit tests for selected stabilizer-ASA emulsions are presented. In the Figure 38 the photographed sample plates after deposition tests are seen. These types of photographs have been taken also before by Lindfors /20/. The smallest deposit values were achieved with starch (MMW, very LCD+) emulsions, around 1-2 g/m², 6.C-PAM (MMW, MCD+) with EE-ASA, values around 3-8.5 g/m².

PAAE (MMW, MCD+) also indicated low amounts of deposit, around 9-15 g/m², with pure ASA emulsion.

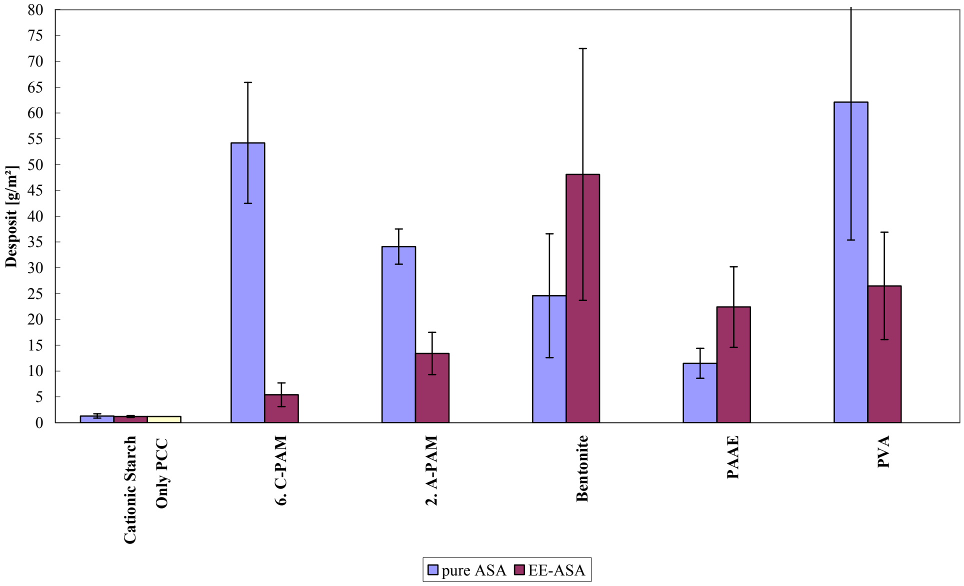

Figure 37. Deposition test plates fouling tendencies for both ASA's. Standard deviation values are presented.

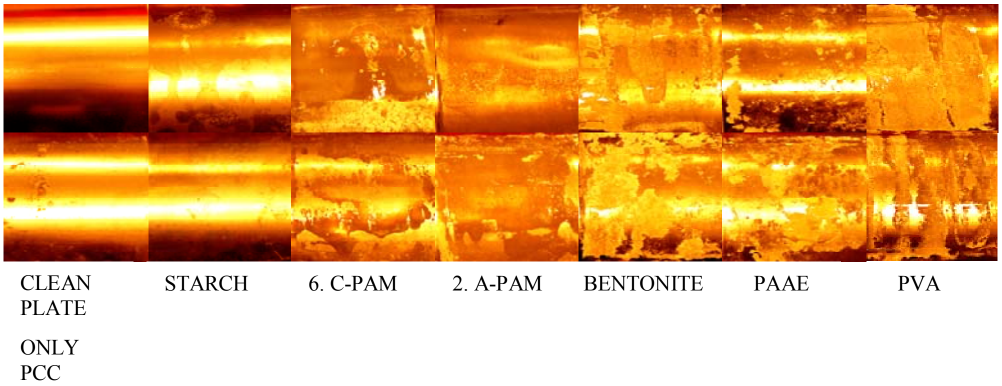

Figure 38. Deposition tester sample plates. The upper ones have been emulsified with, pure ASA, excluding the first from the left which is a clean sample plate. The lower plates are emulsified with EE-ASA, excluding the first from the left which was subjected only to PCC with no sizing emulsion.

Highest amounts of deposit were indicated with PVA (LMW, 0) with both ASA's, pure ASA, showing higher deposit amounts. High amounts were stated also with bentonite (MCD-), and EE-ASA, and with 6.C-PAM (MMW, MCD+), with pure ASA. The deposit amounts of these were 40-95 g/m². The rest of the stabilizers produced deposit amounts of 10-20g/m², showing the average deposit level in these experiments. The test run with PCC had no ASA-stabilizer emulsion included.

All lowest deposit amounts were achieved with medium molecular weight and cationic medium charge density having stabilizers. The stabilizers with highest deposit amounts had in general low or nonionic charge densities. Both ASA's with PCC produced high and low fouling sizing emulsions alike. After the beginning of sample plate fouling, the steel plate surface is no longer clean and the adhesion properties are determined by the deposits on the plate. The stickiness of plate surface is dependent on the plate surface roughness /20/. From Figures 37 and 38 the numerical and visual effects can easily be combined.

