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NOVEL ASA-SUBSTITUTES IN PAPER SIZING BASED ON RENEWABLE RAW MATERIALS

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Kurzfassung

Papierleimungsmittel werden zur Produktion von Papier eingesetzt, um es gegen das Eindringen von Wasser widerstandsfähig zu machen. Dies verbessert die Bedruckbarkeit genauso wie die Haltbarkeit. Die Aufgabe dieser Arbeit war es, ein neues Leimungsmittel zu entwickeln, das auf nachwachsenden Rohstoffen basiert und eine mögliche Alternative zum herkömmlich verwendeten Alkenyl-Bernsteinsäure-Anhydrid (ASA) bietet. So wurden statt dem petrochemisch erzeugten Olefin Leinsamen-, Raps-, Soja- und hoch ölsäurehaltiges Sonnenblumenöl mit Maleinsäureanhydrid umgesetzt.

Wichtige Charakteristika wie Leimungseffizienz, Viskosität, Zusammensetzung der Fettsäurereste am Öl-Triglycerid, Bildung unerwünschter Nebenprodukte und Ausbeute wurden für alle vier maleierten Öle getestet. Der vielversprechendste Ausgangsstoff für pflanzenölbasiertes Leimungsmittel ist das hochölsäurehaltige Sonnenblumenöl (SOHO). Ausgangsstoff sowie maleiertes SOHO (MSOHO) wurden analytisch charakterisiert unter Verwendung von abgeschwächter Totalreflexion Infrarotspektroskopie, ^1H und ^{13}C Nuklearresonanzspektroskopie, Massenspektrometrie und einer Kombination von Ozon-Spaltung und Pyrolyse-Gaschromatographie.

Eine andere wichtige Eigenschaft, mit der Papierleimungsmittel ausgestattet sein müssen, ist Hydrolysestabilität. In verschiedenen Verfahren wurde sie für ASA und MSOHO untersucht, dabei wurde gefunden, dass MSOHO stabiler ist als ASA. Speziell eine erhöhte Calcium-Belastung macht ASA mehr zu schaffen als MSOHO. Dies bedeutet ein geringeres Risiko für Ablagerungen beim Einsatz von MSOHO im Vergleich zu ASA.

Des Weiteren wurden Einflüsse getestet, welche die Leimungseffizienz von MSOHO und ASA beeinflussen, so zum Beispiel die Verwendung von Füllstoff oder Aluminiumsulfat. Eine andere Möglichkeit die Effizienz von MSOHO so zu steigern, dass sie fast jene von ASA erreicht, ist die Beimischung geringer Mengen Fettsäureanhydrids, ein anderes auf nachwachsenden Rohstoffen basierendes Leimungsmittel.

Schlüsselwörter: Alkenyl-Bernsteinsäure-Anhydrid (ASA), ASA-Leimung, hoch ölsäurehaltiges Sonnenblumenöl, maleiertes Pflanzenöl, Papierleimung, nachwachsende Rohstoffe

Abstract

Paper sizing agents are used in paper production to improve the paper's resistance against penetration of water and thus increase its printability and durability. During this thesis plant oils derived from various sources have been modified with maleic anhydride to synthesize a new green sizing agent, which was found to be a suitable candidate to substitute petrochemical-based alkenyl succinic anhydride (ASA) sizes. Relevant characteristics including sizing efficiency, viscosity, composition of fatty acid residues on the triglycerides, formation of by-products, and yield were studied for maleated linseed, rapeseed, soybean, and high oleic sunflower oil. The most promising product - maleated high oleic sunflower oil (MSOHO) - and its raw material were then comprehensively characterized analytically including attenuated total reflection infrared spectroscopy, ^1H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectrometry, and a combination of ozone cleavage and pyrolysis gas chromatography.

As one criterion for the applicability of sizing agents is their hydrolytic stability, several methods were used to predict this feature for the new MSOHO product in comparison with the well established ASA-size. There the higher hydrolytic stability of MSOHO, especially in the presence of Ca^{2+} , was confirmed, which reduces the risk of deposit formation in the paper mill.

Another focus of this thesis was tuning MSOHO's sizing characteristics as to be comparable to highly efficient ASA. The influence of filler or aluminum sulfate addition was investigated. Furthermore blending MSOHO with fatty acid anhydride, another green sizing agent, was found to be suitable for raising its sizing efficiency almost to ASA levels, due to reducing its viscosity significantly.

Keywords: Alkenyl succinic anhydride (ASA), ASA-sizing, high oleic sunflower oil, maleated plant oil, paper sizing, renewable resources

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Aims of work

The application of sizing agents during paper production is essential, as they hinder penetration of water into the sheet. Thus important paper characteristics like printability and durability can be adjusted according the paper makers demands.

For applications in paper sizing, where it is essential that full sizing efficiency is provided to the paper without the need to store the paper for several days (= quick curing), the reactive sizing agent alkenyl succinic anhydride (ASA) is applied. Its only drawback is its dependency on olefin, which so far is mainly derived from petrochemical sources. To be able to substitute the olefin by a vegetable oil based raw material does not only meet the demand for more sustainability in paper production, but also makes it easier to use locally available raw materials; and thus reduces transport costs.

So the aims of the presented PhD thesis were to develop a sizing agent based on vegetable oil that can be produced in a one-step synthesis, has good curing characteristics, and provides sufficient sizing to paper at low dosages. Furthermore the new sizing agent should possibly be more stable against hydrolysis than ASA, and thus minimize deposit formation at paper machines. Another challenge that was faced during this thesis was to comprehensively characterize this new sizing agent as well as to investigate its synthesis mechanism.

The proposed reaction scheme for this renewables based ASA is presented in Figure 1. It comprises the *ene*-reaction of a native vegetable oil with maleic anhydride.

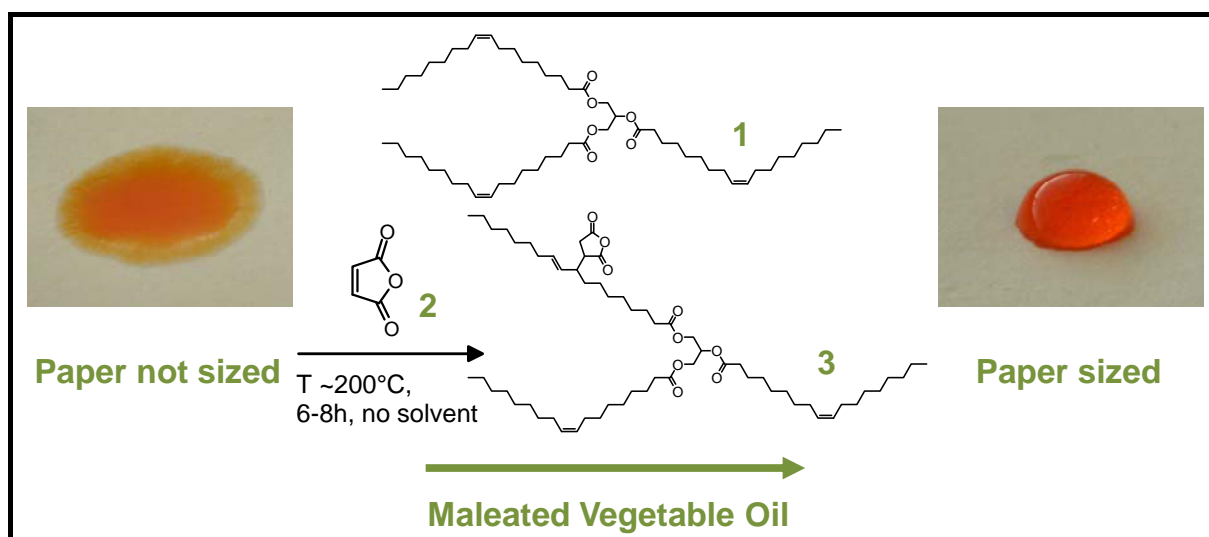


Figure 1: Paper sizing with maleated vegetable oil, production of maleated vegetable oil (3): monomaleation of glycerol trioleate (1) with maleic anhydride (2)

1 History of paper

Ever since people wanted to pass on important thoughts they were searching for objects to record their messages on. Before the first paper like materials were invented they used wood, stone, ceramics, cloth, bark, metal, silk, bamboo, and tree leaves for this purpose. (Alen 2007) After searching for cheaper materials that are also easier to transport papyrus and parchment were developed. Papyrus was first used as early as 3500 B.C. by the ancient Egyptians. It was prepared by making a mat out of sliced papyrus reeds that were pounded together to form a flat sheet. The word paper is derived from papyrus as it is its ancient ancestor. Parchment was invented - most probably also by the Egyptians (2700 B.C.) - as alternative to papyrus. The surface of animal skins is treated until it is smooth enough to write on it. As it is far more flexible than papyrus and even re-useable after scratching of earlier writings, it was used until the middle ages and was only displaced by the far more cost efficient paper. In early American cultures and on the pacific islands other production processes to receive writable sheets were known that were quite similar to papyrus production: Amatl which was used by the Aztecs, Huun invented by the Maya, and Tapa developed on the pacific islands. All of them are based on special treated bark. (Freyer 2003)

1.1 Paper production in the course of time

The first mention of paper by the Chinese court official Cai Lun dates back to 105 AD. He described a papermaking process where a fiber suspension was produced through pounding a mixture of mulberry bark, hemp, old fishing nets, and rags in water. Paper mats were formed by dewatering the pulp through a mold, and pressing. Afterwards the sheets were dried by the sun. From China the art of making paper was brought first to Korea and was further spread to Japan by Buddhist monks around 610 AD. The first non-Asian people learning how to produce paper were the Arabs who learned it from Chinese prisoners of war in 751. Through the Arabs the knowledge of how to make paper finally reached Europe: While Spain was under Moorish rule the first paper mill on European ground was built in Xativa, Spain in 1144. After the Moors were driven out of Spain the knowledge of paper production finally spread across the rest of Europe. After mills were built in Italy and France the first Austrian paper mill was founded near Baden in 1321. (Freyer 2003)

With the invention of the movable type printing press by Gutenberg in 1453 the demand for paper gradually increased and further inventions dealt with the possibility of using new raw materials, wood instead of rags, and with the development of a more efficient process. Big steps towards modern paper production were the invention of the first paper machine by Nicholas-Louis Robert in 1798 and the gradual utilization of wood as raw material with

contributions by F.G. Keller, H. Burgess, C. Watt, B.C. Tilghman, E. Ritter, C. Kellner, and C.F. Dahl. (Freyer 2003)

1.2 Paper treatment for quality improvement

Even in the early days of paper production in ancient China (450 A.D.) the use of starch and gypsum surface treatment were known as important steps to improve paper quality. Later on white mineral powders in combination with wax were used. These treatments filled the cavities and made the paper more water repellent. Whereas during the 8th century the Arabs used talc, gypsum, or chalk which was eventually mixed with starch to increase the whiteness of their paper sheets. (Alen 2007) Even nowadays this concept of using inert pigments (e.g. clay, CaCO_3 , TiO_2 , silicates), dyes, optical brightening agents (OBAs) together with binders or thickeners (e.g. starch, proteins, resins, or CMC) to modify the paper surface has not been outdated.

The first one to size paper by adding chemicals to the pulp before sheet formation was Moritz Illig who invented rosin sizing. This type of internal sizing uses rosin soap or free rosin that is mixed into the pulp and fixed by adding an aluminum salt. (Irving et al. 1866; Kellner 1886; Menzies 1889; Strazdins 1981)

Rosin sizing is still common today. Although for some reasons other sizing agents were developed, in acidic paper making (pH 4-5) there is no established alternative. A more detailed insight into rosin sizing is given below (3.1). However from the 1970s onwards increasing amounts of paper were produced in a neutral to slightly alkaline process. One reason was the instability of acid papers; the free acids cause it to decay. This is troubling librarians and paper restaurateurs all over the world today as they try to find ways to stabilize pieces of art and books based on acid paper grades. (Laine and Stenius 2007) Another reason for the introduction of a neutral to slightly alkaline process was the introduction of CaCO_3 as cheap filler, which cannot be used under acidic conditions. This was perhaps the bigger demand for the papermakers. (Roberts 1996) The most adapted sizing agents are alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). While AKD is known as a paper sizing agent since the 1950s, ASA was introduced in the 1970s. Both are discussed in more detail later on (3.2). Nowadays it is the intended use of the produced paper that demands the use of a certain sizing agent: Sack paper, which needs good frictional properties, is sized with rosin, in the production of liquid packaging board (2.4.2) AKD is used, as it has a high resistance against aggressive liquids like lactic acid, and ASA, reckoned for its fast curing characteristics, is applied in copy paper production. (Laine and Stenius 2007)

2 Modern paper production

While in the early times of papermaking all different steps from the preparation of a cellulose fiber suspension to sheet formation and drying were conducted manually, nowadays it is a highly developed industrial process. Still the main steps have not changed ever since:

- The raw material in use is treated in a way to separate the cellulose fibers.
- The pulp is dewatered on a sieve.
- The readymade sheet is dried.
- The sheet is manipulated to receive a smooth writeable surface.

Additional to these traditional steps following ones are essential for utilizing wood as paper raw material and meeting the demand for a white and printable paper - with regards to chemical treatment of pulp: debarking of wood; cutting the wood into chips; removing lignin (chemical treatment); adding fillers, sizing agents, and additives (Fixatives, retention and drainage aids, dry and wet strength agents, defoamers, dyes, OBAs); applying further surface treatments (calendaring, sealing with polymer films).

The detailed description of the papermaking process below is exclusively focusing on the essential steps of modern paper production. It considers wood as the single raw material source, because technologically it is the most important one besides recycled fibers and annual plants (Sixta 2006). Although many different pulping methods exist today, here only Sulfate and Sulfite process are explained, because no competitive alternative has been found today for chemical pulping. Mechanical pulping is not considered as it is only used to a minor extent for certain paper grades.

2.1 Raw material sources

What provides wood with strength is its construction as composite material. The outer membranes of single wood cells (primary wall and secondary wall) are based on three distinct compounds: Stiffness and resistance against mechanical stress are derived from different layers of cellulose fibers, while elastic properties are gained from amorphous lignin, and hemicelluloses serve as link between those two fractions. Hemicelluloses are responsible for embedding the cellulose fibers in its amorphous matrix. For a detailed description of a wood cell see Figure 2: the different orientations of the cellulose fibrils in different layers of the secondary cell wall can be seen.

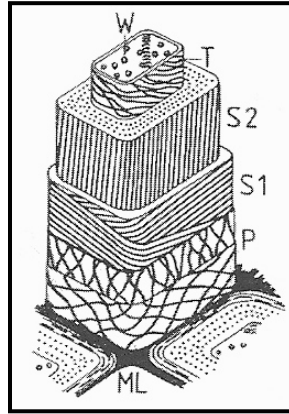


Figure 2: Structure of a wood cell with ML (middle lamella), P (primary wall), S1 (secondary wall, outer layer), S2 (secondary wall, middle layer), T (or S3, secondary wall, inner layer), and W (warty layer) (Alen 2000)

The wood component primarily used in paper production is cellulose, which accounts for around 42-45% of a wood cell depending on its source (Figure 4). It is a homo-polymer made up by β_{1-4} linked glucose units (so called anhydro glucose units AGU). One cellulose polymer may consist of up to 10 000 such AGU's. Neighboring glucose units are rotated by 180° and intra molecular hydrogen bonds are formed between $2\text{-O-H} \rightarrow 6'\text{-O}$ and $3\text{-O-H} \rightarrow 5'\text{-O}$. This renders the fiber strong and stiff. Different cellulose chains aggregate to fiber bundles called micro-fibrils, which are then arranged in fibers; again the structures are stabilized by hydrogen bonds. Due to dense intra- and inter molecular hydrogen bonding systems cellulose cannot be solved in water or any common organic solvent; it is the origin of its physical and chemical stability. (Krainz 2009) If the micro-fibrils are arranged in a perfect parallel structure, these are referred to as crystalline regions, while not so highly organized parts are called amorphous regions. The ratio of these parts is essential for the paper making process, as it is much more difficult for pulping chemicals to enter crystalline regions.

While cellulose is essential for papermaking the hemicelluloses are sometimes wanted, sometimes not. Under conventional treatment, sulfate- or sulfite process, the hemicelluloses are adsorbed on the celluloses. So they increase yield and further more help improving the mechanical properties of the readymade sheets. In contrary to cellulose which is based on one single sugar (glucose), the hemicelluloses are a mixture of different C_5 and C_6 sugars (xylose, arabinose, glucose, mannose, galactose), glucuronic acids, and deoxy hexoses. The composition of hemicelluloses is dependent on its source. While in hardwood there are manly xylose units (Xylans), in softwood there are primarily mannose units (Mannans) (Figure 4).

The third major component in wood is lignin. It is based on p-cumaryl alcohol units that are sometimes functionalized by methoxyl groups at C₃ (coniferyl alcohol) or C₃ and C₅ (sinapyl alcohol) (Figure 3). For the formation of the lignin network phenyl propane units are linked β -O-4 (40-50%), 5-5 (5-20%), α -O-4 (5-10%), β -5 (5-10%), and 4-O-5 (5-10%). To a minor extent also β -1, β - β , γ -O-4, and ester-bonds can occur. Furthermore covalent bonds between parts of the hemicelluloses and lignin were confirmed (Alen 2000; Lawoko et al. 2006).

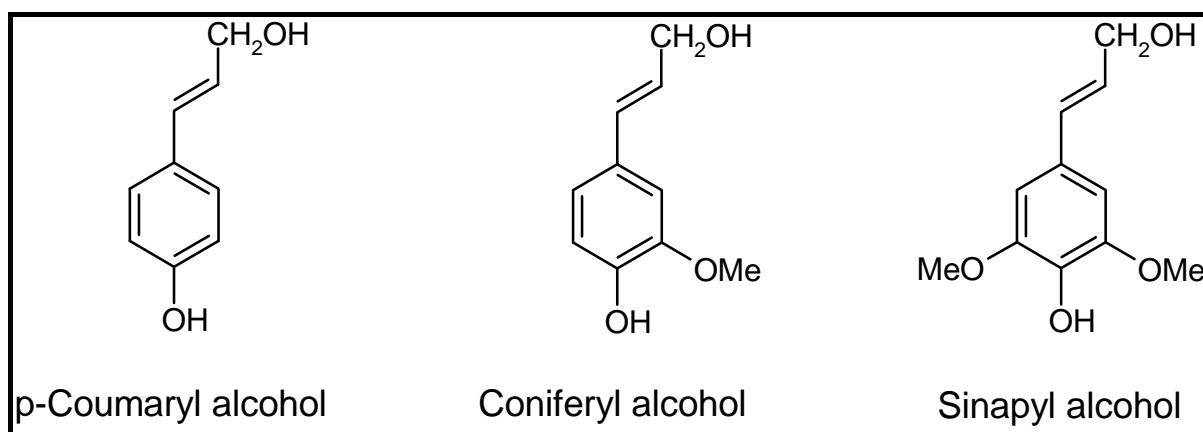
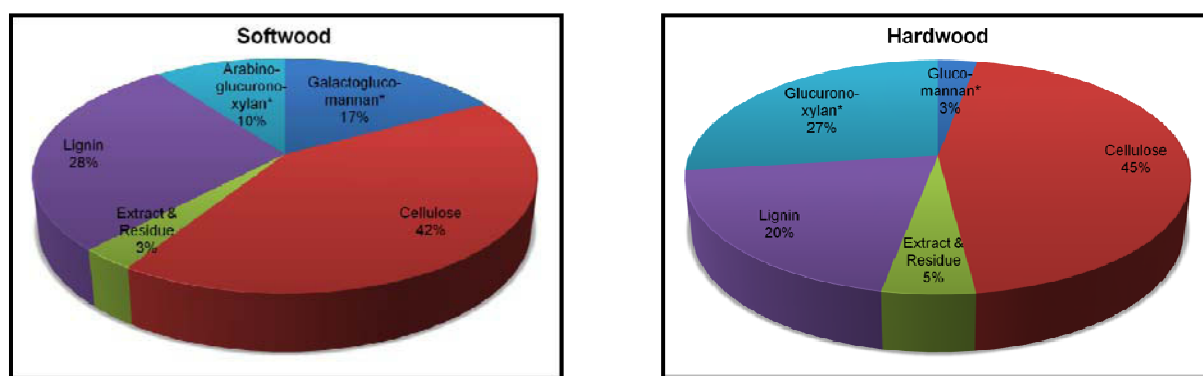


Figure 3: Basis components of lignin

Different trees and annual plants are considered for use in the paper production. Frequently used softwood trees are pine, spruce, and fir, while the most valued hardwood trees are eucalyptus, acacia, beech, and birch. In Figure 4 the distribution of the chemical fractions in softwood and hardwood is given.



*Hemicelluloses

Figure 4: Chemical compounds in wood (data based on: Koch 2006)

2.2 Chemical pulping and bleaching

Wood being the major raw material source for paper production has to be converted into fibrous material by breaking the existing bonds within the wood structure. This process called pulping can be conducted chemically, mechanically or semi-chemically. The largest amount (77%) of all wood based fiber material worldwide is prepared using chemical pulping. (Sixta et al. 2006) In this process lignin is dissolved in the cooking chemicals at elevated temperatures (130-170°C) after facing chemical degradation and modification, whereas cellulose fibers and parts of the hemicelluloses are collected. Extraction of lignin is of mayor importance not only for obtaining the cellulose fibers, but to restrict yellowing caused by residual lignin contained in paper products. Of course not all paper grades need to be lignin free. Newspapers or other paper products with relatively short life times may still contain lignin and are therefore based on fibers gained from other pulping processes (e.g. mechanical pulping).

The processes described in detail below are the two major ones used for the preparation of chemical pulps, the sulfate (=Kraft) and the sulfite process. Their names are derived from the chemicals used to make up for losses during the recovering of the inorganic cooking chemicals. A third group of recently developed pulping processes is summarized under organosolv pulping (2.2.3).

For optimum yields chemical pulping has to be stopped after around 90% of the lignin has been removed, because with ongoing cooking time side reactions degrading the cellulose and hemicelluloses become more frequent (Sixta et al. 2006). To complete delignification the collected chemical pulps are then treated with various bleaching methods.

2.2.1 Kraft process

This process originally invented by C.F. Dahl in 1879 comprises the treatment of wood chips with sodium sulfide (Na_2S) in sodium hydroxide solution (NaOH) at 150-170°C. Due to the alkaline treatment at pH14 lignin's phenolic groups are deprotonated leading to cleavage of the α -ethers and resulting in quinone methides. This structure is attacked by the reactive chemical species being present: hydrosulfide (HS^-) and hydroxide (OH^-) anion in the next step. This nucleophilic species preferably react with the α -position of lignin leading to the cleavage of the β -ether bonds. Thus lignin is cut down to fractions of lower molecular weight. In connection with the introduction of hydrophilic groups, hydrosulfide- or hydroxyl- groups, major parts of lignin become soluble in the cooking chemicals and can be removed. Residual amounts of lignin in cellulose pulp have to be removed afterwards by applying different bleaching sequences. (Sixta et al. 2006) The black liquor remaining after Kraft cooking is

concentrated and either burned for energy production, or treated further to gain valuable chemicals: e.g. crude tall oil.

As the Kraft process is capable of utilizing any wood source it is used for around 90% of all pulp productions (Sixta et al. 2006); especially where mainly wood with a high resin contents is at hand. Further advantages of Kraft pulping are the short cooking times (1-2 h) and the excellent strength properties of the final pulp. The only drawbacks of this chemical treatment are a low bleachability of the pulp and the formation of highly volatile malodorous and toxic sulfur compounds. (Sixta et al. 2006)

2.2.2 Sulfite process

In 1867 B.C. Tilghman patented a process for pulp production using aqueous solutions of calcium hydrogen sulfite ($\text{Ca}(\text{HSO}_3)_2$) and sulfur dioxide (SO_2) in pressurized reactors (Sixta et al. 2006). The modern process treats wood chips, not exceeding a certain length, with sulfur dioxide together with calcium, magnesium, sodium, or ammonium sulfite at a certain pH. Table 1 presents the nomenclature according the used pH range of the resulting cooking liquor.

Table 1: Nomenclature for the sulfite cooking processes (Sixta et al. 2006)

Nomenclature	Initial pH range (25°C)	Base alternatives	Active reagents
Acid bisulfite	1-2	Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+	H^+ , HSO_3^-
Bisulfite (Magnefite)	3-5	Mg^{2+} , Na^+ , NH_4^+	(H^+) , HSO_3^-
Neutral sulfite	6-9	Na^+ , NH_4^+	HSO_3^- , SO_3^{2-}
Alkaline sulfite	10-13,5	Na^+	SO_3^{2-} , OH^-

During treatment with the cooking chemicals in the Bisulfite process lignin structures are first transformed to benzylium cations due to cleavage of α -aryl ethers in acidic pH. In further steps residual lignin is attacked by the hydrogen sulfite ion (HSO_3^-) that is formed from SO_2 and $\text{Mg}(\text{OH})_2$ at the given pH. Thus the lignin's molecular weight is reduced and the solubility is increased even further by sulfonation (=introduction of sulfonic acid groups ($-\text{HSO}_3$)).

Because this process is not capable utilizing wood that is rich in resin, it is only used to a minor extent; for around 5% (Sixta et al. 2006) of the world pulp production. It is mainly applied to hardwood for the manufacturing of “dissolving pulps” which are the raw material for viscose fibers or other cellulose derivatives (Krainz 2009). In comparison to the much more prominent Kraft process less odor problems occur and the ready-made pulp is of higher brightness.

2.2.3 Organosolv pulping

This chemical pulping method comprises the use of organic solvents for delignification of wood or similar biomass. As in the above described pulping methods (2.2.1 and 2.2.2) lignin's molecular weight is reduced and solved in the cooking chemicals. The driving force behind the development of Organosolv processes was to replace the common inorganic ones as well as to be able to utilize not only the cellulose fraction, but also other polysaccharides, lignin, and extractives (Sundquist 1999). Many different processes have been developed, which can be distinguished by their cooking chemicals; some examples are listed in Table 2.

Table 2: Different Organosolv pulping methods (based on Sundquist 1999)

	Cooking Chemicals	Advantages	Disadvantages
Alcell	50% Ethanol, Water (Acid auto-hydrolysis)	Sulfur free process and products Good brightness-stability of pulp Easy cooking liquor regeneration No additional cooking chemicals Good bleachability of pulp	Reduced pulp strength Low pulp yield Only for hardwood pulping High pressure equipment
Organocell	Methanol, NaOH, Water, Anthraquinone	Sulfur free process and products Applicable for hard- and softwood Comparable strength to Kraft pulp	Difficult chemical recovery High pressure equipment
ASAM	10% Methanol, NaOH, Na ₂ CO ₃ , Na ₂ SO ₃ , Water; Anthraquinone	Is suitable for all raw materials Higher yield than with Kraft cooking Pulps are easy to bleach High quality pulp	Sulfur containing process Difficult chemical recovery High pressure equipment
Formacell	Acetic acid / Water / Formic acid 75/15/10	Sulfur free process and products Is suitable for all raw materials Selective O ₃ bleaching No bleaching effluents	Corrosive chemicals Difficult chemical recovery Lab-scale only
Milox	Formic acid Hydrogen peroxide (Peroxyformic acid)	Sulfur free process and products Is suitable for all raw materials Simple totally chlorine free bleaching Simple chemical recovery Low temperatures Unpressurized reactors	Poor quality of softwood pulp Corrosive chemicals Chip drying is needed

2.2.4 Bleaching

After removing major parts of lignin via one of the above described chemical treatments the cellulose fibers are collected and washed. Due to the different pulping processes applied colored substances were formed as unwanted by products. These have to be removed from the manufactured cellulose pulps, as they give the pulp a slightly yellow to brown appearance instead of pure white, which decreases its value in the eyes of the customers. Furthermore residual lignin in ready-made sheets will cause the formation of even more chromophores, leading to increased yellowing with ongoing time.

To avoid problems by residual lignin and to decompose other colored substances, different bleaching sequences are combined with extraction steps. Most common bleaching agents oxidize the chromophores to non colored substances, or introduce functional groups increasing the hydrophilicity and thus making it easier to remove them in the following extraction stage. The bleaching sequences have to be adapted to the used chemical pulping process and are dependent on the utilized wood source. Nowadays bleaching sequences mostly comprise the use of chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), oxygen (O_2), ozone (O_3), peracids (ROOOH), and sodium peroxide (Na_2O_2), while the formerly wide spread use of chlorine gas (Cl_2) was reduced to avoid environmental and corrosion problems (Alen 2007). While the use of ClO_2 is possible in elemental chlorine free (ECF) bleaching sequences, it is - for obvious reasons - not a part of totally chlorine free (TCF) ones. Since it is difficult to substitute ClO_2 , due to its excellent (and selective) oxidizing and brightening properties, over 50% of all bleached chemical pulps are ECF (Alen 2007).

2.3 Web forming - wet end

According to the quality of the pulp, its origin, and the desired application of the latter produced paper, different pulp fractions, derived from chemical and/or mechanical pulping as well as recycled fibers, are mixed with water. This fiber blend is called stock. To enhance paper formation and quality chemical additives and fillers are added to the stock, which is then diluted to less than 1% consistency. Afterwards the so called thin stock is mechanically purified, sizing agents and other chemical additives are added, and pumped towards the wet end of the paper machine. There paper is formed as a continuous web: In a first step the paper web is dewatered on a moving forming wire, afterwards it is pressed through the rolls of the press section, which is followed by the drying section. In this last part of the paper machine the paper is dried on steam heated drying cylinders. (Alen 2007) The ready-made paper is then collected on reels weighing several tons if ready, while the drained water (white water) is recycled and used for thick stock dilution. (Möller 2011)

Paper making is a filtration process. Thus the wire pore size as well as fiber and additive size plays a major role. On the one hand dewatering needs to be quick to guarantee good runability of the paper machine, on the other hand high retention must be ensured. A major part of thin stock components is significantly smaller than typical wire pores. Thus it is an important paper maker aim to agglomerate smaller thin stock components to the bigger fibers. This is usually done by flock formation following different mechanisms. (Möller 2011) The chemical nature of the additives used for reaching the above described aims is described in more detail below.

2.3.1 Fixation and retention

In thin stock a high amount of colloidal or dissolved anionic material - anionic trash - is present which may originate from fresh water, pulp, fillers, or other additives. (For examples see Table 3) As the white water collected after drainage of the paper web is reused in preparation of new thin stock, it is the papermakers aim to prevent accumulation of these charged particles in his machine, but they are too small to be retained in the paper just by filtration process.

To remove anionic trash from white water circles they have to be discarded through the paper with the help of fixatives, which adsorb them onto the considerably large cellulose fibers. For this purpose inorganic fixatives like aluminum sulfate, sodium aluminate, polyaluminum chloride, polyaluminum nitrate, or polyaluminum nitrate sulfate, as well as cationic polymers with low molecular weight and high charge density like polyaminoamide epichlorohydrin (PAE), polyamidoamine, polyamine, polydiallyl dimethyl ammonium chloride (poly-DADMAC), and dicyandiamide formaldehyde can be applied. (Krogerus 2007)

Table 3: Origin of anionic trash (based on Bauer 2009)

Fresh Water	Pulp	Filler	Additives
Humic acids	Lignin derivates	Dispersing agents	Starch
Surfactants	Lignin sulfonates	Biocides	CMC
Biocides	Hemicelluloses		Organic acids
	Fatty acids		Dyes
	Latex binder		Biocides
	Starch coating		Dispersing Agents
			Sodium Silicate

Another class of additives helps improving retention and drainage by flock formation. These so called retention aids are polymers with high molecular weight, but low charge density. One of the used polymers is polyacrylamide (PAM) based on various monomers listed in Figure 5. The ester bond and quaternary amine in DMAEA-PAM makes the polymer water soluble and gives it the positive charge needed for its application, while the benefit of APTAC is its better stability against alkaline hydrolysis. Other retention aids are based on polyethylene oxide, which improves retention of small cellulose fibers (fines), polyethylene imine, and especially modified starches. (Krogerus 2007, Bauer 2009)

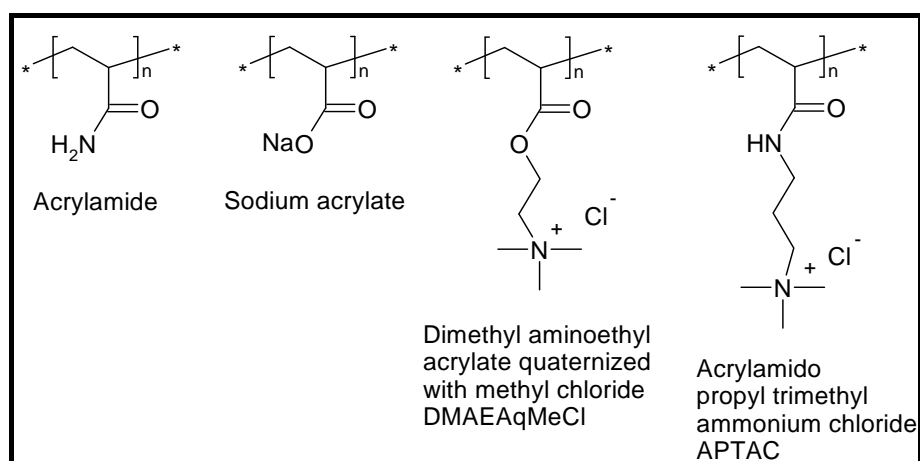


Figure 5: Monomers for polyacrylamides (PAM) used as retention aids

For each paper mill the most suitable combination of fixative and retention aid has to be selected with respect to their molecular weight and charge. No matter what kind of fixative or retention aid is used their addition point has to be chosen carefully with respect to chemical environment (pH) and charge load. Often fixatives are dosed into the white water, while retention aids are added as late as possible to prevent destruction of the once formed flocks.

(Möller 2011) One possible setup used is the primary addition of a cationic fixative to adsorb anionic trash onto fibers while in a second step the fibers are bridged with high molecular weight anionic polymers (dual polymer system; Figure 6).

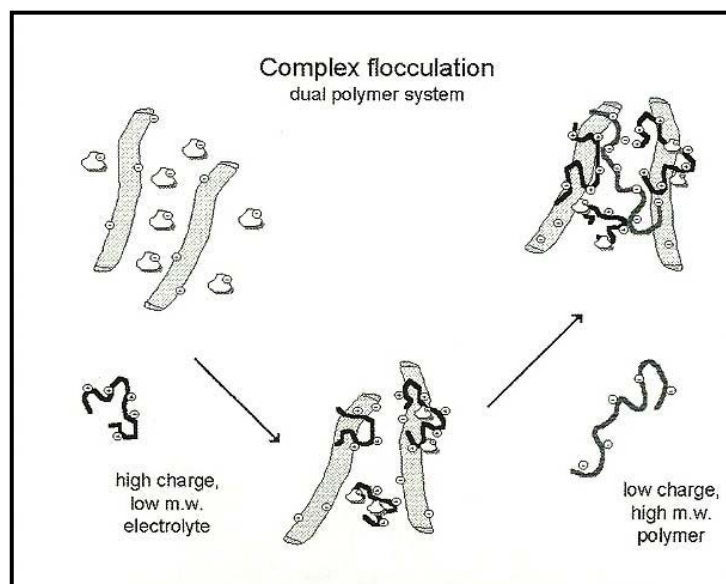


Figure 6: Flocculation using a dual polymer system (Krogerus 2007)

2.3.2 Dry strength

Another important group of additives are responsible for improving strength parameters in the dry sheet. This special paper property is dependent on the number of bonds in the fiber network formed during drying, on the quality of sheet formation, on sufficient retention of fines, and on drainage. Additives that improve dry strength have to be capable of increasing the number of hydrogen bonds, thus hydrophilic, water soluble polymers are used. They may either be derived from renewable resources like starch, vegetable gums, chitosan, carboxymethyl cellulose (CMC), or based on synthetic polymers. (Krogerus 2007)

Starches used for this purpose are isolated from wheat, potato, tapioca, and maize, especially from so called waxy maize. This is a special breed of maize containing of amylopectin only (99%). Amylopectin is a branched high molecular polymer based on 1,4 and 1,6 linked α D-glucose, while the second major fraction in most starches is amylose, another glucose polymer consisting of linear 1,4 α D-glucose. For tuning the starches to fit into different application demands their molecular weight is adjusted by cross linking, while substitution (e.g. with 2,3 epoxy propylene trimethyl ammonium chloride) is able to improve retention on the anionic cellulose fibers. (Krogerus 2007)

The most prominent synthetic dry strength agent is PAM, which was introduced earlier as retention aid. Its amide groups form strong hydrogen bonds with cellulose hydroxyls. If PAM is glyoxalated its addition helps improving dry strength as well as wet strength (see 2.3.3) due to the formation of covalent bonds with cellulose. Other polymers used for the same purpose are polyvinyl alcohol (PVA), latex, and polyvinyl amine. (Krogerus 2007)

2.3.3 Wet strength

During paper formation and in the final product wet paper has to have certain strength adjustable by different chemical aids. While initial wet web strength during papermaking assures machine runability, in the ready-made paper (re-wetted web strength) it is necessary only for special paper products such as tissue or coffee filters. Increasing strength in wet paper can be accomplished by stabilizing existing hydrogen bonds, building new covalent bonds, and formation of a polymer network entangling fibers. There are two different chemical classes of additives to be used: The first class has aldehydes as reactive groups forming acetals or hemiacetals with the hydroxyls of cellulose (temporary wet strength), the second class is able to build hydrolytically stable covalent bonds (permanent wet strength). (Krogerus 2007)

Chemicals used as wet strength agents are typically based on: urea-formaldehyde, melamine-formaldehyde, polyaminoamide-epichlorohydrin, glyoxalated PAM, and polyurethanes. Other wet strength agents are based on renewable resources like dialdehyde starches, modified cellulosic fibers, chitosan, and certain enzymes. The latest mentioned impart initial wet strength by improving drainage and thus increasing the dry content. (Krogerus 2007)

2.3.4 Sizing

To reduce water or ink absorption and to improve the papers resistance against aqueous acids as well as alkaline solutions, it can be treated with various sizing agents. These compounds may be added during the paper making procedure prior to sheet formation wherein the process is called internal sizing. Another opportunity is surface sizing, where sizing agents are applied on the surface of a ready-made paper sheet. The effect of sizing can be made visible easily by adding a drop of water onto two different paper sheets one that has not been sized, whereas the other one has been sized (Figure 7). While the water will be immediately absorbed by the paper in the first case, the water drop will stay visible for some time in the second.

While paper was manufactured without the use of paper machines the only way to improve the papers surface quality was to apply starch or gelatin as a coating, after the invention of

the paper machine internal sizing with rosin became common. It was invented by M.F. Illig in the early 19th century and was the first choice for internal sizing for quite a long time (1830 until 1970s) (Laine and Stenius 2007).

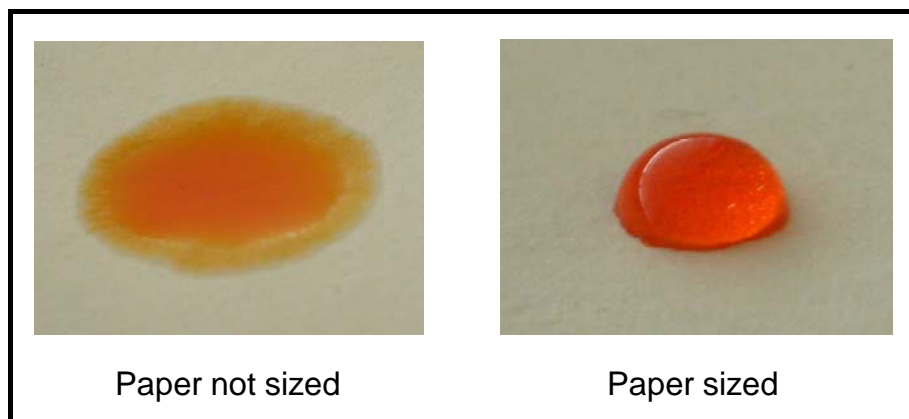


Figure 7: The effect of paper sizing

Rosin soap as well as rosin, both forms are used in rosin sizing, has to be precipitated onto cellulose fibers with the help of aluminum salts, e.g. alum ($\text{Al}_2(\text{SO}_4)_3$). Their use is restricted to acidic paper production. Recent developments shifted paper making from acidic to neutral or slightly alkaline pH regions, because it was found, that the produced papers have higher strength, greater stability and better aging characteristics. Another advantage of neutral to alkaline paper production was the possibility of using the more cost efficient filler CaCO_3 instead of clay which cannot be used in acid paper making due to liberation of CO_2 and foam formation at low pH (Dumas 1981, Roberts 1996, Laine and Stenius 2007). As rosin sizing is only applicable with restrictions at a pH above 6, new sizing agents were invented: The so called reactive sizing agents alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). The concepts of internal sizing with rosin or reactive sizing agents are discussed in a separate part (see section 3).

2.3.5 Fillers

Many different types of filler are used in various paper grades to improve optical properties (opacity) and printing characteristics (Laine 2007). Another reason for using fillers is the possibility to substitute more costly cellulose fibers. While in early times of papermaking exclusively mined minerals and pigments were used, today a shift towards synthetic ones is seen. The reason for this trend is that manufactured minerals have a tighter particle size distribution, controllable shape, and less colored impurities. (Alen 2007)

For each filler application the most suitable candidate has to be chosen according its particle size, shape and surface charge. While fillers are used as wet end additives the pigments

presented in Table 4 may also be used in coating applications. Some selected filler types are listed in combination with their important characteristics in Table 4.