Surprising differences in the adhesion between the plate and the deposit was also stated. For example, the deposits of starch (MMW, very LCD+) 2.A-PAM (HMW, MCD-), and bentonite (MCD-), were stuck extremely well on the surface, whereas the deposits of PAAE (MMW, MCD+), and partly also the deposit of 6.C-PAM (MMW, MCD+), could have been blown away from the surface of the sample plate by strong exhale breathe. In between these ends of adhesion were the plates with PVA (LMW, 0). It seems that the steel surface created higher adhesion with anionic stabilizers.

The deposition results from TGA are presented in Figure 39. In each analysis, both ASA's decompositions were seen in between 580 and 590 °C. The withdrawn amount varied from starches (MMW, very LCD+), 7 % to over 40 % with 2. A-PAM (HMW, MCD-). The differences in decomposition amounts between the two ASA's were insignificant, excluding in the case of 2. A-PAM. The value with pure ASA, was 26 % and with EE-ASA, 42 %, while the difference between other stabilizer-ASA pairs was only around few percents. The decomposition amounts of stabilizer and water also varied among stabilizer. The most notable difference is seen in between A-PAM emulsions. With pure ASA, water-surfactant decomposition amount was over 30% and with EE-ASA under 7 %.

Surfactant charge density would be good to know when evaluating the properties in deposition that surfactants can have an effect on. Nonionic surfactants can stabilize for example tacky particles in water systems and ionic surfactants are said to minimize microbiological deposits. The temperature rise is said to increase the deposit amounts. This might have had effect also on these experiments too. Still, reasons like reduction of the freshwater usage and water systems disclosure are much more significant reasons at the industrial scale. Multivalent cations and ionic polymer stabilizers might be effective in reduction of deposits as were also seen in these experiments in the cases of 6.C-PAM and PAAE. /139/

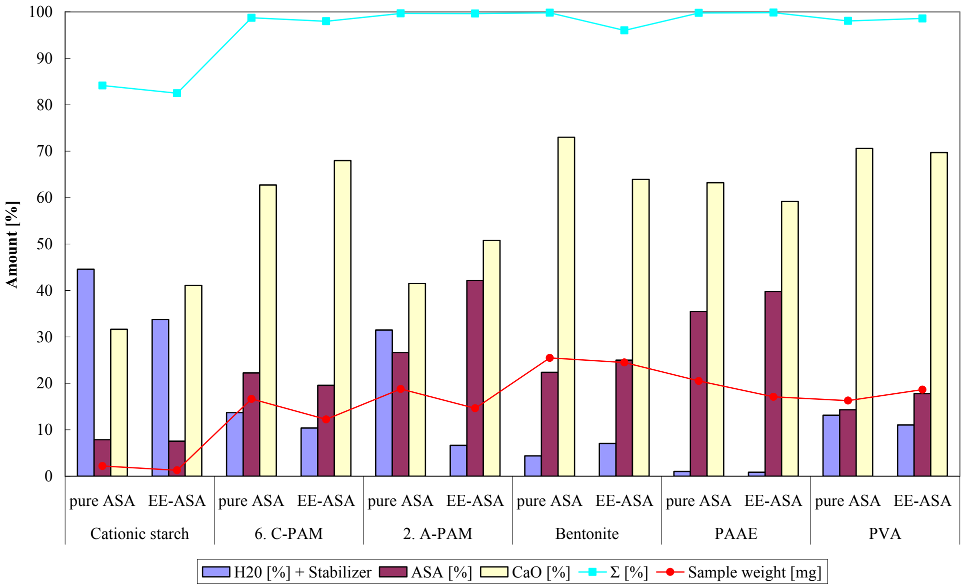

Figure 39. The interpretation of thermal gravimetric analysis (TGA) data. As tolerance levels, the percentual summary (Σ) of total inorganic and organic matter and sample weight are presented. The percentage of each component gives information about the deposit amounts of the sample plates.

Starch (MMW, very LCD+), PVA (LMW, 0) and 6.C-PAM (MMW, MCD+), showed smallest ASA residue amounts. In the case of starch, the small sample amount and low total percentage have to be taken into account, lowering the reliability of the attained TGA result. Starch test plates also included lower amounts of residue CaO.

The decomposition temperature of CO_2 was 815-850 °C with all the other stabilizers but with starch (MMW, very LCD+), it was about 752 °C with both ASA's. Some how starch makes the carbonate decompose in the lower temperature earlier but the reason is not clear /140/. The complexation reaction of calcium and starch is the most probable reason: either with calcium and phosphate groups, or with calcium and glucose units of the starch. In these temperatures all the organic material has already been removed.

8 CONCLUSIONS

The main objective of this thesis was the optimization of ASA emulsions, i.e. improving the stability and sizing efficiency of emulsions and decreasing their fouling tendency. The goal was reached by formulating four-step experimental plan, in which emulsion particle size, pH, zeta potential and turbidity were first studied. Based on these results, hand sheets were prepared with desired emulsions. The paper hydrophobation studies showed suitable emulsions for deposition tests, where differences deposition tendency were indicated visually, by weight differences and by thermal gravimetric analysis (TGA).

Reference cationic potato starch set quite high standards in stability, hydrophobation and deposition tests for other stabilizers to gain. Still successful stabilizers in each experimental step could be found. No stabilizer with superior advantage in all experiments, compared to others was indicated. The optimal properties varied depending on the two different ASA's used, whether it was pure ASA compound or a surfactant-containing EE-ASA. The presence of surfactant caused smaller particle sizes and in some cases weaker long-term stability.