Table 4: Filler types used in papermaking (based on Krogerus 2007)

	Name	Chemical structure	Charge (pH 5-9)	Shape	Particle size (%) <5µm/<2µm
Mined Minerals	Clay (Kaolinite)	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	-	Platelet	75 / 48
	Ground calcium carbonate (GCC)	CaCO_3	-	Cubic, Needles	90 / 40
	Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	-	Lamellas	45 / 16
Synthesized Minerals	Precipitated calcium carbonate (PCC)	CaCO_3	+(-)	Needles, Cubic	100 / 70
	Structured clay (Bentonite, Calcined Clay)	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$	-	Agglomerates	- / 100 (0.3-2µm)
Other Pigments	Titan dioxide	TiO_2	-	Tetragonal crystals	- / 100 (0.2-0.5µm)
	Synthetic silicates	$\text{Na}_2^*\text{Al}_2\text{O}_3^*$ $13.6 \text{ SiO}_2^*\text{H}_2\text{O}$	-	Spherical particles	- / 100 (0.1-0.5µm)

Although fillers are important for tuning paper characteristics their use is limited, because of several effects: If the amount of filler exceeds certain limits it cannot be retained any more. The addition of fillers in the wet end increases the amount of internal sizing agent needed for a certain sizing level. Cationic starch (e.g. used as dry strength agent) is adsorbed to anionic filler particles, therefore on the one hand retention of fillers improve with the addition of such starches, on the other hand filled paper needs a higher starch dosage to reach the same level of dry strength than unfilled paper. Also the chemical nature of the used filler has to be considered carefully. The wide use of CaCO_3 was only possible after shifting paper production from acidic to neutral/alkaline pH and substituting rosin/alum sizing with reactive sizing agents. (Krogerus 2007)

2.3.6 Dyes and optical brightening agents

In production of most paper grades as well as for board manufacturing dyes and optical brightening agents (OBAs) are added to improve their color. It is quite obvious that for production of colored paper dyes need to be added, but the addition of blue or violet dyes to yellowish mechanically pulp is used to make the paper appear more white. The most prominent dyes are direct dyes which have a good affinity to bleached chemical pulp, but there are also basic and pigment dyes. (Krogerus 2007) For an example of an anionic direct dye see Figure 8.

OBAs are able to absorb UV wavelengths and remmit visible blue light; this gives the paper a brighter appearance. As for their brightening effect UV light is needed, OBAs cannot function according to their nature if these wavelengths are missing or are absorbed by other paper

ingredients. Lignin for example is also able to absorb UV light. Therefore OBAs have a limited efficiency in unbleached or wood containing pulp. (Krogerus 2007) The basic structure of OBAs is revealed in Figure 8.

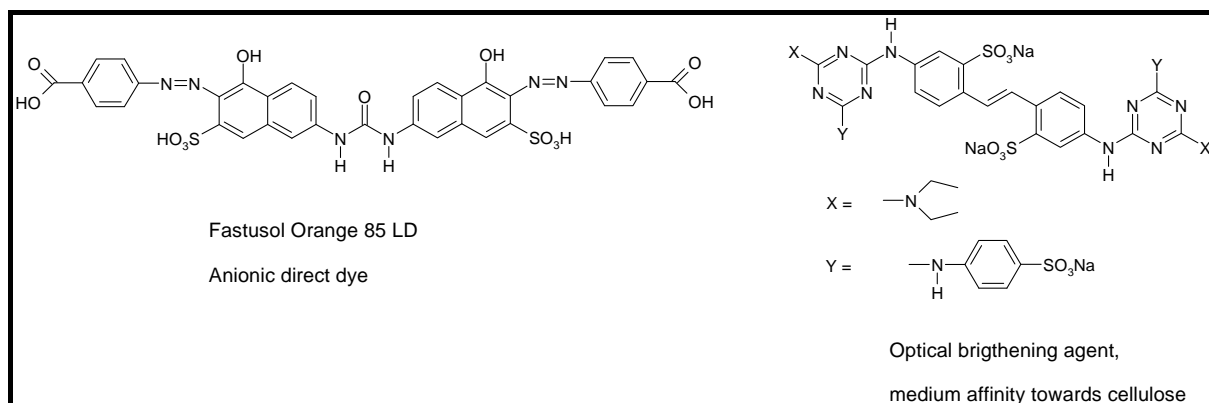


Figure 8: Examples for dyes and OBAs. (Bauer 2009)

2.3.7 Surface treatments

The oldest method to smoothen the paper surface, as to be able to write on it, was surface treatment with starch and gypsum, which was invented in China around 450 A.D. For improving the whiteness of paper sheets also other inorganic fillers like talc or chalk (CaCO₃) were used since the 8th century. During the middle ages the use of casein, animal glue, and china clay (kaolin) was prominent for the same purpose. (Alen 2007) As to modern papermaking nothing much has changed since then: It is still common using coatings on the surface of paper. Today these coatings are complex mixtures consisting of pigments, optical brightening agents (OBAs), binders, rheology modifiers, foam control agents, dispersing agents, and biocides. (Krogerus 2007) Three different concepts for the application of coatings are in use: short dwell time applicators, long dwell time applicators, and film coaters. They may be used alone or in combinations depending on the thickness of the coating that has to be applied. (Haarla 2000)

Another method to improve the quality of ready-made paper is surface sizing. In this method sizing agents are applied as emulsions or dispersions in polymer solution using a size press. The polymers used are often starches whose molecular weight had been adjusted by degradation conducted with acids, enzymes, or oxidation (Krogerus 2007).

Besides the application of surface coatings and sizings the smoothness of paper surfaces can also be adjusted by passing the paper through a calendar, two metal cylinders pressed together with high force.

2.4 Paper grades

Paper production is always mastered according the challenges the ready-made product has to face. For every distinct further use the pulp, chemical environment, production process, and the chemicals added are adapted. Below a rough classification for paper is given according the end use.

2.4.1 Printing and writing paper

Around 30% of the worldwide paper and board production falls within this segment. It may be divided further in papers based on mechanical pulps (mech. pulp) or chemical pulps (chem. pulp). Another important raw material for these grades is recycled fibers. Examples for the uses of this paper grade are as: newspapers, magazines, books, and copy paper. For a possible assignment of selected paper grades according their end-use, fiber raw materials, basis weight, and surface treatment see Table 5. (Haarla 2000)

Table 5: Printing and writing paper grades (based on Haarla 2000)

	Paper Grade	Pulp raw material	Basis weight [g/m ²]	Surface treatment [g/m ² /side]	Filler content [%]	Use
<div style="display: flex; flex-direction: column; align-items: center;"> <div>↓</div> <div>Increasing Quality / Price</div> <div>↓</div> </div>	Standard Newsprint	Up to 100% recycled fibers or up to 100% mech. pulp	~45	calendered	Up to 15	Newspaper, Flyers
	Telephone Directories (Special Newsprint)	100% mech. pulp	28-40	soft calendered		Telephone Directories
	Super-calendered Papers	mech. pulp + 10-30% chem. pulp	52-60	super calendered	Up to 35	Magazines, Catalogs, Commercial Printing
	Coated Mechanical Papers	40-85% mech. pulp + 15-60% chem. pulp	35-90	coated 2-25	20-45*	High quality Magazines, Catalogs, Advertisement
	Uncoated Fine Papers	chem. pulp + max. 10% mech. pulp	25-90	Surface sized (starch) or pigmented	0-25*	Writing Papers, Magazines, Catalogs, Books, Directories
	Coated Fine Papers	chem. pulp + max. 10% mech. pulp	90-170	Sized and / or coated	30-45*	Advertising, Magazines, Catalogs, Books
	Special Fine Papers	chem. pulp + max. 10% mech. pulp	Copy Paper 40-90		5-25	Copy Paper Continuous Stationary

*total filler content including coating

2.4.2 Paperboards

This paper grade can be distinguished from paper by its higher basis weight which normally lies above 150 g/m^2 . It is used for packaging various goods and has to be strong enough that stacking of boxes based on this material is possible. Therefore paperboards are often multi-ply products with elastic top and back plies, while the middle ply is rather bulky or corrugated as is the case for containerboards (Figure 9). (Kiviranta 2000) The second category of paperboard besides containerboard is cartonboard. Consumer goods like food, cigarettes, or milk are packed with this type. For cartonboards in contact with food the fiber raw materials have to be chosen carefully, for example recycled fibers cannot be used. (Kiviranta 2000)

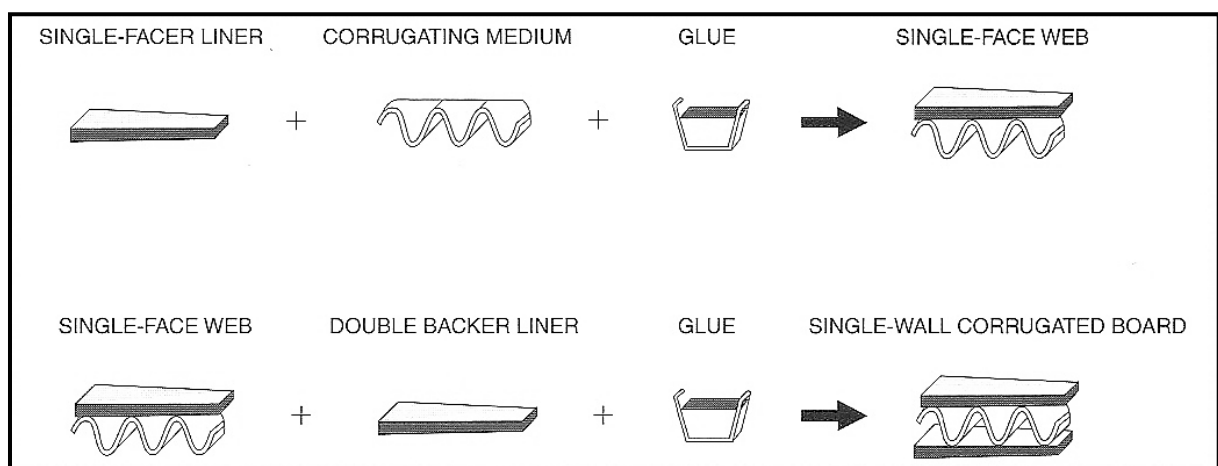


Figure 9: Plies of containerboard. (Kiviranta 2000)

Another challenge for food packages is that some of them have to be complete resistant against penetration of liquids as in the case of liquid packaging board used for example for milk or juice packages. It is conventionally based on paperboard that has been sealed with polyethylene. Although the paper is sealed, it gets in contact with liquid at the cut edges of the folded carton, so sizing agents are added to prevent penetration of liquids into this cut edge. As these packages may contain dairy products the paper used is especially tested for its resistance against penetration of lactic acid. The sizing chemical most adapted to the challenges of this paper grade is AKD for paper board produced at a pH 7-8.5. (Ward et al. 2006)

For liquid packaging boards that are used to carry perishable liquids the packaging board needs to be sterilized by soaking in hot hydrogen peroxide solution. As AKD does not provide enough resistance against edge leaking with hydrogen peroxide, rosin size in combination with alum under acid paper production conditions (pH 4-6) is used in this case. (Ward et al. 2006)

To meet both demands, being resistant to penetration of lactic acid as well as hydrogen peroxide, packaging board may be produced using a dual sizing system, where rosin and AKD size are added in two different steps after pH adjustment. (Walkden 1990)

In an effort to be able using one sizing chemical for both differently used liquid packaging board types a special type of ASA was invented. It is based on symmetrical olefins with a carbon number from 20-28. In both critical tests investigating lactic acid and peroxide resistance it showed improved resistance compared to conventional C₁₈ ASA and comparable results to AKD. In a comparison to rosin sized board the symmetrically olefin based ASA has a comparable resistance to acid ink, but is much more efficient. (Ward et al. 2006)

2.4.3 Tissue

Well known products that fall within this paper grade are toilet paper, handkerchiefs, hand towels, coffee, and cigarette filters. They are produced from lightweight paper and their most obvious characteristics are their high tensile strength and water absorbent characteristics. To achieve high tensile strength wet strength agents are added to the paper stock. Raw materials to be used are chemical pulp (Kraft pulp) and selected grades of recycled fibers. Basis weights can vary from 14 to 50 g/m² according to the planned application of the later produced product. (Kimari 2000)

2.5 Paper testing methods

In the chapter above a short introduction into the various existing paper grades was given. They all have to face very special demands. To make sure, that each produced and sold piece of paper does not fail, when used according to its intended application, several analytical measurements were developed for quality inspection. As it fills whole books (e.g. DIN Taschenbuch 118 and 213, Levlin and Söderhjelm 1999) to describe every testing method that's being used, only some of them, needed to check a paper's sizing degree, will be explained in detail below. Four different methods are common among the paper industry and several research institutions at the moment: Contact angle measurement, the Hercules Sizing test (HST), the Cobb₆₀ test, and the Stöckigt Sizing degree.

2.5.1 Contact angle measurement

This is a basic method to determine the wettability of a surface and measures the contact angle between the paper's surface and a liquid drop that has been placed on top of it. As it is not easy to measure the angle itself, instruments have been developed where the image of the drop is projected onto a screen, so that so that height and base of it can be measured. According to the assumption, that the projected image is a sector of a circle, the contact angle (θ) can be calculated with following equation 1 (Bristow 2007):

$$\theta = 2 \arctan\left(\frac{2h}{b}\right) \quad (1)$$

Whereas h is the height of the image and b is the base.

2.5.2 Hercules sizing test (HST)

With this test the penetration rate of a liquid ink through a piece of paper is measured: The paper is placed on the HST device and a drop of the HST-dye is placed on top of it. A photoelectric cell registers the color change on the bottom side of the paper as the ink penetrates through it. Time measurement is stopped, when the reflectance on the bottom side of the paper falls below a certain level (Hercules sizing tester -instruction manual).

2.5.3 Cobb₆₀ test

The Cobb₆₀ value is to be determined after DIN 53 132. It is an expression of the water absorption over the time period of 60 s given in g/m². A weighed piece of paper is placed between a plastic pad and a metal cylinder with a cross section area of 100 cm², 100 ml water are poured into the cylinder and time measurement is started, after 50 s the water is

discarded and the paper sheet is gauged twice and weighed again. After this the $Cobb_{60}$ value is calculated according to equation 2:

$$Cobb_{60} [gm^{-2}] = \frac{(m_2 - m_1) [g]}{0.01 [m^2]} \quad (2)$$

Whereas m_1 mass of the sample before $Cobb_{60}$ determination [g]; m_2 mass of the sample after $Cobb_{60}$ determination [g].

2.5.4 Stöckigt sizing test

The Stöckigt sizing degree (JIS P 8122) measures the time it takes for a $FeCl_3$ solution to penetrate through small pieces of paper sheet as a gauge for sizing efficiency. Thereby the paper piece is placed on aqueous ammonium thiocyanate solution. The higher the Stöckigt sizing degree in seconds, the better is the paper's resistance to water absorption.

The Stöckigt sizing degree is a quite sensitive method: Small unsized spots on the sheet may lead to small sizing degrees, even if the rest of the paper has a higher resistance to penetration. So this method is also very responsive towards not uniformly distributed sizing agent.

3 Internal sizing

This is one prominent method to modify cellulose fibers in order to control the penetration of liquids into paper sheets. According to the concept of internal sizing the used chemicals are added in the wet end of the paper machine. Depending on the chemical characteristics, application properties of the sizing agent, and the chemical environment of the paper mill the addition points may be varied from thick stock to thin stock addition. The goal is always to adsorb the sizing agent, or sizing agent emulsion on the cellulose fibers, while at the same time limit interaction of sizing agents and fillers.

In order to obtain an uniform distribution of the sizing agents throughout the whole paper web as well as good retention they are emulsified or dispersed prior to their addition to the paper stock. For this purpose aqueous polymer solutions, in most cases starch, but also various synthetic polymers, are used. The quality of these emulsions is characterized by their particle size, which should be around 1 μm . As was mentioned earlier the cellulose fibers in aqueous solution are negatively charged that is why the used starch or polymer is conventionally modified to be cationic for achieving maximum retention of the sizing agent emulsion. The two major existing systems, acid and neutral to slightly alkaline paper production are introduced below.

3.1 Acidic paper making

From the early times of rosin sizing until 20 years ago alkali rosin soaps, as invented by Moritz Illig, were used for paper sizing. The water soluble alkali resinates were added to the paper stock followed by the dosage of alum ($\text{Al}_2(\text{SO}_4)_3$) to fix the resin onto the fiber. This happens, because Al^{3+} immediately forms mono resinate, whose free metal valences act as an anchor for anionic materials like the cellulose fibers. Nowadays the paper industry prefers dispersed rosin size, because it is more efficient, a broader pH range can be covered, and the amount of alum can be reduced. It is manufactured through adding a protective colloid, e.g. casein, soy protein, or synthetic polymers (anionic or cationic modified polyethylene imine or polyacrylamide) to the molten rosin under stirring and dispersing the received mixture into water with the help of high shear equipment. (Bauer 2009, Laine and Stenius 2007)

As the protective colloids of rosin dispersions are often anionic polymers there is no electrostatic interaction helping dispersed rosin particles to precipitate on the anionic cellulose fibers, so alum has to be added to the stock beforehand. Thus where the alum precipitates cationic charged areas are formed which are needed to retain the rosin particles. In a later stage of the paper production, when the paper is dried, rosin starts spreading over the fibers and reacts with the alum present. In this way it is fixed onto the fibers in the most

effective orientation to provide sizing. (Laine and Stenius 2007) One major benefit of dispersed sizes compared to rosin soap is the delay of reaction with alum until the paper web is passing through the drier section of the paper machine. This leaves enough time for the cellulose fibers to form inter fiber bonds which cannot be interfered by rosin, so the produced papers have better dry strength than rosin soap sized ones. (Strazdins 1981)

In the cases of rosin soap or dispersed rosin size with anionic protective colloid the pH range is strictly limited to the acidic pH (4-6), because only under these conditions the needed positively charged alum species exist. One way to overcome this limitation is using a cationic protective colloid. Although these rosin dispersions are more expensive, they in applications where only rosin size can be used and the pH is between 6 and 6.8. (Bauer 2009)

The rosin used for the preparation of rosin soap or rosin dispersions is the natural resin of pine trees and can either be derived from living trees (gum rosin), or is gained after fractionated distillation of pulp mill residues (tall oil rosin). Because rosin is a natural product it is a mixture of resinous substances occurring in wood, to about 90% resin acids, mainly abietic and pimaric acid. For an increased sizing efficiency modern rosin products use maleated or fumarated rosin, known as fortified rosin. These products have a lower softening point which makes them easier to emulsify in order to prepare dispersed rosin size. Furthermore it was found that adsorption of such dispersed rosin size is increased as well as spreading on fiber surfaces. (Laine and Stenius 2007)

In recent years, from the 1970s onwards, papermakers switched from acid to neutral or slightly alkaline papermaking. The reasons for this change were most probably the possible use of CaCO_3 as very inexpensive filler. Other key advantages for the change are reduced corrosion on machine parts and increased strength in the produced paper, due to less fiber swelling under the given pH conditions. (Roberts 1996) But nonetheless rosin is still used in certain applications, where its special properties are needed. For example there are only limited possibilities to size liquid packaging boards with other sizing agents than rosin (see 2.4.2) and its use is mandatory if the produced paper is in direct contact with food (Möller 2011).

3.2 Neutral to alkaline sizing

Although many attempts were made to adopt rosin sizing to higher pH, for example by preparing dispersed rosin sizes with cationic protective polymer, which reduces the need for alum addition, other sizing agents were invented which were better adapted to the conditions of a paper machine run at neutral pH. The most prominent are alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA), which are discussed in detail below.

3.2.1 Alkyl ketene dimer (AKD)

The first long chain hydrocarbon alkyl ketene dimer to be used in paper sizing was patented by Hercules (Downey 1953). An emulsion of decyl- and hexyldecyl ketene dimers in aqueous solutions of carboxymethyl cellulose or starch was prepared with the help of emulsifiers to give the sizing agent dispersion.

Today AKD production comprises the use of stearic acid converted to acid chloride with thionyl chloride. With the addition of triethylamine the acid chlorides form ketenes which then dimerize to form AKD. AKD is a solid wax which is not soluble in water. Its melting point is around 50°C, depending on the length of the alkyl chains. For the use in paper mills AKD emulsions are prepared by dispersing the molten AKD wax in aqueous polymer solutions; in most cases cationic modified starch. These emulsions may have an AKD content of up to ~15%, emulsions with higher AKD levels lack stability. For a better performance of AKD emulsions small amounts of retention aids and surfactants may also be present to a minor extent. (Roberts 1996) Commercial AKD emulsions are acidified after preparation to limit hydrolysis. This step is necessary, to make sure these products are stable enough to ship to customers and store them for several weeks. (Laine and Stenius 2007)

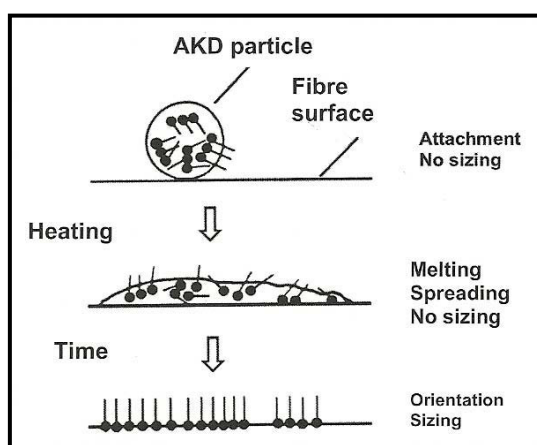


Figure 10: AKD-sizing mechanism. (Laine and Stenius 2007)

The sizing mechanism of AKD is based on electrostatic attraction of cationic size particles and negatively charged cellulose fibers in the wet end. Once AKD is retained on the fibers and reaches the drying section in the paper machine, the heat applied melts it and evenly distributes it throughout the paper web. In a last step the high temperature helps in orientating the AKD on the cellulose surface providing the produced paper with the demanded water repellency (Figure 10). It was found that only 15% of the fibers' surface needs to be covered by AKD to provide sufficient sizing. (Laine and Stenius 2007) However the actual development of sizing with AKD takes some time. It might only reach its peak after

storage of produced paper on-reel for several days (=curing). Storage at elevated temperature accelerates the sizing development. (Roberts 1996)

The clear advantage of AKD is its applicability at pH ranging from 6-9 and its resistance against lactic acid, which is needed for sizing liquid packaging board (see 2.4.2). But its use is limited where the produced paper has to show some frictional properties, e.g. sack paper, where rosin sizing is still used (Roberts 1996). AKD's slow curing characteristics may also be problematic where paper needs to be treated further immediately after production, e.g. surface sized. For these applications a fast curing sizing agent is needed and can be provided with ASA.

3.2.2 Alkenyl succinic anhydride (ASA)

While only slight changes in the original production of ASA were made from 1946 up to now, its application has spread. The original ASA was based on olefins with carbon lengths from 4-12, derived from distilling cracked petroleum hydrocarbons (Kise and Engle 1946). In that time ASA derivatives were used as lubricant (transformer) oil additives as they were found to reduce rust formation (Trigg et al. 1949, Osuch 1966). Later on scientists used the emulsifying capacity of ASA, and searched for further applications.

The first ASA used in paper production contained an alkyl chain with 5-18 carbon atoms and was linked to starch. It was originally invented as emulsifying agent and thickener to be used in paints, cold creams, liquid cleaners, stabilizer for lattices, and as laundry starch. (Caldwell and Wurzburg 1953).

Later on the capability of providing resistance to the penetration of water on paper when used as paper sizing agent was investigated (Wurzburg and Mazzearella 1963). The ASA used for this application was applied in neutral to alkaline paper production and its alkyl chain consisted of 5-12 or even more carbon atoms. Today ASA mostly is based on C₁₆ or C₁₈ internal olefins and is applied as an emulsion in cationic polymers; in most cases cationic modified starch. For the production of ASA, alkenes react with maleic acid anhydride (MAA) at high temperatures around 200°C in an *ene*-reaction (Figure 11).

So far, the olefin starting materials are exclusively from petrochemical sources. In many cases, olefins with terminal or near-terminal double bonds are isomerized to products with more centered double bonds before maleation since alpha ASA is solid at room temperature and thus more complicated to apply.

The basic reaction procedure remained unchanged, but earlier patents introduced several antioxidative additives, because they inhibit the formation of unwanted byproducts during the *ene*-reaction of olefin and MAA. Mäkipäura et al. (1997) proposed the application of benzoquinone, hydroquinone, dialkylsulfoxide, or acetylacetonate complexes of transition

metals in concentrations between 0.05 – 2 mol% related to the amount of MAA. In another patent, the addition of 0.2% BHT and 0.2% boric acid related to the total mass of olefin and MAA was claimed to decrease the amount of by-products (Kapanen et al. 1999). Other developments increasing quality of ASA focused on the search for additives, which reduce the force needed to emulsify it. (Schmid and Sartori 2010)

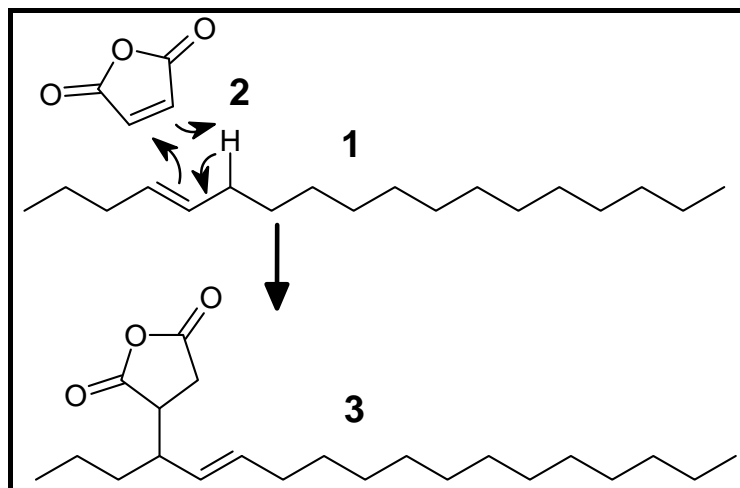


Figure 11: ASA (3) production: ene-reaction of internal olefin (1) with maleic anhydride (2) (based on Publication 1)

Besides the advantage that ASA can be used in neutral to alkaline sizing, it is also able to develop its - almost - full effectiveness (over 80%) without curing. This makes it especially attractive, when it comes to paper grades that are processed further directly after drying (e.g. surface sized). (Gess and Rende 2005) Furthermore it may be used with alum, CaCO_3 or any other pigment or filler and is not restricted to any particular pH. Although its hydrolysis rate accelerates with rising pH and temperature (Gess and Rende 2005), in conventional ASA applications, where it is emulsified on-site into cationic polymers and directly fed to the paper stock, this might not lead to considerable amounts of hydrolyzed ASA, because of the short dwell time.

Because of increasing environmental awareness and the general trend to sustainability, an alternative to petrochemically derived sizing agents like ASA would be highly desirable. Of course such new sizing agents should have a comparable efficiency with well-known ones like ASA and AKD. Some interesting developments concerning new raw materials are going on in this field and are presented in the next part.

4 The challenges of sustainable paper manufacturing

In recent years scientists came up with several alternative sizing agents that are based on renewable raw materials. The main driving force for this development is not only the higher awareness for environmental issues, but also the even higher demand for chemicals that are not based on crude oil products; as prices for crude oil are constantly rising. Expectations regarding the properties of these new compounds are big: They should provide alternatives for conventional products without lacking efficiency; furthermore their stability under papermaking conditions ought to be the same as for common products; and last but not least also the price for these products plays an important role. Products developed for use as internal sizing agents are presented below.

4.1 Green sizing agents

Substances that were found to provide hydrophobicity to paper, when used as internal sizing agents, can be divided into three groups:

- The oldest ones were developed around 1980 and comprise the use of maleated vegetable oils (Hiskens and Dudley 1979; Roth and Nevin 1980; Trzasko et al. 1988). Because they were rather viscous and lacked efficiency, when compared to ASA, in later publications the focus lay on maleated fatty acid esters (Hiskens and Dudley 1979; Quesada et al. 2003; Quesada 2003; Isogai and Morimoto 2004; Candy et al. 2005; Sundberg et al. 2006).
- As second class of new sizing agents anhydrides based on long chain fatty acids and rosin acids were discussed (Isogai 1999, Fallmann et al. 2007).
- Another substance proposed to size paper was fatty acid, which is applied like ASA (De Oliveira 2003).

4.1.1 Maleated vegetable oils and fatty acid esters

Knowing the efficiency of reactive sizing agents like ASA the applications and production procedure of more sustainable substitutes was investigated by various scientists. Conventionally olefins that are the bases for most ASAs are petrochemically derived. They are reacted with maleic anhydride (MAA) using an *ene*-reaction mechanism. To receive a sizing agent with comparable sizing features the maleation of fatty oils or fatty acid esters is one proposed strategy.

4.1.1.1 Sizing agent emulsion with maleated oils and special emulsifiers

In a Canadian patent (Roth and Nevin 1980) a method for emulsion preparation using trialkylamines (alkyl moiety is methyl or ethyl) or ammonium hydroxide as emulsifiers and any kind of sizing agent, from ASA and AKD to maleated fatty acid ester and maleated vegetable oil, in water is claimed.

Their preferred sizing agent is maleated vegetable oil derived from soy beans. But other vegetable oils with highly unsaturated fatty acids are also claimed, like cotton seed, corn, safflower, linseed, peanut, hempseed, oiticica, and dehydrated castor oil. Fish oil is said to be another alternative. The oils are maleated under nitrogen atmosphere at around 200-230°C for 20-40 min using a ratio of maleic anhydride to triglyceride of 0.9-2.

For emulsion preparation the emulsifier is first dispersed in the sizing agent and this blend is then added to water while stirring with a propeller mixer. This sizing agent emulsion can be used with the common additives present in the wet end of the paper machine: alum, aluminum chloride, cationic starch, and synthetic polymers and the like. The tested ratios of the sizing agent per dry weight of pulp were 5-15 kg/t for a pulp with a pH of 6.5.

The tested ratios are comparable to the ones used in rosin sizing, thus it might be hard to implement such a sizing system at a paper mill. Having a reactive group like the succinic anhydride group present in the size, emulsions can only be prepared on site, like it is standard for ASA applications. This means the size would have to compete against the much more efficient ASA, which provides sufficient sizing at dosage levels of around 1 kg/t; depending on the paper grade and demanded sizing level.

4.1.1.2 Sizing with maleated oils and oleic acid esters

Other scientists (Hiskens and Dudley 1979) patented similar sizing agents which comprise the use of tung, linseed, olive, castor oil, or oleic acid esters (methyl-, ethyl-, propyl-, butyl-, pentyl-, hexyl-, heptyl-, and octyl-) that are reacted with MAA at 200-240°C and 30-60 psi under nitrogen atmosphere, for several hours. The used ratios MAA per fatty acid ester or oil component vary between 0.3:1 and 2:1. To limit polymeric by-products polymerization inhibitors can be added during reaction. Residual MAA present after the reaction can be removed by distillation.

The products were emulsified in cationic starch and were tested in surface and internal sizing. Good internal sizing properties were found for maleated methyl oleate (Cobb₆₀: 28 g/m² at 4 kg/t), maleated tung oil (Cobb₆₀: ~30 g/m² at 2 kg/t), maleated isooctyl oleate (Cobb₆₀: 29 g/m² at 4 kg/t), and maleated octyl oleate (Cobb₆₀: 32.5 g/m² at 2 kg/t). In surface sizing some sizing was provided to the test sheets, but for various maleated alkyl oleates the

sizing efficiency improved with decreasing amounts of sizing agent. This was explained with the contents of surface active substances present as by-products.

The developed sizing agents seem to be very useful for internal paper sizing although they might lack some efficiency compared to conventional ASA which will provide sufficient sizing at dosage levels of around 1 kg/t.

4.1.1.3 Production of fatty acid methyl ester based ASA

As an inexpensive raw material for a new kind of ASA, different fatty acid methyl esters (FAMES) were investigated (Quesada et al. 2003; Quesada 2003). Especially interesting are the natural FAME mixtures gained after transesterification of rapeseed (RSO), sunflower (SO), or oleic motif enriched sunflower oil (SOHO). The production procedure of maleated FAME was investigated with the goal finding the optimum settings regarding temperature, reaction time, and the ratio of MAA per olefin compound. Therefore a second-order Doehlert uniform network design was used observing their influences on yield, by-products, color, viscosity, and residual amount of MAA.

The best working production procedure for maleated SOHO-FAMES to obtain a maximum yield (95%) was using a 1.5:1 ratio MAA per FAME and 235°C during 8 h under nitrogen. For an improved low content of polymeric by-products (<1.5%) and a low viscous end product the optimum setting was: a 0.8:1 molar ratio, 220-230°C during 8 h under nitrogen, which resulted in a yield of 35-60%. The same settings can be used for conventional SO, although viscosity will be higher and the color a little darker. The reason for this is the higher content of polyunsaturated fatty acids present in SO compared to SOHO. (Quesada et al. 2003)

One optimized set of reaction parameters for RSO based maleated FAMES to gain maximum yield (78%) were using a molar ratio of 1.5 (MAA per fatty acid methyl ester), 210-220°C during 8 h under nitrogen. Thereby 6% of by-products are produced and 16% of residual MAA were found in the product. If the most important characteristics of the new ASA are a low content of by-products (<1.5%) and residual MAA (<15%), it was best to use following reaction parameters: a 0.85:1 ratio MAA per FAME and 220°C during 8 h under nitrogen to gain ASA with a yield between 30 and 40%. (Quesada 2003)

4.1.1.4 Use of solvent in production of FAME based ASA

Based on two earlier studies (Quesada et al. 2003; Quesada 2003) the reaction conditions for the production of ASA from SOHO-FAMES were adjusted for a 50% xylene medium (Candy et al. 2005) using a pressure batch reactor. Through altering molar ratio of MAA per FAME, temperature, and reaction time the optimum reaction conditions concerning yield,

methyl oleate conversion, unwanted by-products, viscosity, and optical appearance were adjusted.

Conducting the synthesis in a solvent reduced the amount of polymeric by-products, but increased the demanded ratio of MAA per FAME and the needed temperature. Furthermore the solvent has to be removed through distillation afterwards. It was shown that for limiting the reversion of the *ene*-reaction it is necessary to keep temperature below 250°. The optimized reaction parameters to gain a maximum yield of 55% FAME based ASA were 220-235°C, 1.2-1.35:1 ratio of MAA per FAME, a reaction time of 8-10 h and the use of nitrogen atmosphere.

4.1.1.5 Sizing efficiency and hydrolytic stability of fatty acid ester based ASA

Practical application properties of four different alkyl oleate succinic anhydrides were investigated in a study conducted by Isogai and Morimoto (2004). The selected alkyl groups were methyl, ethyl, propyl, and butyl. These ASA substitutes were used in unfilled hand sheet making after emulsifying them in cationic starch; as it is standard for commercial ASA applications. While the sizing level of ASA was almost reached with ethyl oleate succinic anhydride, the other alkyl oleate succinic anhydrides lacked efficiency. In a second step conventional ASA and ethyl oleate succinic anhydride were compared for their sizing efficiency in hand sheets filled with 20% PCC. There ethyl oleate succinic anhydride provided the sheets with a higher sizing level than ASA, when used at the same dosage. The authors concluded, that ethyl oleate succinic anhydride must have higher stability the under alkaline conditions of filled paper making (pH 8.3) than conventional ASA. So they investigated hydrolytic stability of ethyl oleate succinic anhydride and conventional ASA and found that the first mentioned was considerably more resistant to hydrolysis than ASA, especially at higher pH (pH 9).

4.1.1.6 Paper sizing with FAME based ASA

This invention (Sundberg et al. 2006) describes the production and application of a reaction product of MAA and mixtures of FAMEs. The used fatty acids are natural mixtures originating from rapeseed, soybean, linseed, and sunflower oil with the limitation that monounsaturated fatty acids are at least present to 50% and poly-unsaturated or saturated ones are only present in minor amounts. Synthesis of this product used in paper sizing is carried out at 210-220°C, where MAA reacts with unsaturated FAMEs in an *ene*-reaction. To hinder formation of polymeric by-products it is suggested to use radical inhibitors and nitrogen atmosphere during synthesis. Another way to limit polymerization and keeping viscosity in a certain range is using oil sources with only monounsaturated fatty acids. This can be

accomplished by using the right vegetable oil source e.g. a special breed of sunflower oil (SOHO) or by partially hardening (hydrogenation).

The maleated FAMEs is used as an internal sizing agent after dispersion in water or polymer solution (e.g. starch). Conventional emulsifiers can be used to adjust particle size; they are added to the sizing agent in the range of 0.5-2%. In a test series the invented sizing agent was tested in comparison to ASA and two interesting effects were shown: Addition of alum ($\text{Al}_2(\text{SO}_4)_3$) improved sizing performance significantly, and Cobb_{60} values were lower (better), when the sizing agent was allowed to react with the fiber suspension for 2 min before sheet formation. Thus following Cobb_{60} values were obtained at a size dosage of 1.5 kg/t: maleated FAME (without alum, or waiting for 2 min before sheet formation): 205 g/m^2 ; maleated FAME (with alum, but without waiting for 2 min before sheet formation): 29.5 g/m^2 ; maleated FAME (with alum, and waiting for 2 min before sheet formation): 19.9 g/m^2 ; ASA (with alum, and waiting for 2 min before sheet formation): 20.2 g/m^2 .

In further studies hydrogen peroxide and lactic acid resistance were investigated. Here the new sizing agent lacked efficiency compared to conventional ASA, although the difference in the hydrogen peroxide test was smaller than in the lactic acid test.

4.1.2 Fatty acid anhydrides

Another proposal for new paper sizing agents was to use liquid fatty acid anhydrides (FAAs) derived from mixtures of saturated and unsaturated fatty acids with a chain length from C_{12} to C_{24} (Fallmann et al. 2007). Possible raw materials are tall oil fatty acids, rosin acids, and fatty acids derived from vegetable oils like sunflower, rapeseed, soybean, or linseed oil. FAA is formed after reaction of the fatty acids with acetic acid anhydride at 120°C for 5 hours. Formed acetic acid is removed through distillation afterwards.

In internal sizing the invented compounds are used as emulsions in cationic starch hereby the paper may contain filler like CaCO_3 . Furthermore it was shown that the addition of aluminum compounds like alum or poly aluminum chloride (PAC) are beneficial for its sizing efficiency. Thus sizing ($\text{Cobb}_{60} \sim 30 \text{ g/m}^2$) was possible with as low amounts as 0.7-0.9 kg/t.

The formed sizing agent is not only based on renewable raw materials, which may be derived from pulping by-products like tall oil, but also had beneficial effects on the runability of paper machines: No sticky deposits were found in calcium rich aqueous environments as sometimes is the case with ASA.

In a study conducted by Isogai (1999) fatty acid anhydrides (FAA) based on palmitic and stearic acid whose carboxyl carbon atoms were labeled with ^{13}C were produced and their binding behavior was investigated. These FAAs were emulsified in cationic starch and used for internal paper sizing with or without PAE as retention aid. Measureable sizing degrees

(24 s), expressed as Stöckigt sizing degrees, were found for FAA at an addition level of 3.2 kg/t, but only after heat treatment of the finished sheet. For ASA sizing degrees over 20 s are possible at a dosage of 1.5 kg/t.

Analysis of FAA sized sheets with pyrolysis-GC showed that about 15% FAA were present in the hand sheet, whereas the rest is hydrolyzed to the corresponding fatty acids. Solid state ^{13}C -NMR spectra were used to investigate the possibility of FAA to form covalent bonds during sheet formation: While in sheets with 8 kg/t FAA without PAE no such bonds were found, they were detected for sheets with PAE and 1.6 and 3.2 kg/t FAA. It is believed, that the formed esters are ester bonds between FAA and the azetidinium groups of PAE, which do not contribute to sizing.

4.1.3 Fatty acids

In the patent literature also fatty acids were claimed as sizing agents. De Oliveira (2003) used pure fatty acids in an internal sizing emulsion. His sizing agent is prepared using the natural fatty acid mix derived from soy bean oil by blending it with starch solution (5% solids), alum, and water for 20 min at 35°C at maximum velocity in an “emulsifier container”.

4.2 Main challenges for the production of green sizing agents

To be able to synthesize a reactive sizing agent from native vegetable oils or their fatty acid alkyl esters and maleic anhydride of course only fatty acid residues that are unsaturated may react according to the *ene*-reaction mechanism. Thus Roth and Nevin (1980) concluded that it was best to use oils which have high amounts of polyunsaturated fatty acid residues. When examining the possible use of maleated vegetable oils for paper sizing during the work on my thesis I made the experience that the use of oils rich in polyunsaturated fatty acids was detrimental to product quality. Whereas the use of oils with low contents of polyunsaturated fatty acids (especially rapeseed, and high oleic sunflower oil) resulted in products having a lower viscosity, contained less polymeric by-products, and were more effective in paper sizing (Publication 1). This is in good correlation with other studies also proposing the use of oils, or their fatty acid alkyl esters, that have a low content of polyunsaturated fatty acids, but a high content of monounsaturated ones, especially oleic acid residues (Hiskens and Dudley 1979; Quesada et al. 2003; Quesada 2003; Candy et al. 2005; Sundberg et al. 2006).