Most stabilizers gave stabilizing effect on ASA oil droplets by steric and electrostatic stabilization. Bentonite and colloidal silica stabilized ASA oil droplets by microparticle stabilization effect. With EE-ASA, the surfactants took a part in stabilization/destabilization phenomena. The presence of surfactants might have caused some overlapping of stabilization mechanisms due to its presence. ASA emulsions with particle size, of 0.5-1.5 µm showed high stability and high sizing efficiency. Examples on these emulsions were those of PVA and pectin with pure ASA and reference starch and 6.C-PAM, with EE-ASA. Based on zeta potential, microparticle stabilization systems of bentonite and colloidal silica worked well. In turbidity measurements, the emulsions of starch, PVA and medium molecular weight, medium charge density 6.C-PAM with both ASA's showed high stability.

In emulsification, the stabilizer and the absence or presence of surfactant had greatest impact on the resulting emulsion. The ASA dosage, stabilizer and the absence or presence of surfactant had the greatest impact on hydrophobation and tensile strength properties. The highest hydrophobation was received with 6.C-PAM, PVA and pectin emulsions. The pure ASA compound did well with most of the stabilizers in hydrophobation tests. The highest tensile strength values were gained with reference starch and galactoglucomannan in the case of ASA. With EE-ASA, high molecular weight, medium charge density A-PAM showed the best results. PAAE worked well in wet tensile strength showing superior values compared to others.

In deposition tests, the stabilizer and the absence or presence of the surfactant had greatest impact on results. Both ASA's showed low and high deposition amounts. The best results were achieved with reference starch and PAAE in the case of ASA and with reference starch and E-HS Plus in the case of EE-ASA. Surprising differences in the adhesion between sample surface and deposits was seen. The mechanism with ASA and PCC and the effect of surfactant and stabilizers should be studied more in-depth, but cationicity seemed to result smaller contamination. TGA showed lowest residue ASA with reference starch and with PVA.

Medium molecular weight and medium charge density PAAE had many properties important for cost-efficient internal sizing: with PAAE, the need of wet strengthening chemicals is reduced due to the stabilizer properties. Internal sizing can gain high cost-efficiency by reducing the dosage of chemicals due to this multi-purpose chemical, but the limitations in use with and without surfactant and process temperature conditions need to be taken in notice. The novel field of application for unmodified galactoglucomannan in ASA stabilization is also welcome, because the applications for galactoglucomannan are under investigation. High cost-efficiency is expected when extraction of galactoglucomannan from wood material can be done without expensive and time-consuming modification procedures.

For further studies, the effect of stabilizer saturation on the results was not studied in this work, but would give valuable information in stabilizer selection for different internal sizing systems. Many potential stabilizers were left out after stability and sizing tests and their sizing and deposition testing would be interesting. For example pectin is stated to have special characteristics with calcium but it was left out of deposition tests because of the limited experimental plan. From deposition point of view, it would also be interesting to study the adhesion properties of formed deposits on papermachine surfaces, when different stabilizers are used. In stability comparison, valuable information would be the knowledge on stabilizer and surfactant specific surface areas with both ASA's. This information would require hydrophile-lipophile balance experiments for each stabilizer. In these experiments, the hydrolysis tendency of ASA was not studied, so it was rather difficult to clearly state its effect on emulsification, emulsion stability and on hydrophobation or deposition tendency, during the experiments. It would be advisable to study this tendency and use the information when interpreting the results.

In the paper- and boardmaking point of view, efficient ASA emulsions showed high stability, proper hydrophobation in neutral internal sizing and low deposition tendency in process conditions. Cost-efficient ASA sizing could be materialized with reference cationic starch, PVA, E-HS Plus, pectin and PAAE. Starch, PVA and pectin worked better with ASA, whereas PAAE and C-PAM showed optimal results with EE-ASA. To move the findings on many emulsions to industrial scale would be easy, since most of the products are already in commercial production. The utilization of these products would in most cases require only pilot scale tests before commercializing as internal sizing systems.