The most prominent oils and the amount of their most important fatty acids are listed in Table 6. Linseed and soybean oil have rather high amounts of polyunsaturated fatty acids like linoleic or linolenic acid, and according to the more recent studies are not so well suited for the production of paper sizing agents. Whereas rapeseed and especially high oleic sunflower oil are well suited for this purpose as they contain more than 50% oleic acid and only minor amounts of polyunsaturated fatty acids.

Table 6: Important fatty acids of selected vegetable oils (based on Publication 1)

Oil	Fatty acid distribution %				
	16:0	18:0	18:1	18:2	18:3
Linseed	6	4	18	16	54
Soybean	10	4	23	56	4
Rapeseed	4	2	56	21	6
Sunflower (high oleic)	3	2	72	10	0

16:0 Palmitic acid, 18:0 Stearic acid, 18:1 Oleic acid, 18:2 Linoleic acid; 18:3 Linolenic acid

For the use of maleated alkyl esters there are several proposals how to tune reaction parameters to gain a product most suitable for paper sizing. Although in some studies good sizing results were obtained (Hiskens and Dudley 1979; Sundberg et al. 2006), they do not fully reach the efficiency of conventional ASA. Here Isogai and Morimoto (2004) came up with other arguments to promote these new vegetable based sizing agents: They proved that

maleated ethyl oleate was more stable against hydrolysis than conventional ASA. Thus a sizing agent emulsion containing maleated ethyl oleate has a prolonged life time compared to a conventional ASA emulsion, which is an important application feature.

For FAA the situation is quite similar: Although the efficiency of ASA was not fully reached with the use of pure FAA as internal sizing agent, there are some beneficial properties that are superior to ASA. First of all the used raw materials can be derived from tall oil which is a pulping by-product. Secondly observations were made that FAA-use does not lead to deposit formation in hard water cycles as sometimes occurs when using ASA.

5 Summary and conclusions

As it was presented within the papers published during the work on this thesis it is possible to size paper with maleated vegetable oils derived from linseed, soybean, rapeseed, and a special breed of sunflower oil. These products are promising substitutes for conventional olefin-based ASA sizing agents, because the starting plant oils are renewable raw materials with reduced logistic efforts and transportation costs. Moreover these green sizing agents can be produced in a one-step synthesis, whereas conventional ASA production at least comprises one more additional step, the isomerization of α -olefin, before conducting the maleation step.

Nonetheless some of the vegetable oils tested are less qualified for the intended purpose; for example those with high amounts of polyunsaturated fatty acid residues (linseed or soybean oil). They tend to give overly viscous products when maleated, because the polyunsaturated fatty acid residues preferably react with MAA and form polymeric by-products. The case of soybean oil maleated with the threefold amount of MAA per triglyceride (Figure 12) is a particularly illustrative example for the higher reactivity of multiple unsaturated acids in the maleation: while the oleic acid part remained unchanged, about 80% of the double unsaturated acids (linoleic-) reacted, and the triple unsaturated acids (linolenic-) were even completely converted (100%). The percentages in Figure 12 represent the amount of fatty acid residues that were modified with MAA related to the amount of the respective starting fatty acid residue in the unmodified vegetable oil.

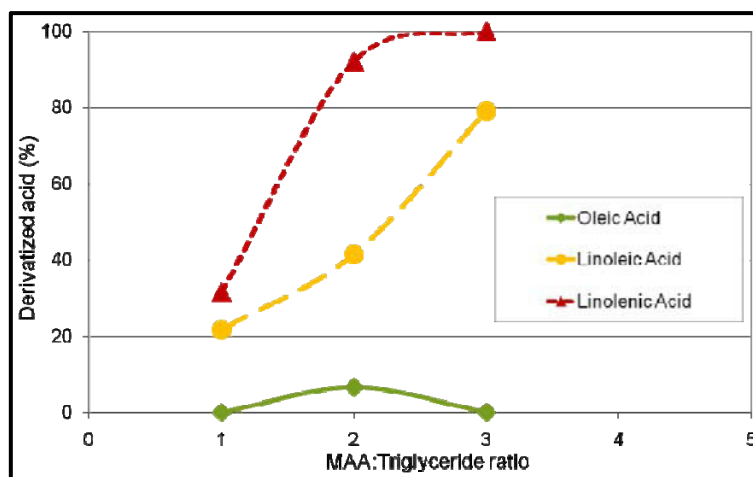


Figure 12: Preferential maleation of polyunsaturated fatty acids in maleated soybean oil (GC analysis after transesterification into the fatty acid methyl esters (based on Publication 1))

Most promising results were obtained for oils with a high content of monounsaturated fatty acids (oleic-). Rapeseed oil (RSO) and in particular high-oleic sunflower oil (SOHO) were

preferred raw materials for the new sizing agents. They are less likely to form polymeric by-products during the maleation step, and a higher yield of maleated triglycerides can be reached. To further limit unwanted polymer formation and maximize yield of the maleated product, the maleation procedure was thoroughly optimized: the reaction was carried out at 200°C under inert gas pressure (3.3 bar) for 6 h, a mixture of BHT and BHA (0.02%) was added as stabilizer, and the MAA-to-triglyceride ratio was set to 4:1.

In Table 7 some important analytical characteristics of SOHO raw material and two maleated SOHOs (MSOHOs) are listed. While MSOHO 2:1 was produced using a conventional setting, for MSOHO 4:1 the optimized reaction parameters were used. Reacting SOHO with the double amount of MAA gave a product in which 20% of unchanged oil remained. At a 4:1 ratio of MAA per triglyceride, the amount of residual oil in MSOHO was reduced to about 10% (Table 7). This higher MAA-to-triglyceride ratio also resulted in an increased viscosity of the product, even though the amount of polymers was lower. It can be assumed that this behavior is due to higher viscosity of the polar succinic anhydride moieties in the modified triglycerides.

Table 7: Analysis results for different maleated oils (based on Publication 1)

Oil resp. MAA:Triglyc. ratio ^a	Residual oil by		R ^b	Viscosity (mPas)	Polymers by GPC (%)
	HPLC (%)	GC (%)			
SOHO	100	99	-	78	0.1
MSOHO 2:1	15	20	1.1	2085	14.2
MSOHO 4:1 ^c	7	10	1.4	5775	8.8

^a Numbers are the ratio between maleic anhydride and triglyceride during *ene*-reaction.

^b R, maleic anhydride-to-triglyceride ratio in the product, calculated from soap numbers.

^c produced using the optimized setting.

Using various analytical methods including attenuated total reflection infrared spectroscopy, ¹H and ¹³C nuclear magnetic resonance spectroscopy with full resonance assignment, and mass spectrometry the MSOHO sizing agent was comprehensively analyzed. Thus the *ene*-reaction mechanism with the conversion of the natural occurring *cis* double bonds in vegetable oils into *trans*-configuration after maleation was confirmed (Figure 13). In a related study using ozonolysis and the characterization of the gained fragments with pyrolysis gas chromatography - mass spectrometry it was found that there is no apparent selectivity for the placement of the double bond on the fatty acid residues after maleation (Publication 5).

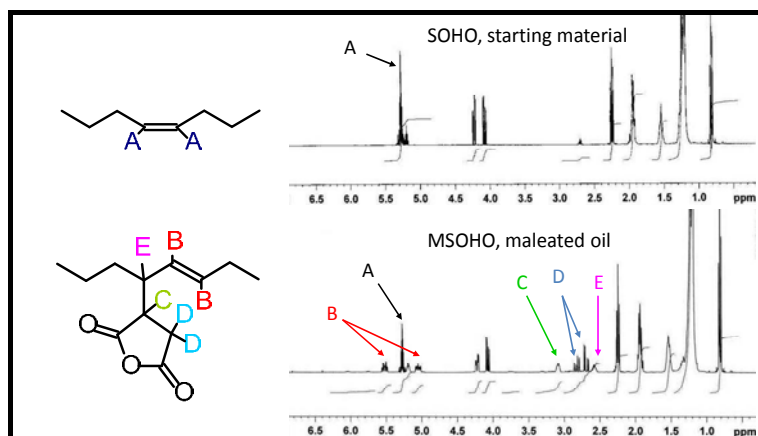


Figure 13: ^1H NMR spectra (400 MHz, CDCl_3) of high oleic sunflower oil (SOHO, starting material for maleation) and MSOHO (maleated product) (based on Publication 2)

The new, renewables-based sizing agent also has a succinic anhydride moiety as reactive group, similar to conventional ASA sizes. In general, it will also be affected by the same hydrolysis mechanisms as ASA. This could be confirmed conducting hydrolysis of the pure sizing agents in organic solvent (THF), excluding any viscosity and diffusion effects. The observed first order reaction rates, that were almost the same for ASA and MSOHO, are governed by the reactive group (succinic anhydride) only. If the sizing agents are used according their application they are added to the paper stock as aqueous emulsions. Therefore hydrolytic stability of ASA and MSOHO was also tested as emulsions in cationic starch. Zero-order rate laws were found, pointing out, that these hydrolysis rates are only influenced by diffusion of water into emulsion droplets. Conducting hydrolysis in its emulsion state MSOHO was considerably more stable than ASA, especially under conditions where a high Ca^{2+} ion concentration was present.

An improved hydrolytic stability for MSOHO was also confirmed in a sizing test, where it was possible to size hand sheets with MSOHO emulsions that were stored at 25°C for 30 h, whereas the ASA emulsion treated in the same way could not provide any water repellency to hand sheets (Figure 14).

In a sizing test where blends with increasing amounts of MSOHO and a commercial ASA type were tested against pure ASA almost no difference in efficiency was observed (Figure 15). The used pulp was a standard Kraft pulp (30% short fiber and 70% long fiber) containing 1% fibers and 0.25% ground calcium carbonate (GCC). As additives for sizing and sheet formation a retention aid and alum were added.

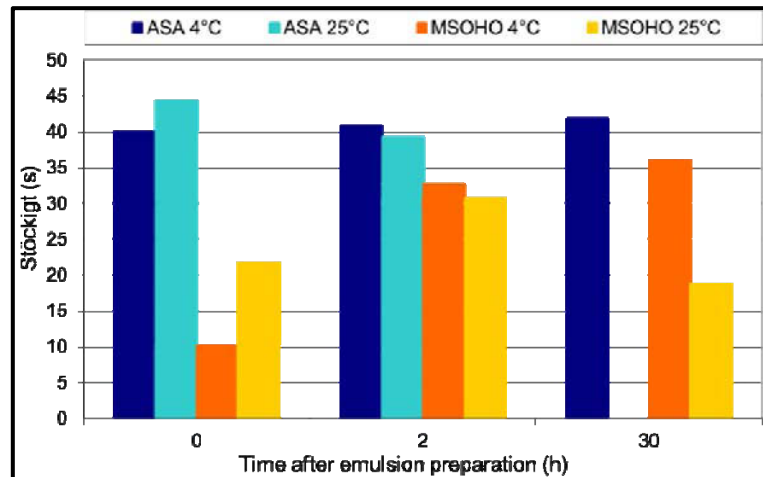


Figure 14: Development of the sizing efficiency of ASA and MSOHO emulsions stored at 4°C and 25°C with time (based on Publication 3)

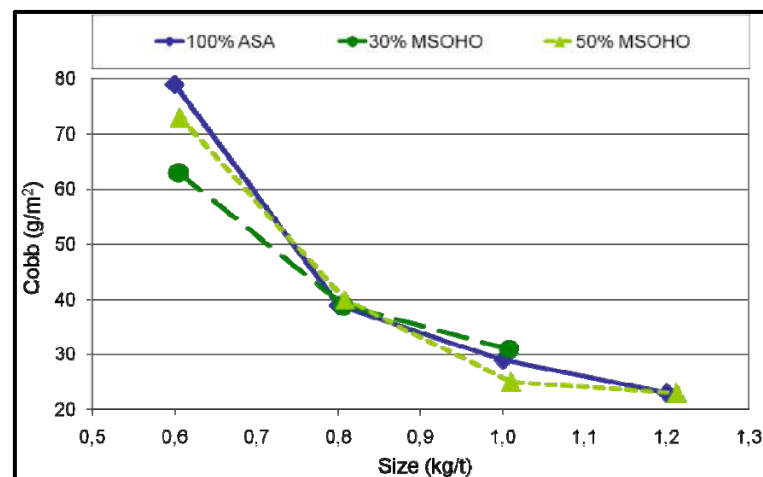


Figure 15: Sizing efficiency of MSOHO - ASA blends compared to pure ASA. (based on Publication 6)

One outstanding characteristic of MSOHO in comparison to ASA is its high viscosity. Common ASA has a viscosity from 100 to 250 mPas, while for MSOHO it can be considerably higher (Table 7). While the high viscosity positively influences the stability of MSOHO in an aqueous environment (hydrolytic stability), it is detrimental to sizing, because it makes spreading on cellulose fibers more difficult. A very convenient way was invented to overcome this problem: Another green sizing chemical with a very low viscosity (FAA) can be blended into MSOHO. The gained mixtures exhibited an unexpected synergistic effect in terms of sizing efficiency and ASA sizing efficiency could almost be reached (Figure 16).

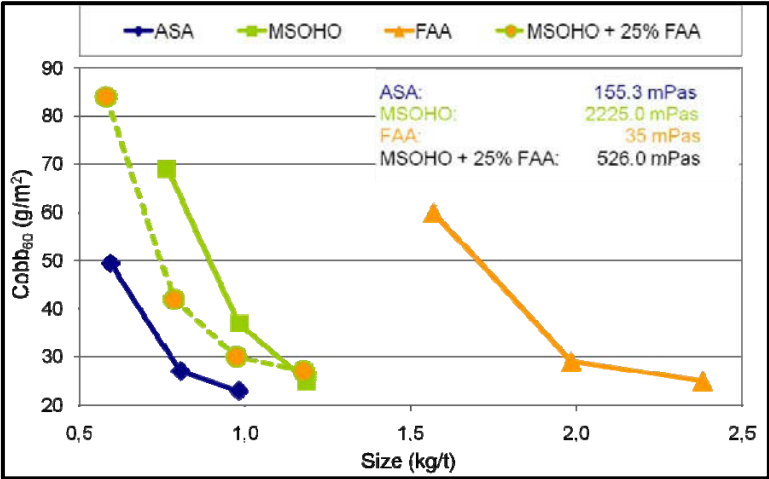


Figure 16: Sizing efficiency of ASA, MSOHO, FAA, and an MSOHO - FAA blend (based on Publication 6)

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9 Abbreviations

AD	Anno Domini, “in the year of lord”
AGU	anhydro glucose unit
AKD	alkyl ketene dimer
APTAC	acrylamido propyl trimethyl ammonium chloride
ASA	alkenyl succinic anhydride
B.C.	before Christ
BHA	butylated hydroxyanisole
BHT	butylated hydroxytoluene
BOKU	short for: University of Natural Resources and Life Sciences, Vienna
chem. pulp	chemical pulp
CMC	carboxy methyl cellulose
DIN	Deutsches Institut für Normung, standards registered by the German Institute for Standardization
DMAEA-PAM	dimethyl aminoethyl acrylate polyacrylamide
DMAEAqMeCl	dimethyl aminoethyl acrylate quaternized with methyl chloride
ECF	elemental chlorine free
FAA	fatty acid anhydride
FAME	fatty acid methyl ester
GC	gas chromatography
GCC	ground calcium carbonate
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
HST	Hercules sizing test
MAA	maleic anhydride
mech. pulp	mechanical pulp
ML	middle lamella
MRSO	maleated rapeseed oil
MSOHO	maleated high oleic sunflower oil
m.w.	molecular weight
NMR	nuclear magnetic resonance
OBA	optical brightening agent

P	primary wall
PAC	poly aluminum chloride
PAE	polyaminoamide epichlorohydrin
PAM	polyacrylamide
PCC	precipitated calcium carbonate
Poly-DADMAC	polydiallyl dimethyl ammonium chloride
PVA	polyvinyl alcohol
RSO	rapeseed oil
S ₁	secondary wall (outer layer)
S ₂	secondary wall (middle layer)
SO	sunflower oil
SOHO	high oleic sunflower oil
T	= S ₃ secondary wall (inner layer)
TCF	totally chlorine free
THF	tetrahydrofuran
W	warty layer

Publications 1-7

Publication 1

Novel paper sizing agents from renewables.

Part 1: Preparation of a paper sizing agent derived from natural plant oils

Lackinger, E.; Schmid, L.; Sartori, J.; Isogai, A.; Potthast, A.; Rosenau, T.

Published Jan 2011, Holzforschung 65, 3-11

Publication 2

Novel paper sizing agents from renewables.

Part 2: Characterization of maleated high oleic sunflower oil (MSOHO)

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Part 4: Application properties in comparison to conventional ASA sizes

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Novel paper sizing agents based on renewables.

Part 5: Characterization of maleated oleates by ozonolysis

Lackinger, E.; Sartori, J.; Potthast, A.; Rosenau T.

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Publication 6

Novel paper sizing agents based on renewables.

Part 6: Sizing properties of maleated high oleic sunflower oil

Lackinger, E.; Fallmann, J.; Sartori, J.; Potthast, A.; Rosenau T.

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Modified fatty oils in paper sizing as green alternative to conventional sizing agents based on crude oil

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Novel paper sizing agents from renewables. Part 1: Preparation of a paper sizing agent derived from natural plant oils

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Abstract

Natural oils derived from linseed, rapeseed, soybean, and a special breed of sunflower were tested for the production of maleated fatty oils for paper sizing in the *ene*-reaction with maleic anhydride. All these maleated oils were subjected to a conventional sizing test proving their ability to hydrophobize handsheets. Natural oils having only monounsaturated fatty acid residues (oleic acid) in the triglycerides worked best by having lower product viscosity and higher yields. The optimized production procedure employs antioxidant addition, an increased maleic anhydride:triglyceride ratio of 4:1, as well as increased pressure to reduce undesired polymeric byproducts and to increase yield.

Keywords: alkenyl succinic anhydride (ASA); ASA sizing; green chemistry; high oleic sunflower oil; maleated oils; paper sizing; plant oils; renewable resources.

Introduction

Sizing of paper is needed to hinder penetration of water into the sheet. This repellence improves durability and other paper characteristics such as printability (Figure 1). For this purpose, synthetic sizing agents based on petrochemicals have been applied so far, but the demand for “green” sizing agents has increased considerably. This demand was also the central impetus for our research.

For paper sizing, amphiphilic molecules are used which are able to attach to the cellulosic fiber surface with their hydrophilic, polar side, whereas their hydrophobic, apolar side is directed away from the surface and repels water and thus water penetration into the paper sheet is hindered. This process is commonly called internal sizing. Today alkenyl succinic anhydrides (ASAs) and alkyl ketene dimers (AKDs) are the most common chemicals used for this purpose in neutral to slightly alkaline paper production (Roberts 1996). Frequently, ASA is the preferred option because it is more cost-efficient and has a shorter curing time compared to AKD.

For the production of ASA, alkenes react with maleic acid anhydride (MAA) at high temperatures around 200°C in an *ene*-reaction (Figure 2a). So far, the olefin starting materials are exclusively from petrochemical sources. In many cases, olefins with terminal or near-terminal double bonds are isomerized to products with more centered double bonds before maleation. Because of increasing environmental awareness and the general trend to sustainability, an alternative to such products from petrochemistry would be highly desirable. Some interesting developments based on renewable raw materials are ongoing in this field. Pure fatty acids were used in a sizing dispersion as well as unsaturated fatty acid methyl esters that were modified with maleic anhydride (De Oliveira 2003; Isogai and Morimoto 2004; Candy et al. 2005; Sundberg et al. 2006). Another proposal focused on liquid fatty acid anhydrides derived from mixtures of saturated and unsaturated fatty acid mixtures with chain lengths from C₁₂ to C₂₄ (Fallmann et al. 2007).

Highly unsaturated vegetable oils can also be applied (such as soy bean, cotton seed, corn, safflower, linseed, or peanut oil) or fish oil with a high amount of free unsaturated fatty acids. These oils are combined (by low-shear mixing) with emulsifying agents, trialkylamines, and ammonium hydroxide as sizing agents (Roth and Nevin 1980). The high degree of unsaturation apparently caused problems in maleation due to polymerization and increased product viscosity as well as in the aging and yellowing characteristics of the products.

In the literature, some maleated oils have been described, although for purposes somewhat different from paper sizing: additives for electrodeposition of metals, components of hair care products, emulsifiers, or as components in latexes, coatings, and textile finishes (Bussell 1974; Force and Starr 1987; Höffkes et al. 2000; Aarts et al. 2005; Lange and Bartley 2005; Thames et al. 2006).

In our approach in the present series, a novel paper sizing agent was developed based on natural plant oils. Their unsat-

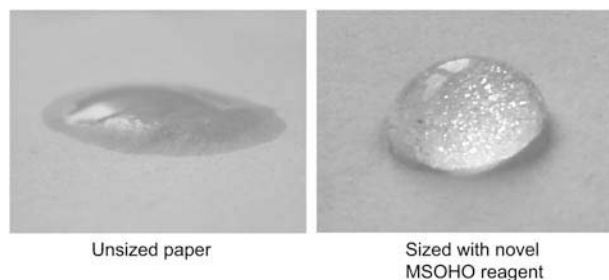


Figure 1 Effect of paper sizing.

urated fatty acids, as part of triglycerides, were the co-reacting moieties in the maleation reaction with MAA (Lackinger et al. 2009). This approach completely eliminates the use of isomerized petrol-based olefins and meets the general demand for greener products. Another driving force for developing new sizing agents was the inferior hydrolytic stability of ASA that decreases its sizing ability (Nishiyama et al. 1996). Furthermore, conventional ASA can react to calcium salts in the presence of the most common paper filler CaCO_3 and form sticky deposits which negatively affect paper production.

In the present, first part of the series, selection of the natural sources is addressed. Various analytical methods will be applied and the raw materials and production procedures will

be adjusted with regard to minimizing side reactions and unwanted byproducts. First results based on four different natural oils will be presented. The subsequent parts of the series will address detailed structural characterization, hydrolytic stability under different conditions, sizing effectiveness, an in-depth comparison to conventional sizes, and a report on practical applicability and usage.

Experimental

Materials

For handsheet production, a paper stock solution made from commercial bleached Kraft pulp with 2% dry content consisting of 30% short fiber and 70% long fiber was beaten to 30° SR (ISO 5267-1, ISO standard 1999). The standard stock solution was prepared diluting the 2% paper stock solution to 1% dry content; the solution contained 1% fibers and 0.25% ground calcium carbonate.

Samples of the new sizing agent were produced from fatty oils: linseed, rapeseed, soybean, and high oleic sunflower oil (SOHO) from C. Thywissen GmbH, Germany, and maleic anhydride (MAA) of synthesis grade from Merck, Germany. The abbreviations MLSO, MRSO, MSBO, and MSOHO are used for maleated linseed, rapeseed, soybean, and high oleic sunflower oil, respectively.

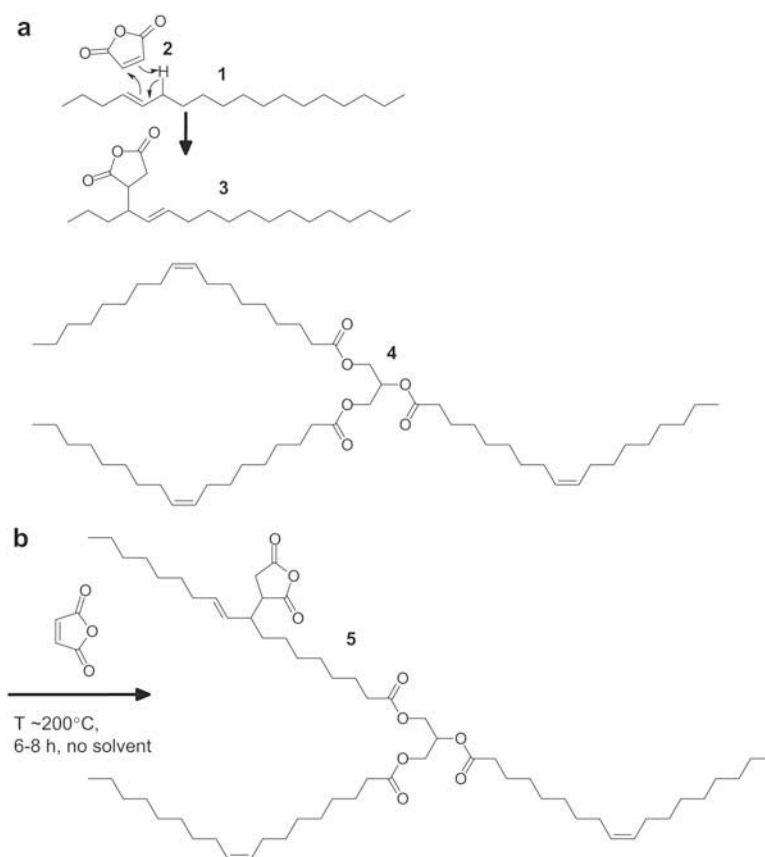


Figure 2 (a) Conventional ASA (3) production: *ene*-reaction of internal olefin (1) with maleic anhydride (2). (b) Production of maleated vegetable oil (5): monomaleation of glycerin trioleate (4) with maleic anhydride (2).

The following antioxidants were tested during production of the maleated oils: Anox 330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-4-hydroxybenzyl)benzene, Great Lakes Manufacturing Italy S.r.l., Italy; butylated hydroxytoluene (BHT, di-*tert*-butyl-hydroxy-toluene), purity >99%, Sigma Aldrich, Austria; butylated hydroxyanisole (BHA, *tert*-butyl-hydroxy-anisole), food grade, Eastman Chemical Company, USA; and vitamin E acetate (α -tocopheryl acetate), 98%, Haupt Chemicals Trading GmbH, Austria. Cationic starch (HICAT 5103A, 4%), Roquette Co., France, was used for emulsion preparation.

Chemicals for characterization of the new sizing agents included veratrylamine (3,4-dimethoxybenzylamine) 97%, borontrifluoride-methanol complex (50 wt%), hexatriacontane, 1,2,3-trilinoleoyl glycerin (purum), glycerin trioleate (puriss.) from Sigma-Aldrich, Austria, margoric acid (heptadecanoic acid), puriss., from Fluka Chemie GmbH, Austria, and ortho-phosphoric acid (p.a.) from Merck, Germany.

Acetonitrile, toluene, tetrahydrofuran, and methanol (all HPLC grade) were purchased from Fisher Scientific GmbH, Austria. Ethanol (abs.) and n-pentane (analytical reagent) were purchased from VWR, Austria, and acetone (techn.) from Brenntag CEE GmbH, Austria.

Working procedure for the preparation of maleated natural oils Vegetable oil (150 g, 0.17 mol) was charged into a reactor in an inert gas atmosphere and then heated to 180–220°C under stirring. MAA was added in one step, the amount of the anhydride was varied between 16.61 and 66.45 g (0.17–0.68 mol). The reaction was performed under inert gas at a pressure of 1.0–3.3 bar for 6–8 h. The reaction mixture was cooled to r.t., the pressure was released, and excess MAA was distilled off at a reduced pressure of 10 mbar at 120–140°C. The general reaction of this process is shown in Figure 2b. Antioxidants can be added in the range of 0.01–0.4 wt% related to weight of the reaction mixture.

Preparation of handsheets Paper handsheets were formed on a Rapid-Köthen sheet former (Type G8-E, Gockel & Co. GmbH, Germany) from ground cellulose (standard stock solution). In a first step, 1% of the tested sizing agent was emulsified in a carrier polymer solution (4% cationic starch in water) with an Ultra Turrax homogenizer (IKA Werke GmbH & Co. KG, Germany) for 1 min at 10 000 rpm and r.t. This emulsion was diluted 1:10 with deionized water and used within 15 min. The respective amounts of this sizing dilution were added to approximately 190 g standard stock solution to form sheets with a basis weight of 70 g m⁻².

The freshly prepared sheet was dried in the drum dryer at 115°C at a speed of approximately 1 turn/40 s. The air-conditioned sheet was then used for further analysis (*Cobb*₆₀ tests).

Instrumental analysis

Gel permeation chromatography (GPC) Substances with high molecular weight, such as polymeric material

formed during maleation of natural oils, were separated and analyzed on a GPC system of the following setup: autosampler AS-2000, interface D-6000, pump L-2600 (all three Hitachi High Technologies Corporation, Tokyo, Japan), degasser DG-2410 (Degasys, Uniflows Co. Ltd., Tokyo, Japan), column oven (Jetstream 2 Plus) held at 40°C, refractive index (RI) detector (RI 2414, Waters Corp.), and a set of four columns (250 mm×7 mm×5 μ m, Hibar, Merck, Germany) packed with divinylbenzene-crosslinked polystyrene (PS 20/PS 4/PS 1/PS 1). Eluant: tetrahydrofuran (THF).

***Cobb*₆₀ test (DIN 53 132, DIN standard 1990)** The *Cobb*₆₀ value, an expression of the water absorption over the time period of 60 s given in g m⁻², is calculated according to Eq. (1):

$$Cobb_{60} [g\ m^{-2}] = \frac{(m_2 - m_1)[g]}{0.01[m^2]} \quad (1)$$

where m_1 is mass of the sample before *Cobb*₆₀ determination [g]; m_2 is mass of the sample after *Cobb*₆₀ determination [g].

Gas chromatographic analysis of fatty acid methyl esters To find a relationship between the fatty acid composition of the vegetable oils and the sizing efficiency of the corresponding maleated products, the starting oils and the maleated product oils were transesterified into the corresponding methyl esters by treatment with BF₃-methanol complex. Afterwards, the fatty acid methyl esters are extracted with pentane. Then, 1 μ l of the pentane solution was injected for gas chromatography (GC) (Thermo Electron Corporation instrument, Italy, with FID detection). GC setup: DB-1 column (100% dimethyl polysiloxane, J&W Scientific, USA), H₂ as carrier gas, autosampler AS 3000 (Thermo Electron Corporation, Italy), split flow 150 ml min⁻¹, temperature program 170°C to 215°C at 2°C min⁻¹, further to 245°C at 4°C min⁻¹, and to 300°C with 15°C min⁻¹ with a hold time of 5 min.

Viscosity The viscosity was determined on a rota-viscosimeter (Rheometer MC1, Anton Paar GmbH, Austria) at 20°C and a shear rate of 50 s⁻¹.

Quantification of unmodified oil in the maleated product

Gas chromatography (GC) Focus instruments (Thermo Electron Corp.) with autosampler and FID detection as described above. Thermo TR5 column (5% phenyl/methyl polysiloxane column, Thermo Electron Corporation, Italy) with H₂ as the carrier gas at a split flow of 400 ml min⁻¹. Temperature program: 200°C, ramped to 350°C at 20°C min⁻¹, and a final hold time of 5 min. Injected volume: 1 μ l. For sample preparation, hexatriacontane (20 mg, internal standard) and either 70 mg of unmodified oil or 250 mg of maleated oil were dissolved in toluene (7 ml). Then, 1 ml of

this solution was put into the autosampler vial and subjected to GC analysis. The amount of unchanged triglycerides in the sample was quantified by comparison of the triglyceride peak area with that of the internal standard.

High performance liquid chromatography (HPLC)

HPLC separation was carried out on a system consisting of an L-2130 quaternary-gradient-pump, autosampler L-2200, refractive index detector L-2490, UV detector L-4250 at 215 nm (Hitachi High Technologies Corporation, Tokyo, Japan) and degasser DG-2410 (Degasys, Uniflows Co., Ltd., Tokyo, Japan). The triglycerides were separated on a Supelcosil C₈ column (Supelcosil LC-8 58297, 25 cm × 4.6 mm, ID 5 µm, Supelco, USA) with the ternary eluant acetonitrile/ethanol/deionized water (v/v/v = 56:38:6) in an isocratic mode, at a flow rate of 1.5 ml min⁻¹. For sample preparation, either 400 mg of unmodified oil or 1 g of maleated oil were weighed into a 10 ml volumetric flask which was filled up with acetone. Then, 1 ml of this solution was transferred into the autosampler vial; the injection volume was 20 µl.

The method was calibrated with rapeseed oil as triglyceride standard (eight dilutions in acetone in the range from 4.6 to 60 mg ml⁻¹, and a pure acetone sample) with all runs in triplicate. The standard deviation for the triglyceride content was 0.17% (*n* = 3). Pure glycerin trilinoleate and glycerin trioleate were measured as retention time markers for calculation of limit of detection (LOD) and of limit of quantification (LOQ) of these triglycerides. The peak assignment with regard to possible fatty acid distribution (double bond distribution) is given in Table 1, the calculated LOD and LOQ values are presented in Table 2.

Table 1 Assignment of HPLC peaks of fatty oils.

RT (min)	No. of DBE	Possible fatty acids composition per triglyceride ^a
5.8	9	3×CXX:3
6.8	8	2×CXX:3+1×CXX:2
8.2	7	1×CXX:3+2×CXX:2 2×CXX:3+1×CXX:1
10.0	6	2×CXX:3+1×CXX:0 1×CXX:3+1×CXX:2+1×CXX:1 3×CXX:2
12.9	5	1×CXX:3+2×CXX:1 1×CXX:3+1×CXX:2+1×CXX:0 2×CXX:2+1×CXX:1
16.7	4	2×CXX:2+1×CXX:0 1×CXX:3+1×CXX:1+1×CXX:0 1×CXX:2+2×CXX:1
22.2	3	1×CXX:3+2×CXX:0 1×CXX:2+1×CXX:1+1×CXX:0 3×CXX:1
26.1	2	1×CXX:2+2×CXX:0 2×CXX:1+1×CXX:0

^aCXX:n corresponds to the conventional nomenclature of fatty acids: XX denotes the number of C-atoms in the chains (most probably 16 or 18), the number behind denotes the number of double bonds.

RT, retention time; No. DBE, number of double bond equivalents.

Table 2 HPLC method parameters of standard triglycerides.

Oil	LOD (mg ml ⁻¹)	LOQ (mg ml ⁻¹)
1,2,3-trilinoleoyl glycerin	0.10	0.33
Glycerin-trioleate	0.15	0.49

LOD, limit of detection; LOQ, limit of quantification.

Wet-chemical analysis of the maleated products

Soap number (ASTM D464-95, ASTM standard 1996)

Soap numbers were determined. From these values, the amount of MAA equivalents on the triglycerides was calculated according to Eq. (2), using the approximation of 885.5 g mol⁻¹ for the molecular weight of the oils and thus the assumption that the oil consisted solely of glycerin trioleate:

$$R = \frac{MW_{(Oil)}}{\left(\frac{2000 \times MW_{(KOH)}}{(SN_{(Maleated_Oil)} - SN_{(Oil)})} - MW_{(MAA)} \right)} \quad (2)$$

where $MW_{(Oil)}$ is 885.5 g mol⁻¹ (with the above assumption); $MW_{(KOH)}$ is 56.1 g mol⁻¹; $MW_{(MAA)}$ is 98.1 g mol⁻¹; SN is mg KOH per g of sample.

Iodine number (DIN 53 241-1, DIN standard 1995)

Iodine number denotes the amount of iodine [g] that is consumed per 100 g of sample by addition to the double bonds, thus being an indicator of unsaturation (amount of double bond equivalents) in a fatty acid or triglyceride.

Fatty acid methyl esters Vegetable oil or maleated oil (100 mg) and margaric acid (20 mg, internal standard) were dissolved in THF (1 ml) in a 10 ml vial. The methylation agent [3 ml, consisting of 35% BF₃-methanol complex (1:1), 35% MeOH, and 30% toluene] was added and the mixture was mixed vigorously. After stirring the closed vial it is stored at 105°C for 40 min. Then it is cooled to r.t., 2 ml of deionized water and 2 ml of pentane were added, and the mixture was stirred for 1 min. After phase separation, 1 ml of the organic (upper) phase was transferred into a GC autosampler vial and analyzed with the gas chromatographic method for analysis of fatty acid methyl esters described above.

Results and discussion

Selection of the raw material and maleation procedure

A wide range of plant oil raw materials were screened with regard to their fatty acid composition, their ability to be maleated according to procedures generally used in ASA production, and their suitability as sizing agents and thus as ASA substitutes. The most suitable candidates were: linseed oil (LSO), soybean oil (SBO), rapeseed oil (RSO), and high

oleic sunflower oil (SOHO). The latter is a special breed of sunflower, containing more than 80% oleic acid.

Analysis of the triglycerides is possible by either GC or HPLC. By GC, separation of triglycerides is performed at 350°C (Rezanka and Rezanková 1999). A big drawback of this method is the high temperature, as only special GC instruments and columns can be used. More gentle conditions are afforded by HPLC with different detection modes, which can be UV detection at wavelengths of 220 nm or lower, or mass-sensitive detection (Shukla et al. 1983; Kumagai 2006). Reversed-phase HPLC with C₁₈-columns in combination with differential refractive index (DRI) detection and an acetone/acetonitrile mixture as the eluant give reliable results and robust performance, as do C₈-alkyl columns in combination with refractive index (RI) detection (Dotson et al. 1992; Gratzfeld-Huesgen 2001; Lee et al. 2001; Deineka et al. 2003).

In the next step, the maleation of the oils with MAA was performed. The conversion is a so-called *ene*-reaction, in which a double bond reacts with an allylic hydrocarbon via a pericyclic transition state consisting of 4 π -electrons and 2 σ -electrons (Christen 1982). The reaction thus somewhat resembles the classical Diels-Alder process (a 4 π +2 π process) in which the diene (4 π system) is replaced by an allyl system (2 π +2 σ). The *ene*-reaction generally requires relatively drastic conditions to proceed (temperatures above 140°C), but is a relatively neat reaction with few byproducts, of which most result from (auto)oxidation and rearrangements of the involved double bond systems. In the process, the MAA (the 2 π system) is attached to an unsaturated fatty acid residue on the triglyceride, resulting in a 1,2-shift of the existing double bond on the fatty acid residue, whereas the anhydride moiety is transformed from maleic to succinic under loss of the double bond (Figure 2b).

In the case of multiple unsaturated fatty acids, the MAA is attached to the bis-allylic position, and migration of one of the adjacent double bonds forms a conjugated double bond system, which is a major additional driving force in this special case.

The reaction procedure in the case of vegetable oils is similar to that of conventional ASA production (Figure 2a), but there is one important difference and benefit: there is no need to modify (isomerize) the raw material before the maleation step. Although α -olefins are usually isomerized into olefins with internal double bonds prior to ASA production, there is no need for this additional step for natural oils, as the double bonds of the fatty acids are already present in central positions along the chain.

Maleation behavior and application properties

Finding raw materials with the most suitable fatty acid composition The ratio between MAA and triglyceride in the product can be adjusted by ratio of the co-reactants, i.e., with higher amounts of MAA the product will reach a higher degree of maleation. From the experimentally determined soap number, the anhydride-to-triglyceride ratio (R) in the product is calculated according to Eq. (2). The different starting oils, the ratio MAA:triglyceride – that was used during

production – and the ratios R in the product (anhydride-to-triglyceride) are listed in Table 3.

The double bond equivalents as determined by GC or HPLC might translate into different fatty acid compositions in the triglyceride. As an example, six double bond equivalents might correspond to either of the following patterns: two triple unsaturated acids plus one saturated acid, one triple unsaturated plus one double unsaturated plus one single unsaturated acid, or three double unsaturated fatty acids. Only in the case of nine, eight, or one double bond equivalent, the iodine number and GC data, respectively, unambiguously translate into a certain fatty acid pattern. High numbers of double bond equivalents (more than 3) are less probable, because the percentage of double or triple unsaturated fatty acids is rather low as compared to the percentage of monounsaturated (oleic) acids (Table 4). However, fatty acids with two or even three double bonds react preferentially with the MAA and are thus enriched in the maleated products, see Table 4. This general trend was confirmed with all starting materials throughout all maleation attempts. As an example, SOHO contained approximately 72% oleic acid, and 10% of double unsaturated fatty acids (in addition to 3% and 2% of C₁₆ and C₁₈ saturated acids), respectively. Whereas maleation with three (four) equivalents of MAA converts 36% (58%) of the oleic acid, the double unsaturated acids are almost completely maleated (90% and 100%, respectively).

This phenomenon was subject to a more detailed analysis which employed transesterification of the triglycerides to the fatty acid methyl esters and subsequent GC analysis, both before and after the reaction with MAA, see Table 4 for all used oils and Figure 3 for MSBO in particular. The percentages represent the amount of fatty acids that were modified with MAA related to the amount of the respective starting fatty acid in the unmodified vegetable oil. The case of soybean oil maleated with the threefold amount of MAA (see Table 4, MSBO 3:1, and Figure 3) is a particularly illustrative example for the higher reactivity of multiple unsaturated acids in the maleation: whereas the oleic acid part remained unchanged, approximately 80% of the double unsaturated acids reacted, and the triple unsaturated acids were even completely converted (100%). Thus, the succinic acid residues in the maleated oils are preferably located on

Table 3 Maleic anhydride-to-triglyceride ratios (MAA:Triglyc.) during the *ene*-reaction and in the maleated oils.