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LIST OF APPENDICES

APPENDIX I

Stabilizer selection procedure tables for pure ASA and EE-ASA experiments

Stabilizer	pH	Particle size numerical	Particle size graphical	Charge	Mobility	Turbidity	Visual	Total
Cationic Starch	G	A	G	GG	GG	GG	G	23
1. C-PAM	A	A	GG	B	B	A	G	12
2. C-PAM	G	B	A				A	
3. C-PAM	G	BB	A				A	
4. C-PAM	A	A	G	BB	BB	G	B	11
5. C-PAM	A	BB	G	BB	BB	G	G	11
6. C-PAM	A	G	A	A	A	GG	GG	15
7. C-PAM+P-DADMAC	G	B	A			BB	A	
1. A-PAM	A	B	BB	G	GG	BB	B	20
2. A-PAM	G	A	GG	GG	GG	A	GG	19
3. A-PAM	A	A	GG				G	
4. A-PAM	G	G	GG				GG	
5. A-PAM	G	A	B				B	
5. A-PAM	G	A	GG				B	
1. CMC	GG	G	G	GG	GG	B	B	20
2. CMC	G	G	G				A	
3. CMC	A	GG	G				A	
4. CMC	A	G	G				G	
5. CMC	G	A	G				A	
1. Bentonite	G	B	GG	GG	GG	GG	A	21
1. Silica	B	B	G	G	GG	A	B	14
G-PAM	A	B	A	BB	BB	A	BB	7
A-VAM	A	GG	A	BB	BB	B	B	9
P-VAM	G	A	G	BB	BB	BB	B	9
P-DADMAC	A	G	G	B	B	BB	B	11
PVA 3-96	G	A	B	A	A	GG	GG	18
Pectin 76280	GG	GG	G	GG	GG	BB	A	21
PAAE	G	GG	G	GG	GG	A	G	23
1. Amphoteric polymer	G	G	G	G	G	A	G	18
2. Amphoteric polymer	G	G	GG				G	
3. Amphoteric polymer	B	BB	BB				BB	
Dicyandiamide	B	G	G				BB	
Bonding agent	B	B	GG	B	B	B	G	12
GGM	A	G	A	G	G	G	GG	

🟥 = selected for turbiscan
🟦 = selected for sheet prep

GG	**Perfect**	**4**
G	**Good**	**3**
A	**Average**	**2**
B	**Poor**	**1**
BB	**Very poor**	**0**

Stabilizer	pH	Particle size numerical	Particle size graphical	Charge	Mobility	Turbidity	Visual	Total
Cationic Starch	G	G	B	GG	GG	G	G	21
1. C-PAM	A	G	GG	B	B	BB	GG	15
2. C-PAM	G	A	A				A	
3. C-PAM	G	B	B				B	
4. C-PAM	G	GG	B	BB	BB	GG	BB	21
5. C-PAM	A	B	G	BB	BB	G	G	12
6. C-PAM	A	GG	A	BB	BB	GG	GG	16
7. C-PAM+P-DADMAC	G	B	B				B	
1. A-PAM	G	A	B	GG	GG	A	BB	16
2. A-PAM	G	B	GG	GG	GG	G	GG	20
3. A-PAM	GG	G	GG				GG	
4. A-PAM	A	G	GG				G	
5. A-PAM	G	G	B				BB	
5. A-PAM	G	A	GG				G	
1. CMC	GG	G	B	G	G	B	A	17
2. CMC	G	GG	B				G	
3. CMC	G	GG	B				B	
4. CMC	G	G	A				GG	
5. CMC	G	G	B				A	
1. Bentonite	G	GG	B	GG	GG	GG	GG	20
1. Silica	A	B	BB	GG	GG	GG	BB	15
G-PAM	G	BB	A	BB	BB	GG	BB	6
A-VAM	G	A	A	BB	BB	B	A	10
P-VAM	G	G	B	BB	BB	BB	GG	11
P-DADMAC	B	G	GG	GG	GG	BB	BB	16
PVA 3-96	G	GG	BB	GG	GG	GG	GG	23
Pectin 76280	GG	GG	B	B	B	BB	G	14
PAAE	G	GG	G	B	B	A	GG	18
1. Amphoteric polymer	G	G	G	G	G	G	G	21
2. Amphoteric polymer	G	GG	B				G	
3. Amphoteric polymer	B	BB	BB				BB	
Dicyandiamide	G	BB	A				BB	
Bonding agent	G	GG	A	BB	BB	GG	GG	17
GGM	A	A	B	GG	GG	GG	G	20

🟥 = selected for turbiscan
🟦 = selected for sheet prep

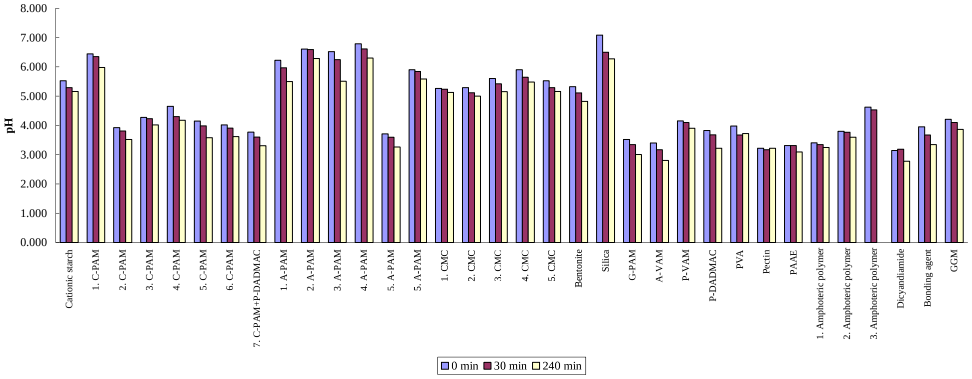
GG	**Perfect**	**4**
G	**Good**	**3**
A	**Average**	**2**
B	**Poor**	**1**
BB	**Very poor**	**0**

Sheet preparation procedure table

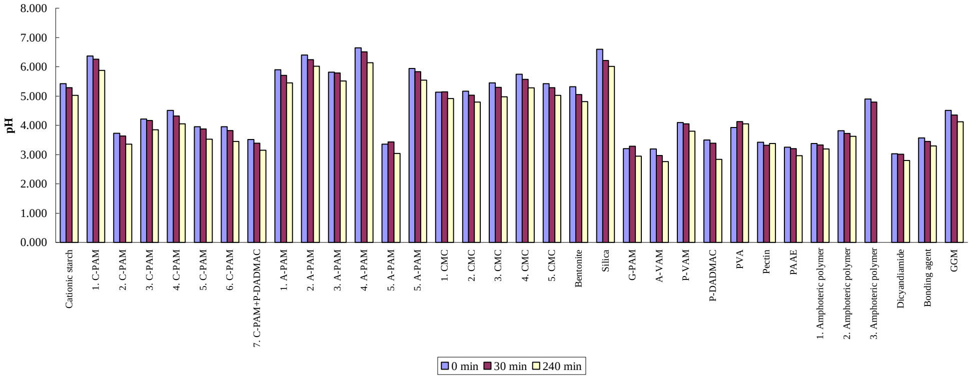
Handsheet preparation with ISO 3688 sheet mould
Weighin of pulp according to test sheet; (weight goal/weight of the test sheet)* 500 ml
Addition of ASA to the pulp with Finnpipette 1 or 2 kg/t
Wait for 10 seconds
Addition of retention aid 200g/t
Wait for 10 seconds
Pouring the pulp to sheet mould
Starting of mixing
Emptying of the sheet mold
Infiltration (sound) for 10 seconds
Opening of the sheet mould and setting of blotters, on the sheet, one new, two used
Putting the weight of ISO 3886 on blotters
Wait for 20 seconds
Taking both used blotters away and putting one new to the other side while removing from the wire
Wet pressing for 2 minutes at 4 bar pressure, on top of the sheet 20 used blotters
Removing the new blotter from the other surface of the sheet and placing it the bare side facing to vacuum dryer
Vacuum drying for 3 minutes at - 0.9 bar
Sheet conditioning according to ISO 187 and testing

pH graphs of pure ASA and EE-ASA

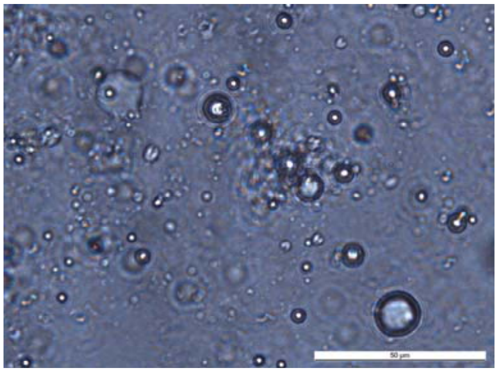
pure ASA emulsion pH during 4 hours time



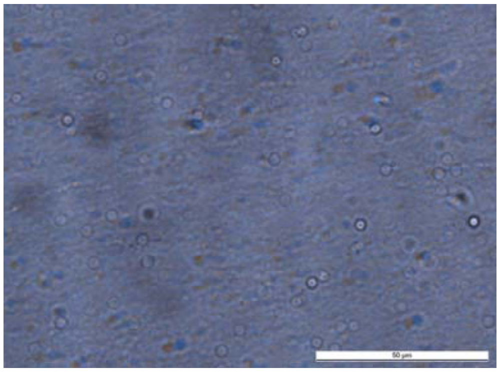
EE-ASA emulsion pH during 4 hours time



Microscopic pictures of selected emulsions



Bentonite_pure ASA_0min.



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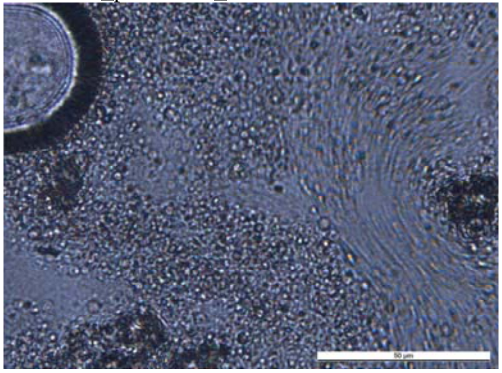
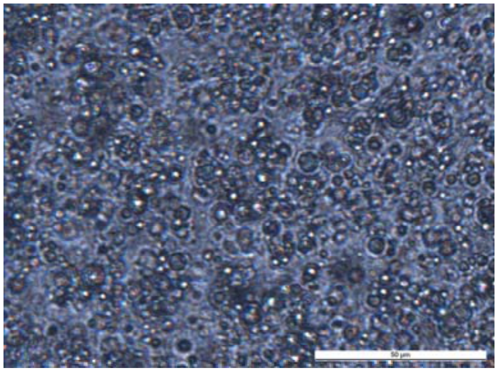
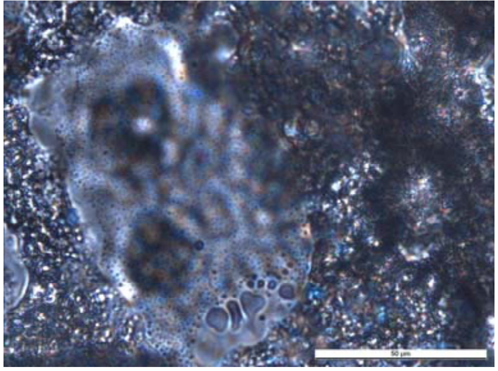