Maleated oil	MAA:Triglyc. (<i>ene</i> -reaction)	MAA:Triglyc. (in product)
Rapeseed (MRSO)	2:1	1.2
Rapeseed (MRSO)	3:1	1.5
Rapeseed (MRSO)	4:1	1.7
Sunflower high oleic (MSOHO)	3:1	1.2
Sunflower high oleic (MSOHO)	4:1	1.3
Soybean (MSBO)	1:1	0.5
Soybean (MSBO)	2:1	1.0
Linseed (MLSO)	2:1	1.2
Linseed (MLSO)	3:1	2.0

Table 4 Fatty acid composition of vegetable oils and their derived maleated products measured with GC in %.

Oil resp. MAA:Triglyc. ratio ^a	Number of C in fatty acid:number of double bonds							
	16:0	18:0	18:1	18:1 (%) ^b	18:2	18:2 (%) ^b	18:3	18:3 (%) ^b
RSO	4	2	56	–	21	–	6	–
MRSO 2:1	4	1	40	16	5	16	1	5
MRSO 3:1	4	1	31	25	2	19	<1	6
MRSO 4:1	3	1	20	36	1	20	<1	6
SOHO	3	2	72	–	10	–	0	–
MSOHO 3:1	3	2	46	26	1	9	0	0
MSOHO 4:1	2	2	30	42	<1	10	0	0
SBO	10	4	23	–	56	–	4	–
MSBO 1:1	11	4	23	0	44	12	3	1
MSBO 2:1	11	4	21	2	33	23	<1	4
MSBO 3:1	16	6	23	0	12	44	<1	4
LSO	6	4	18	–	16	–	54	–
MLSO 2:1	5	4	17	1	12	4	24	30
MLSO 3:1	6	5	20	0	11	5	18	36

^aNumbers are the ratio between maleic anhydride and triglyceride during *ene*-reaction.

^b(%) is the part of the respective fatty acid that has reacted with maleic anhydride.

RSO, rapeseed oil; MRSO, maleated RSO; SOHO, sunflower oil high oleic; MSOHO, maleated SOHO; SBO, soybean oil; MSBO, maleated SBO; LSO, linseed oil; MLSO, maleated LSO.

polyunsaturated fatty acid chains, whereas in the presence of those multiple unsaturated chains the monounsaturated ones (oleic acid residues) remain largely unchanged. Thus, the MAA is not evenly distributed over all triglycerides. If relatively large percentages of polyunsaturated acids are contained, a high amount of triglycerides remain without maleation.

Preliminary sizing efficiency tests of the maleated oils

Handsheets were produced from the maleated vegetable oils listed in Table 3 after emulsification in cationic starch. For each sheet, a new emulsion was prepared and used within 15 min. Sizing efficiency was tested by means of the standard *Cobb*₆₀ test (DIN 53 132, DIN standard 1990). Figure 4 gives selected results for the maleated oils. In a simplified way, the *Cobb*₆₀ test assesses the quality of

a sizing agent by the amount of water absorbed by the test paper sheet in a time of 60 s. To compare the sizing efficiency, *Cobb*₆₀ values are determined for different amounts of sizing agent. For a satisfying sizing behavior, *Cobb*₆₀ values around 30 g m⁻² or lower at dosages as low as possible are desired.

As evident from Figure 4, MSBO does not seem to be suitable as sizing agent compared to the other oils. Whereas MRSO, MLSO, and MSOHO generally showed the same efficiency at higher charges of the sizing agent, MSOHO was clearly superior at lower charges.

For the production of sizing emulsions in starch solution as well as for pumping and dosing, the viscosity of the sizing agent is of major importance. It is generally aimed at keeping viscosity as low as possible. Oils with a high content of polyunsaturated fatty acids (linseed, soybean oil) tended to afford highly viscous products due to polymerization and

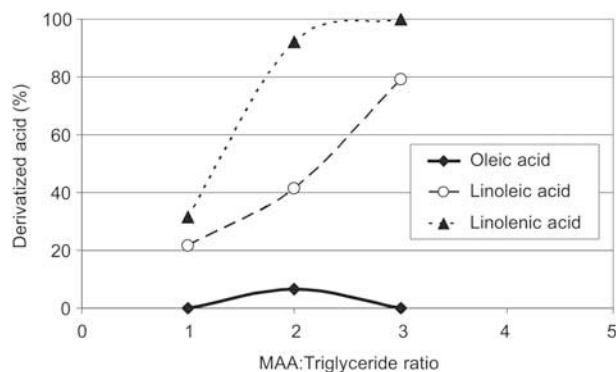


Figure 3 Preferential maleation of polyunsaturated fatty acids in maleated soybean oil (GC analysis after transesterification into the fatty acid methyl esters, percentages of “derivatized acid” are relative values).

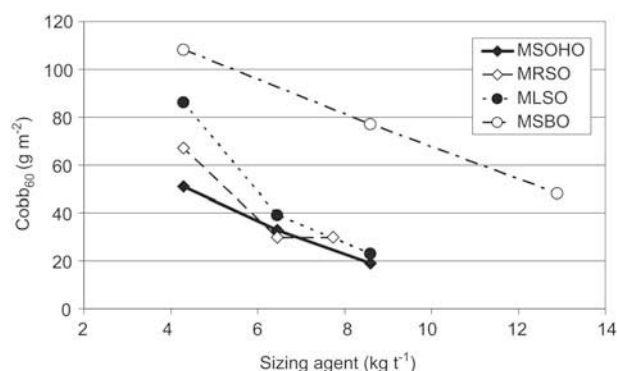


Figure 4 Preliminary sizing results (*Cobb*₆₀ values) of selected maleated oils: MSOHO, high oleic sunflower oil; MRSO, rapeseed oil; MLSO, linseed oil; MSBO, soybean oil.

side reactions. The maleated products from such oils were thus difficult to handle and difficult to emulsify with starch solutions. Consequently, oils having mostly monounsaturated fatty acids, such as rapeseed or high oleic sunflower oil, were more suitable for the use as sizing agent.

The aim of reacting triglycerides with MAA is evidently to anchor at least one MAA per triglyceride and to avoid having unmodified oil in the product which does not contribute to sizing. To reach this goal, the content of polyunsaturated acids should be low, as these react preferably with MAA and leave those fatty acids and triglycerides unchanged, which have lower reactivity, especially those containing mainly oleic acids. It is generally beneficial to have a high amount of structurally similar fatty acids in the oil, which results in a similar reactivity towards MAA. This requirement is met exemplarily by the high content of oleic acids in SOHO. Furthermore, oils with polyunsaturated fatty acid residues tend to polymerize and form high viscous products, as mentioned above. Accordingly, oils were sought for with a high amount of oleic acid and low amounts of polyunsaturated fatty acids. Thus, the raw materials selected were RSO and SOHO.

Optimization of the production parameters and minimization of side reactions RSO yielded products with significantly higher viscosity than SOHO at the same ratio of MAA per triglyceride (Table 5). This is caused by the higher content of polymeric substances in maleated RSO and thus by the high content of polyunsaturated fatty acids with their inherent tendency for polymerization. The amount of polymeric substances in the products was quantified with GPC. A typical GPC spectrum of MSOHO 4:1 product (Table 5) is shown in Figure 5. Owing to the superiority of maleated SOHO, further optimization of the reaction conditions for the maleation concentrated on this raw material.

Another criterion for the quality of the maleated oils is the content of unchanged triglyceride (residual fatty oil), which should be as low as possible. Evidently, any triglyc-

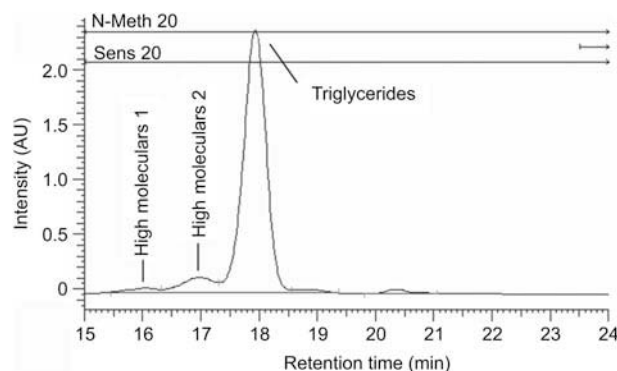


Figure 5 GPC chromatogram of a maleated high oleic sunflower oil product (maleic anhydride-to-triglyceride ratio 4:1, cf. Table 5, reference standard non-maleated SOHO).

eride containing exclusively saturated fatty acids cannot be chemically modified by maleation; fortunately, the overall content of such triglycerides is very low. However, also triglycerides containing one or two oleic acid residues remain partly unchanged. Reacting SOHO with the double amount of MAA yielded a product in which 20% of unchanged oil remained. At a 4:1 ratio of MAA and triglyceride, the amount of residual oil in MSOHO was reduced to approximately 10% (Table 5). An increased ratio of MAA-to-triglyceride in the *ene*-reaction naturally decreased the amount of unchanged triglyceride. This higher MAA-to-triglyceride ratio also resulted in an increased viscosity of the product, even though the amount of polymers was lower. It can be assumed that this behavior is due to higher amount of polar succinic anhydride moieties in the modified triglycerides. The content of polymeric products was not the only, although the most important, factor influencing product viscosity. When the MAA-to-triglyceride ratios exceeded 4:1, the products became so viscous that they were difficult to be handled and to be emulsified. Thus, this MAA-to-triglyceride ratio might be the upper limit for the maleation reaction.

Table 5 Analysis results for different maleated oils.

Oil resp. MAA:Triglyc. ratio ^a	Residual oil by		R ^b	Viscosity (mPas)	Polymers by GPC (%)
	HPLC (%)	GC (%)			
RSO	99	98	–	71	0.5
MRSO 2:1 ^c	22	29	1.0	4488	27.1
MRSO 2:1 ^d	16	21	1.1	8530	22.5
SOHO	100	99	–	78	0.1
MSOHO 2:1	15	20	1.1	2085	14.2
MSOHO 4:1	7	10	1.4	5775	8.8

^aNumbers are the ratio between maleic anhydride and triglyceride during *ene*-reaction.

^bR, maleic anhydride-to-triglyceride ratio. Values differ slightly from those in Table 3 since different preparations were used.

^cWithout addition of antioxidant.

^dWith addition of antioxidant.

RSO, rapeseed oil; MRSO, maleated RSO; SOHO, sunflower oil high oleic; MSOHO, maleated SOHO.

Table 6 Preventing the formation of polymeric material by antioxidative additives during maleation of SOHO with two equivalents of maleic anhydride.

Additives	Polymeric material (%)
Without	15.2
0.4% Boric acid/BHT	18.0
0.02% AnoxPP18S	19.2
0.02% Vitamin E acetate	13.0
0.02% BHT	12.9
0.2% BHT	13.6
0.02% BHT/BHA	10.3

Antioxidative additives were found to be beneficial for the production of ASA, because they inhibit the formation of unwanted byproducts during the *ene*-reaction of olefin and MAA. Mäkipieura et al. (1997) proposed the application of benzoquinone, hydroquinone, dialkylsulfoxide, or acetylacetonate complexes of transition metals in concentrations between 0.05 and 2 mol% related to the amount of MAA. In another patent, the addition of 0.2% BTH and 0.2% boric acid related to the total mass of olefin and MAA was claimed to decrease the amount of byproducts (Kapanen et al. 1999). As the reaction mechanism of maleation of vegetable oils is similar to that of ASA production from olefins, some of the above-mentioned additives were expected to be active as well. They were tested in the maleation of SOHO based on MAA-to-triglyceride ratio of 2:1 (Table 6). The additives were admixed to the vegetable oil before filling into the pressure reactor. The effect of the antioxidants can be explained by the prevention of radical chain reactions that cause polymerization and autoxidation of the material. The impact of the additives was quantified by GPC. All materials with molecular weights beyond those of maleated triglycerides were regarded as “polymeric” and as an indicator of side reactions. The expectation was that additives diminish the side reactions and byproducts. As seen in Table 6, the most effective additives were Vitamin E acetate, BHT, and a 1:1 blend of BHT and BHA. Because the 10-fold increase of the BHT concentration did not improve the results concerning the polymer content, it was sufficient to use 0.02% of the additive.

The iodine number of the products, reflecting the content of reactive double bonds, was measured for MRSO and MSOHO as well as for the unmodified starting oils. Both maleated oils were produced according the working procedure in the experimental section based on the MAA-to-triglyceride ratio of 2:1 and in the presence of 0.0122% of Anox additive. The iodine number decreased from 114.4 g/100 g (RSO) to 70.0 g/100 g (MRSO) and from 75.7 g/100 g (SOHO) to 65.1 g/100 g (MSOHO). The double bonds of MSOHO were almost preserved during the maleation step, but MRSO had far fewer double bonds than its starting oil. This finding confirms the presence of more unwanted side reactions in the RSO case and is in agreement with the above-discussed maleation reactivity and GPC results.

Conclusions

Sizing paper with maleated natural plant oils is possible; these products are promising substitutes for conventional olefin-based ASA sizing agents. The starting plant oils are renewable raw materials, which implies reduced logistic efforts and transportation costs. Moreover, an isomerization step is not needed before production as is the case for conventional olefins.

Some of the oils are less eligible for this purpose, for example, those with high amounts of polyunsaturated fatty acid residues (linseed or soybean oil), which tend to give overly viscous products when maleated. Vegetable oils with a high content of monounsaturated fatty acids (oleic acid) yielded the most promising sizing results. RSO and in particular SOHO were preferred raw materials for new sizing agents. They are less likely to form polymeric byproducts during the maleation step, and a higher yield of maleated triglycerides can be reached.

To limit unwanted side reactions and to maximize the yield of maleated products, the maleation procedure was thoroughly optimized: the reaction was carried out under pressure, a mixture of BHT and BHA (0.02%) was added as stabilizer, and the MAA-to-triglyceride ratio was set to 4:1.

Preliminary sizing results (deduced from *Cobb*₆₀ tests and emulgation behavior), as presented in this paper, were promising. Further studies will focus on the characterization of the novel renewables-based ASA substitute, on applicability, emulsion stability and hydrolytic stability, paper sizing characteristics, as well as on application tests in combination with other sizing agents. These studies will be reported in the subsequent parts of this series.

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Novel paper sizing agents from renewables. Part 2: Characterization of maleated high oleic sunflower oil (MSOHO)

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Abstract

Maleated oils derived from high oleic sunflower oil (MSOHO) have promising applications in paper sizing as a green alternative to conventional reactive sizing agents, such as alkenyl succinic anhydride. In this study, MSOHO was comprehensively characterized analytically by attenuated total reflection infrared spectroscopy, ¹H and ¹³C nuclear magnetic resonance spectroscopy with full resonance assignment, and mass spectrometry.

Keywords: alkenyl succinic anhydride (ASA); ASA sizing; attenuated total reflection infrared (ATR-IR) spectroscopy; green chemistry; high oleic sunflower oil; maleated oils; nuclear magnetic resonance (NMR) spectroscopy; paper sizing; plant oils; renewable resources.

Introduction

The mechanisms of internal paper sizing have been addressed in the literature (Roberts 1996), such as sizing with alkenyl succinic anhydride (ASA), but central issues are still unclear and are a matter of current discussion.

Whereas McCarthy and Stratton (1987) presented evidence that formation of ester bonds between ASA and cellulosic hydroxyl groups is possible even under papermaking conditions, more recent studies have revealed a more complex system: Nishiyama et al. (1996a) demonstrated that

ASA is mostly present as ASA acid in sized hand sheets and ester bonds can only be formed to a minor extent, whereas it has been argued that ASA acid does not contribute to sizing (Wasser and Brinen 1998). Further investigations by Nishiyama et al. (1996b) and Isogai (2000) revealed that genuine ASA was needed in terms of retention and neat distribution of ASA throughout the paper sheet, and that hydrolyzed ASA (i.e., ASA acid), once immobilized, was not at all detrimental to sizing. The explanation might be that once immobilized ASA acid can form Ca-salts during drying and curing of CaCO₃ filled paper sheets. This Ca-salt has a positive effect on sizing level of a paper as was shown by Wasser and Brinen (1998).

One prerequisite to a better understanding of sizing in general and to the development of novel sizing agents is a precise knowledge of the chemical structure of the sizing molecules involved. We have recently developed sizing agents based on maleated fatty oils of plants, i.e., based on fully renewable resources, such as rapeseed oil (RSO) or high oleic sunflower oil (SOHO) (Lackinger et al. 2009, 2011) and have optimized their production. In this study, these sizing agents were characterized comprehensively by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and attenuated total reflection infrared (ATR-IR) spectroscopy. Emphasis was placed on structure elucidation, including a full NMR assignment in the ¹H and ¹³C domains.

Experimental

Materials

Sources of oil and chemicals: high oleic sunflower oil (SOHO) from C. Thywissen GmbH, Germany; maleic anhydride (MAA) of synthesis grade from Merck, Germany; butylated hydroxytoluene (BHT, di-*tert*-butyl-hydroxytoluene), purity > 99%, Sigma Aldrich, Austria; and butylated hydroxyanisole (BHA, *tert*-butyl-hydroxy-anisole), food grade, Eastman Chemical Company, USA. The abbreviation MSOHO means maleated SOHO. Chemicals for analysis included deuteriochloroform from Sigma-Aldrich, Austria; acetonitrile (HPLC grade) from Fisher Scientific GmbH; and formic acid from Merck, Germany.

Working procedure for the preparation of maleated natural oils Vegetable oil 150 g (0.17 mol) was charged into a reactor in an inert gas atmosphere together with 0.02 w% of a BHT/BHA mixture (w/w = 1:1) and then heated to 200°C under stirring. Then, 66.45 g (0.68 mol) MAA was added in one step. The reaction was performed under inert gas at a pressure of 3.3 bar for 6 h. The

reaction mixture was cooled to r.t., the pressure was released, and excess MAA was distilled off at a reduced pressure of 10 mbar at 120–140°C.

Instrumental analysis

Attenuated total reflection infrared (ATR-IR) spectroscopy

Instrument: AVATAR 370 FT-IR device with a Smart DuraSamplIR probe head (Thermo Nicolet Corporation, USA). The spectra were analyzed by means of the Omnic 6.2 package (Thermo Nicolet Corp., 1992–2001). One drop of the neat substance was placed on top of the probe head and the measurement was started immediately.

Nuclear magnetic resonance (NMR) spectroscopy

Spectra were recorded at 400.13 MHz for ^1H and at 100.41 MHz for ^{13}C at a Bruker Avance II instrument, with CDCl_3 as solvent, if not otherwise stated. Chemical shifts, relative to TMS as internal standard, are given in δ values and coupling constants in Hz. ^{13}C peaks were assigned by means of APT, HMQC and HMBC spectra. In total, 30 mg of the sample was dissolved in 0.6 ml of CDCl_3 for NMR analysis.

Mass spectroscopy (MS) Instrument: ESI Q-TOF mass spectrometer (Q-TOF Ultima, Waters Micromass). Capillary voltage was adjusted to obtain approximately 200 counts s^{-1} . Data analysis was performed with MassLynx 4.0 SP4 Software (Waters Micromass). The sample was dissolved in acetonitrile containing 5% water and 0.1% formic acid before introduction into the MS system.

Results and discussion

Infrared (IR) results

ATR-IR spectra of the unmodified (SOHO) and the MSOHO showed some distinct differences (Table 1 and Figure 1). In the spectrum of MSOHO, the appearance of the new bands at 1862, 1782, 1062, 974, and 915 cm^{-1} are the most significant differences compared to SOHO IR spectra. Most bands originate from the succinic anhydride moiety: at 1862 and 1782 cm^{-1} from the asymmetric and symmetric carbonyl stretching vibrations, the 1062 cm^{-1} band from the symmetric C-O-C vibration, and band at 915 cm^{-1} from the ring-stretching vibration of the saturated five-membered ring. The somewhat prominent band at 974 cm^{-1} is due to the C-H out-of-plane bending vibration of a C=C-H *trans*-alkene structure. Unmodified SOHO contains exclusively double bonds in *cis*-configuration. After reaction of these bonds with MAA in an *ene*-reaction via a cyclic transition state (Christen 1982), the double bond in the product is mainly *trans*-configured, although deviations from this regular product geometry can occur by thermal isomerization due to the usually high reaction temperatures. The IR results thus clearly confirm the presence of succinic anhydride moieties in the product and thus the success of the maleation reaction.

IR spectroscopy is also useful for the control of the purification of the product. Namely, the excess MAA is removed

Table 1 IR band assignment of SOHO (starting material) and MSOHO (maleated product).