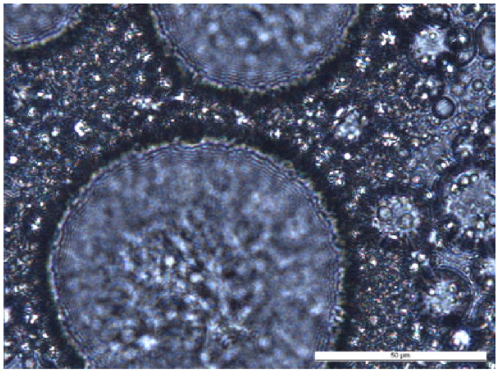
Starch_pure ASA_0min.



Starch_EE-ASA_0min.

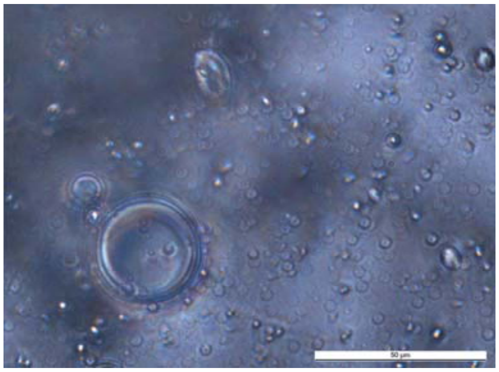


1. amphoteric polymer_pure ASA_0min.

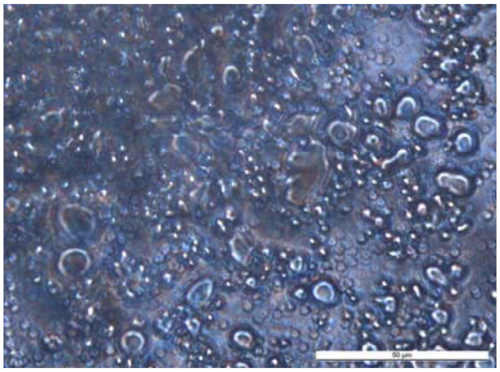


1. amphoteric polymer_EE-ASA_0min.

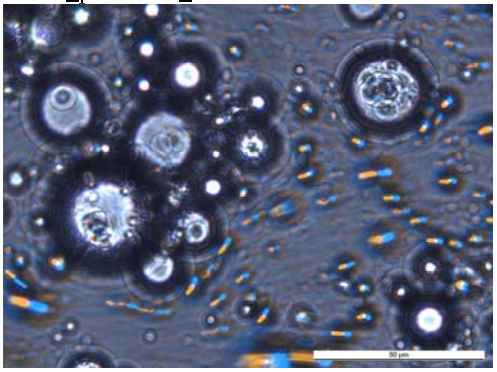
Microscopic pictures of selected emulsions



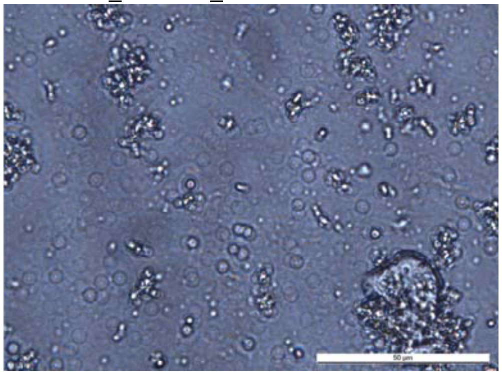
Pectin_pure ASA_0min.



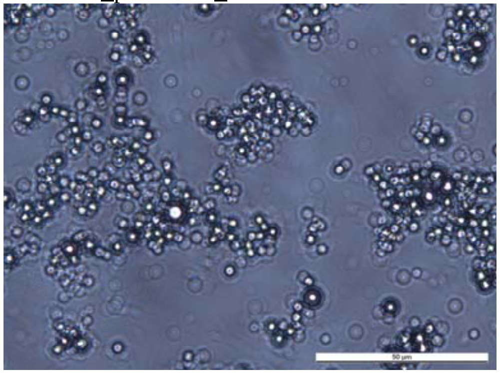
Pectin_EE-ASA_0min.



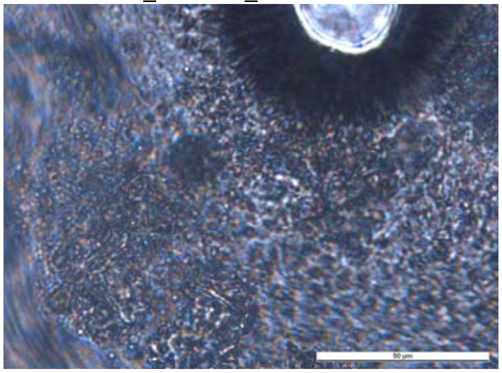
Bentonite_pure ASA_30min.



Bentonite_EE-ASA_30min.

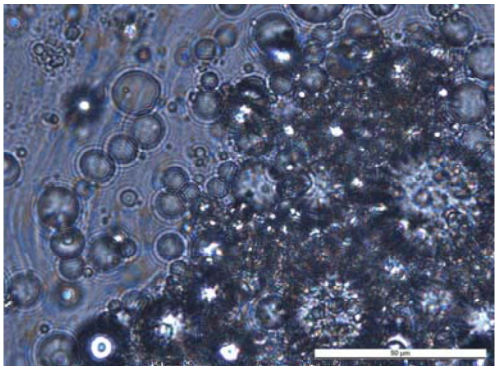


Starch_pure ASA_30min.

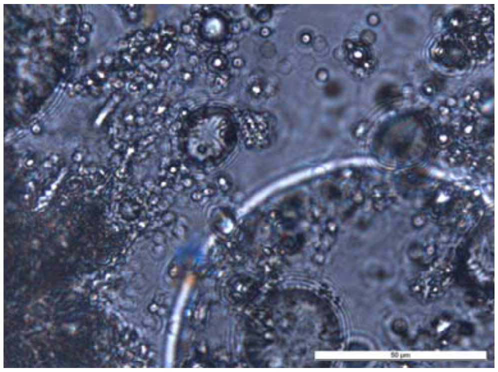


Starch_EE-ASA_30min.

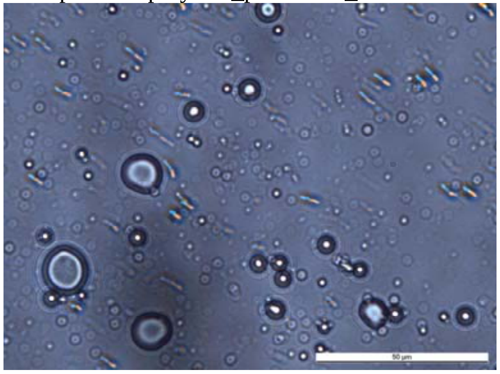
Microscopic pictures of selected emulsions



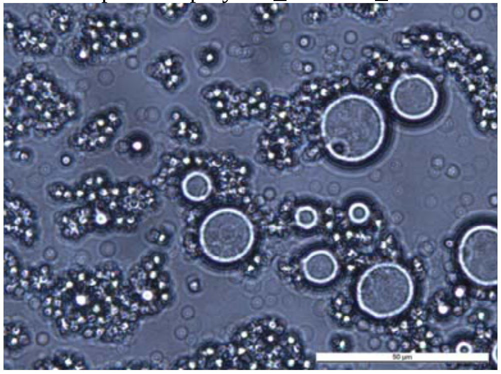
1. amphoteric polymer_pure ASA_30min.



1. amphoteric polymer_EE-ASA_30min.



Pectin_ pure ASA_30min.



Pectin_EE-ASA_30min.

APPENDIX V

Sheet test numerical tables

Polymer	ASA	Dosage [kg/t]	Polymer:ASA	Cobb$_{60}$ [g/m²]	SD	Dry tensile index [Nm/g]	SD	Wet tensile index [Nm/g]	SD	Grammage [g/m²]	SD	Air permeability [ml/min	SD	Thickness [µm]	SD
Cationic starch	**pure ASA**	1	2:1	26.8	0.5	74.2	2.4	3.8	0.1	79.6	0.7	172.8	4.9	109.4	1.6
		2	2:1	23.9	0.4	80.6	4.2	4.2	0.3	80.1	1.2	170.4	12.8	110.3	2.1
	EE-ASA	1	2:1	29.0	1.0	90.2	8.4	3.4	0.1	79.4	0.7	166.0	7.8	107.9	1.6
		2	2:1	25.1	0.7	78.7	0.4	3.9	0.1	79.6	1.2	183.8	8.5	109.7	1.5
4. C-PAM	**pure ASA**	1	0.1:1	27.5	1.5	77.7	0.8			79.4	0.8	305.2	17.5	107.7	2.6
		2	0.1:1	23.4	0.5	85.1	3.4			79.0	1.1	330.2	18.2	115.6	12.4
	EE-ASA	1	0.1:1	27.1	1.0	85.6	3.7			79.1	0.7	278.2	27.4	108.4	1.6
		2	0.1:1	24.0	0.6	74.3	9.4			79.8	0.8	308.0	29.1	111.2	3.5
6. C-PAM	**pure ASA**	1	0.1:1	37.2	3.0	64.8	6.3			82.8	1.6	170.2	10.5	117.4	4.1
		2	0.1:1	21.9	0.5	62.4	8.4			83.9	0.5	192.5	15.0	120.7	7.0
	EE-ASA	1	0.1:1	40.1	11.7	62.4	7.4			83.0	1.5	148.8	15.9	118.4	1.3
		2	0.1:1	25.1	0.9	69.2	2.1			82.3	1.1	191.5	9.4	114.8	3.2
2. A-PAM	**pure ASA**	1	0.1:1	33.1	3.1	87.9	16.8			79.4	0.8	200.2	12.6	104.9	2.1
		2	0.1:1	35.2	6.2	87.5	13.1			79.0	1.0	205.0	16.5	105.9	2.8
	EE-ASA	1	0.1:1	77.5	3.0	76.9	7.7			78.3	1.6	126.2	13.1	104.1	3.7
		2	0.1:1	40.6	3.7	86.7	3.4			76.9	1.7	135.3	11.2	101.1	9.3
1. CMC	**pure ASA**	1	0.1:1	48.1	4.5	70.9	13.9			83.3	0.9	147.0	8.5	118.4	9.6
		2	0.1:1	23.0	0.2	69.0	13.7			82.7	1.2	149.5	14.7	114.0	19.5
	EE-ASA	1	0.1:1	35.9	5.0	79.8	1.5			83.1	1.1	140.3	12.4	111.9	1.6
		2	0.1:1	27.1	2.1	73.3	3.2			83.4	1.4	139.2	21.7	116.9	10.6
Bentonite	**pure ASA**	1	0.1:1	34.3	6.1	65.6	1.5			86.7	3.8	150.3	10.3	117.0	3.3
		2	0.1:1	31.4	5.3	69.1	13.1			89.1	1.8	163.0	11.2	120.6	2.0
	EE-ASA	1	0.1:1	56.5	9.1	72.5	2.9			87.3	1.5	145.8	5.7	117.7	2.9
		2	0.1:1	27.1	1.8	73.9	2.5			87.1	3.3	154.8	14.1	116.1	5.1
Pectin	**pure ASA**	1	0.1:1	26.7	1.2	81.7	1.7			83.8	1.0	133.7	14.7	112.1	3.3
		2	0.1:1	22.9	0.2	77.4	2.3			83.6	0.4	143.2	8.1	114.0	3.3
	EE-ASA	1	0.1:1	28.2	2.0	79.1	5.3			84.2	0.7	134.8	4.5	96.2	42.2
		2	0.1:1	24.0	2.0	75.4	1.5			83.8	0.9	147.2	8.1	115.6	3.0
1. A-PAM	**pure ASA**	1	0.1:1	25.2	0.8	69.71	10.61	3.4	0.0	79.2	0.9	287.8	9.1	111.1	5.9
		2	0.1:1	23.9	0.4	70.15	5.06	3.8	0.6	79.9	0.7	282.4	11.8	111.2	2.9
			0.3:1	28.5	1.1	61.44	5.64	2.9	0.0	80.9	1.3	248.9	24.6	110.7	2.2
	EE-ASA	1	0.1:1	25.7	0.3	70.59	0.77	3.5	0.1	80.7	0.6	241.3	14.9	110.2	2.0
		2	0.1:1	23.7	1.0	44.27	46.95	4.4	0.6	80.4	1.0	240.0	12.7	107.7	2.5
			0.3:1	28.6	1.0	76.94	15.88	3.2	0.5	81.6	1.3	230.8	18.5	110.5	2.9
PVA	**pure ASA**	1	0.1:1	24.8	0.3	66.4	9.9	3.4	0.1	81.9	0.9	289.6	15.4	116.2	3.8
		2	0.1:1	22.4	0.8	76.1	13.5	4.1	0.1	81.4	0.9	309.4	12.5	114.4	1.6
			0.3:1	29.1	1.0	77.0	24.7	3.5	0.0	81.9	0.8	246.3	16.6	112.5	4.0
	EE-ASA	1	0.1:1	23.8	0.6	72.1	3.2	3.6	0.7	81.0	1.4	274.9	16.2	109.7	2.8
		2	0.1:1	22.4	0.5	75.6	14.9	3.8	1.1	82.6	1.5	290.3	17.3	114.6	4.7
			0.3:1	25.2	0.6	74.7	9.9	4.3	1.1	81.2	2.8	293.4	38.0	111.3	6.7
PAAE	**pure ASA**	1	0.1:1	27.2	1.2	72.1	1.3	3.9	0.6	81.5	1.2	285.5	14.5	112.8	2.8
		2	0.1:1	23.4	1.4	74.1	5.4	4.5	0.1	82.1	0.8	296.1	17.4	117.4	3.5
			0.3:1	29.9	0.6	81.1	1.0			81.8	0.7	263.8	9.2	114.8	3.5
	EE-ASA	1	0.1:1	25.4	1.4	75.1	11.9	4.3	1.8	83.1	1.4	293.3	46.9	119.2	8.7
		2	0.1:1	23.7	0.4	74.4	6.6	6.5	0.3	83.1	0.7	269.5	17.1	117.4	4.5
			0.3:1	24.3	0.3	72.4	12.9	5.3	0.5	79.9	2.8	278.8	10.8	117.2	9.7
GGM	**pure ASA**	1	0.1:1	25.1	0.5	73.9	2.0	3.6	0.0	79.6	0.9	300.4	34.1	108.4	3.4
		2	0.1:1	24.1	0.2	77.1	10.8	5.1	0.4	80.2	0.8	297.5	23.0	111.0	2.4
			0.3:1	29.5	2.1	87.5	6.6	3.2	0.5	80.4	0.6	307.6	95.3	112.5	4.7
	EE-ASA	1	0.1:1	24.7	0.5	81.4	10.0	3.6	0.4	80.1	0.6	315.6	13.0	110.0	2.4
		2	0.1:1	24.6	0.6	68.2	6.9	4.6	0.3	80.6	0.8	281.3	16.4	111.0	2.2
			0.3:1	25.7	0.1	69.2	0.0	3.7	0.6	80.2	3.4	301.1	29.4	114.8	8.6