SOHO		MSOHO		Assignment
Wave number (cm^{-1})	Absolute intensity	Wave number (cm^{-1})	Absolute intensity	
3006	0.024	3005	0.015	ν (C-H) stretching vibration of -CH=CH-
2953	0.065	2953	0.061	ν_{as} (CH_3)
2922	0.221	2923	0.193	ν_{as} (CH_2)
2852	0.155	2853	0.134	ν_{sy} (CH_2)
		1862	0.047	ν_{as} (C=O) of saturated five-membered ring of anhydride (Dauben and Epstein 1959; Socrates 2001)
		1782	0.234	ν_{sy} (C=O) of saturated five-membered ring of anhydride (Dauben and Epstein 1959; Socrates 2001)
1744	0.252	1740	0.242	ν (C=O) of fatty acid esters
1461	0.077	1462	0.073	δ (CH_2) C-H deformation
		1413	0.043	δ (CH) CH_2 scissoring from - CH_2 -CO-
1376	0.045	1376	0.048	δ (CH) CH deformation vibration
1237	0.074			ν_{as} (-C-O-C=) of the fatty acid esters
		1220	0.132	ν_{as} (=C-O-C=) of the cyclic five-membered ring of anhydride
1162	0.165	1164	0.174	ν_{sy} (-C-O-C=) of the fatty acid esters
		1062	0.155	ν_{sy} (=C-O-C=) of the cyclic five-membered ring of anhydride (Socrates 2001)
		974	0.094	δ (C-H), C=C-H out of plane bending vibration of <i>trans</i> -alkene
		915	0.233	ν (C-C), ring stretching vibration of saturated cyclic five-membered anhydride
723	0.1	724	0.115	r (C-H) rocking vibration of chain -(CH_2) $_n$ - and δ (C-H) of -CH=CH- out-of-plane bending vibration of <i>cis</i> -alkene ^a

^aDifficult to assign due to overlap of bands.

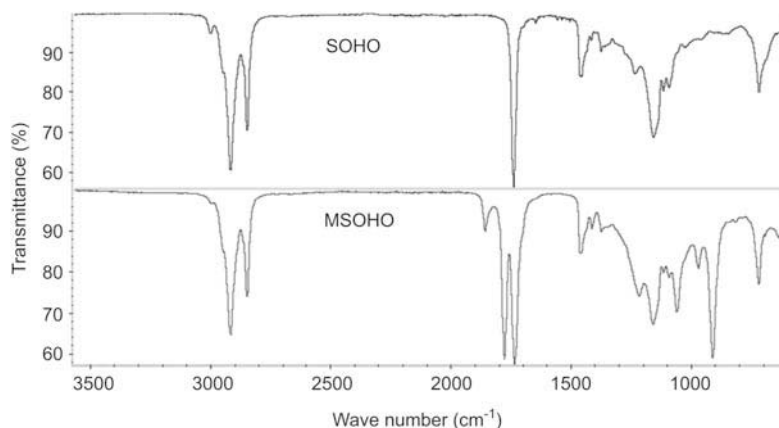


Figure 1 Comparison of the ATR-IR spectra of SOHO (starting material, upper trace) and MSOHO (maleated product, lower trace).

through vacuum distillation after completion of the maleation and the progress of this purification step is visible by the disappearance of bands assigned to free MAA. These include the C-H stretching vibration (3110 cm^{-1}) and the C-H bending vibration (694 cm^{-1}) of $-\text{CH}=\text{CH}-$ in the five-membered MAA ring.

Nuclear magnetic resonance (NMR) results

NMR allowed structural elucidation of the maleated oils most directly and most comprehensively, especially by combination of 2D techniques. In the present case, a signal assignment of all relevant resonances in the ^1H and ^{13}C domains was possible for the starting oil and the maleated product. These assignments are reported here for the first time. We used a combination of 1D proton and carbon spectra, the latter in the APT variant (attached proton test) as well as 2D homonuclear (H,H-COSY), and heteronuclear (HSQC, HMBC) experiments.

The proton spectrum (Figure 2a) as well as the ^{13}C spectrum (Figure 3a) of the starting oleate-rich sunflower oil (SOHO) showed the presence of a rather homogeneous and neat product. The assignments of the resonances to structural elements are given in Table 2 for the ^1H domain and in Table 3 for the ^{13}C domain. The resonance at 0.81 ppm originates in the terminal methyl groups of the fatty acids, the resonances between 1.12 and 1.30 ppm from methylene units other than the $\alpha\text{-CH}_2$ ($\sim 2.25\text{ ppm}$) and the $\beta\text{-CH}_2$ ($\sim 1.55\text{ ppm}$). All allylic methylene groups, i.e., such in α -position to an isolated double bond ($\text{HC}=\text{CH}-\text{CH}_2$), resonated around $1.91\text{--}2.02\text{ ppm}$. The minor resonance at 2.70 ppm originates from a methylene group in allyl position to two double bonds (the central 3-CH_2 in a $1,4\text{-pentadiene}$ structural unit). This signal is useful to approximate the degree of double (and triple) unsaturation in the oil, i.e., to determine the content of linoleic and linolenic fatty acids. The integral indicates a content of 0.48 protons in allylic positions and thus 0.24 equivalents of double unsaturated structures: approximately one double unsaturated structure (linoleic/linolenic acid) was contained per four isolated double bonds (oleic acid) in the starting oil. The well-resolved double-doublets at 4.07 and 4.22 ppm originate from the two enantiotopic methylene pro-

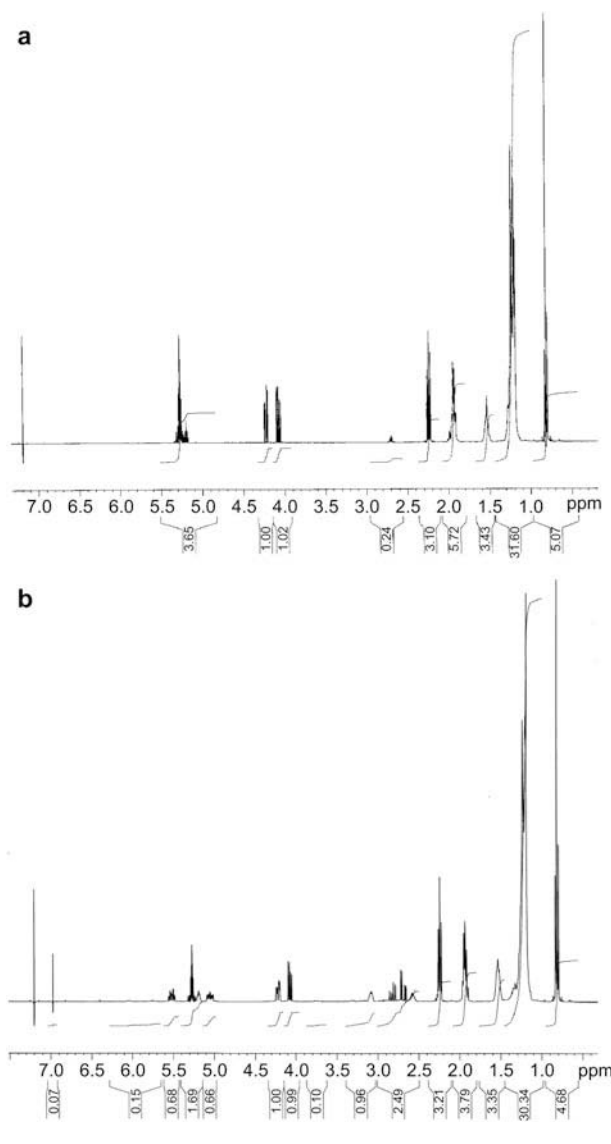


Figure 2 ^1H NMR spectra (400 MHz , CDCl_3) of (a) high oleic sunflower oil (SOHO, starting material for maleation) and (b) MSOHO (maleated product).

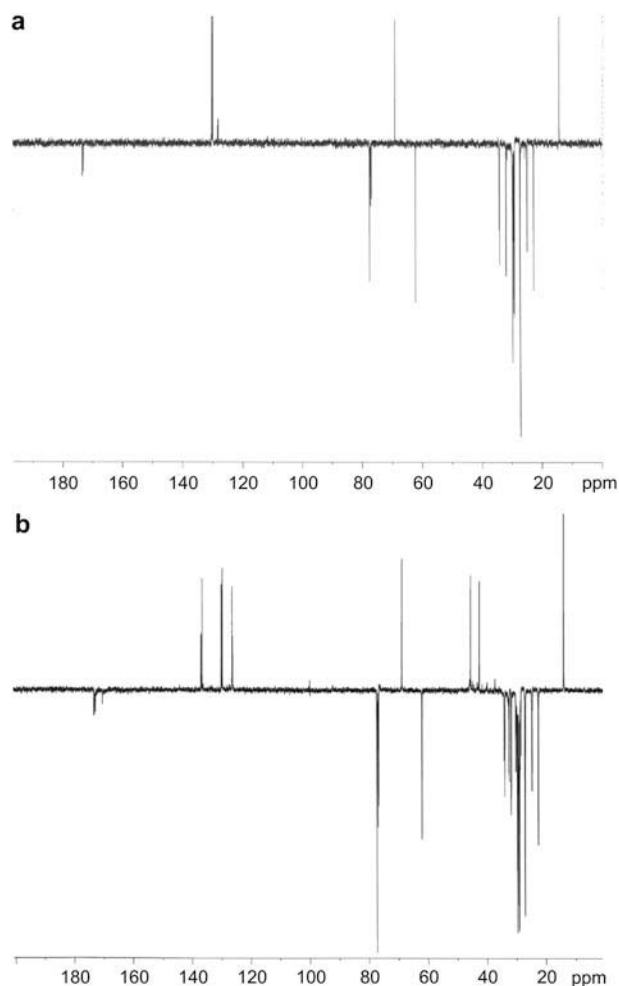


Figure 3 ^{13}C NMR spectrum (100 MHz, CDCl_3 , APT) of (a) high oleic sunflower oil (SOHO, starting material for maleation) and (b) MSOHO (maleated product).

tons at C-1 and C-3 of the glycerol moiety, the multiplet at 5.17–5.21 ppm from the central methine proton at C-2 of glycerol.

The overall content of double bonds can be retrieved from the multiplet resonance at 5.17–5.34 ppm, encompassing H-2 of glycerol (integral 1) and all olefinic protons (integral

6.3). Assuming only oleate residues and the above determined amount of 0.24 equivalents of double unsaturated residues, an integral of 6.48 is the result. The lower experimental value of 6.3 indicates the presence of a small amount saturated fatty acids (0.09 double bond equivalents). Thus, the overall composition of the oil is a trioleate with 0.24 equivalents of double unsaturated structures and 0.09 equivalents of saturated fatty acids. In other words, approximately five double unsaturated and two saturated fatty acids are contained in the starting material per 20 isolated double bonds in oleate residues.

Also, the maleated product (MSOHO) appeared as a neat substance with well-resolved spectra (Figures 2b, 3b) and their full ^1H and ^{13}C assignments are given in Table 4 and Table 5, respectively. The additional resonances introduced by maleation can readily be identified and assigned: the methine CH of the fatty acid, to which the succinic anhydride residue (succ.) is attached, appears as a broad multiplet at 2.53–2.62 ppm (^{13}C : 42.6 ppm) and the adjacent methine proton in the succinic anhydride as broad multiplet at 3.05–3.12 ppm (^{13}C : 45.5 ppm). The three protons in the succinic moiety form an ABX spin system. The two diastereotopic protons of the methylene groups in the succinic anhydride produce two well-resolved dd patterns (doublet of doublets) centered at 2.68 and 2.82 ppm (^{13}C : 30.2 ppm), the geminal coupling constant being $^2J=19.2$ Hz, and the two vicinal ones $^3J=9.8$ Hz and $^3J=5.4$ Hz. One of the two methylene protons showed a long-range 4J coupling of 1.2 Hz to the proton at the junction methine moiety (^1H : 2.53–2.62 ppm, ^{13}C : 42.6 ppm) of the acyl chain.

The olefinic protons of the newly rearranged double bond were found as multiplets at 5.00–5.10 ppm and 5.47–5.57 ppm and the corresponding carbon resonances around 126.2 and 136.5 ppm, respectively. Otherwise, the typical resonances of the (non-converted) starting material are also found in the maleated product.

Detailed evaluation of the spectra allows some interesting insights. The degree of maleation can easily be determined from the integral ratio between the two glycerin methylenes (4.04–4.26 ppm, integral 4.0) and the three succinic anhydride protons (2.53–2.90 ppm, integral 4.98). Regarding the oil as an ideal trioleate that would give an integral of 9 upon maleation at every double bond. Thus, the degree of malea-

Table 2 ^1H NMR peak assignment for SOHO (starting material).

Chemical shift (ppm)	Peak characteristics	Integral	Structural element
0.81	t, $^3J=6.8$ Hz	9 H	CH_3
1.12–1.30	m	60 H	CH_2 other than below
1.50–1.58	m	6 H	$\text{OOC-CH}_2\text{-CH}_2$
1.91–2.02	m	12 H	HC=CH-CH_2
2.22–2.27	m (dt), $^3J=7.6$ Hz	6 H	$\text{OOC-CH}_2\text{-CH}_2$
2.70	m	<1 H	$\text{HC=CH-CH}_2\text{-CH=CH}$
4.07	dd, $^2J=12$ Hz, $^3J=6$ Hz	2 H	$\text{O-CH}_A\text{H}_B\text{-CH(OR)-}$
4.22	dd, $^2J=12$ Hz, $^3J=4.4$ Hz	2 H	$\text{O-CH}_A\text{H}_B\text{-CH(OR)-}$
5.17–5.21	m	1 H	$\text{O-CH}_A\text{H}_B\text{-CH(OR)}$
5.22–5.34	m	6 H	-HC=CH-

Table 3 ^{13}C NMR peak assignment for SOHO (starting material).

Chemical shift (ppm)	Characteristics	Structural element
14.1		CH_3
22.6		$\text{CH}_3\text{-}\underline{\text{CH}}_2$
24.8		$\text{OOC-CH}_2\text{-}\underline{\text{CH}}_2$
25.6		$\text{HC=CH-}\underline{\text{CH}}_2\text{-CH=CH}$
27.2	m	$\text{HC=CH-}\underline{\text{CH}}_2$
29.1–29.8	m	CH_2 other than above and below
31.9		$\text{CH}_3\text{-CH}_2\text{-}\underline{\text{CH}}_2$
34.1	m	$\text{OOC-}\underline{\text{CH}}_2$
62.1		$\text{O-}\underline{\text{CH}}_2\text{-CH(OR)-}$
68.8		$\text{O-CH}_2\text{-}\underline{\text{CH}}(\text{OR})\text{-}$
127.8		$\text{HC=}\underline{\text{CH}}\text{-CH}_2\text{-}\underline{\text{CH}}\text{=CH}$
129.8–130.5	m	$\text{HC=CH-CH}_2\text{-CH=}\underline{\text{CH}}$ and $\text{-}\underline{\text{CH}}\text{=}\underline{\text{CH}}\text{-}$
172.8 and 173.2		-COO-

tion was approximately 1.66, i.e., around 5 out of 9 double bonds were maleated.

All allylic positions within double unsaturated structures (1,4-diene structure) were completely consumed, confirming the earlier discussed observation that upon maleation multiple unsaturated fatty acids reacted preferably. Upon such reaction, a conjugated double bond system (1,3-diene) is formed. The carbon resonances of isolated double bonds in fatty acids appear at 130 ppm, no matter if a succinic anhydride residue is placed in α -position, and also independent on the stereochemical configuration of the double bond. However, conjugated double bonds – 1,3-butadiene structural motifs – show a distinct downfield shift of the two outer carbons and a highfield shift of the two inner carbons, accounting for the resonances at approximately 136 ppm and 126 ppm, respectively. These resonances thus originate from conjugated double bonds formed upon maleation of doubly unsaturated structures.

The *ene*-reaction, that introduced the succinic anhydride residue by reaction with MAA, shifts a new double bond into 2,3-position of the former *cis*-1,2-olefin. Following from the transition state of the pericyclic reaction, the configuration of this rearranged double bond would be always *trans*, in theory. However, owing to the rather harsh conditions of this thermally induced process, *cis-trans* isomerization might occur, so that configurational mixtures are often obtained in practice. In the case of the maleated oils, configuration of the new double bonds was *trans* exclusively. This cannot be deducted from the ^{13}C shifts of the double bond carbons themselves, as they are insensitive towards possible configurational change (see above). However, the methylene carbons next to the double bond experience typical changes depending on the configuration of the double bonds. Whereas methylene carbons remote from double bond systems in fatty acids resonate around 30 ppm, this value is shifted upfield to around 27 ppm for $\text{RCH=CH-}\underline{\text{CH}}_2$ with *cis*-con-

Table 4 ^1H NMR peak assignment for MSOHO (maleated product).

Chemical shift (ppm)	Peak characteristics	Structural element
0.81	t, $^3J=6.8$ Hz	CH_3
1.12–1.28	m	CH_2 other than below
1.29–1.38 ^a	m	$\text{-CH=CH-CH(succ.)-}\underline{\text{CH}}_2$
1.48–1.59	m	$\text{OOC-CH}_2\text{-}\underline{\text{CH}}_2$
1.89–1.96	m	$\text{HC=CH-}\underline{\text{CH}}_2$
2.22–2.27	m (dt), $^3J=7.6$ Hz	$\text{OOC-}\underline{\text{CH}}_2\text{-CH}_2$
2.53–2.62 ^a	m	$\text{-}\underline{\text{CH}}\text{-CH(succ.)}$
2.68 ^a	dd, $^2J=19.2$ Hz, $^3J=5.4$ Hz	$\text{CH}_\text{A}\text{H}_\text{B}\text{-CH in succ.}$
2.82 ^a	ddd, $^2J=19.2$ Hz, $^3J=9.8$ Hz, $^4J=1.2$ Hz	$\text{CH}_\text{A}\text{H}_\text{B}\text{-CH in succ.}$
3.05–3.12 ^a	m	$\text{CH}_\text{A}\text{H}_\text{B}\text{-}\underline{\text{CH}}$ in succ.
4.07	dd, $^2J=12$ Hz, $^3J=6$ Hz	$\text{O-CH}_\text{A}\text{H}_\text{B}\text{-CH(OR)-}$
4.18–4.26	dd, $^2J=12$ Hz, $^3J=4.4$ Hz	$\text{O-CH}_\text{A}\text{H}_\text{B}\text{-CH(OR)-}$
5.00–5.10 ^a	m	$\text{-CH(succ.)-}\underline{\text{CH}}\text{=CH-}$
5.15–5.22	m	$\text{O-CH}_\text{A}\text{H}_\text{B}\text{-}\underline{\text{CH}}(\text{OR})\text{-}$
5.22–5.33	m	$\text{-}\underline{\text{HC}}\text{=}\underline{\text{CH}}\text{-}$
5.47–5.57 ^a	m	$\text{-CH(succ.)-CH=}\underline{\text{CH}}\text{-}$

succ.=2-substituted succinic anhydride residue.

^aPeaks newly occurring through maleation (in comparison to the starting material).

Table 5 ^{13}C NMR peak assignment for MSOHO (maleated product).

Chemical shift (ppm)	Characteristics	Structural element
14.3		CH_3
22.6		$\text{CH}_3\text{-}\underline{\text{CH}}_2$
24.7; 24.8		$\text{OOC-CH}_2\text{-}\underline{\text{CH}}_2$
25.6		$\text{HC=CH-}\underline{\text{CH}}_2\text{-CH=CH}$
27.0–27.2	m	$\text{HC=CH-}\underline{\text{CH}}_2$
28.6–29.7	m	CH_2 other than above and below
30.2 ^a		CH_2 in succ.
31.8	m	$\text{CH}_3\text{-CH}_2\text{-}\underline{\text{CH}}_2$
32.6–32.7	m	$\text{CH(succ.)-CH=CH-}\underline{\text{CH}}_2$
33.9–34.2	m	$\text{OOC-}\underline{\text{CH}}_2$
42.6 ^a		$\text{-}\underline{\text{CH}}\text{-CH(succ.)-}$
45.5 ^a		CH in succ.
62.1		$\text{O-}\underline{\text{CH}}_2\text{-CH(OR)-}$
68.8		$\text{O-CH}_2\text{-}\underline{\text{CH}}\text{(OR)-}$
126.2 ^a ; 126.4 ^a		$\text{-HC=}\underline{\text{CH}}\text{-CH=CH-}$
129.7–130.0 ^a	m	$\text{HC=}\underline{\text{CH}}\text{-}$ and $\text{-CH(succ.)-}\underline{\text{CH}}\text{=}\underline{\text{CH}}\text{-}$
136.5 ^a ; 136.8 ^a		$\text{-HC=CH-CH=}\underline{\text{CH}}\text{-}$
170.3 ^a		C(=O)-O-C(=O) in succ.
172.7–173.2		-COO-

succ.=2-substituted succinic anhydride residue.

^aPeaks newly occurring through maleation (in comparison to the starting material).

figuration as it is encountered in the starting SOHO oil, and downfield to approximately 33 ppm for $\text{RCH=CH-}\underline{\text{CH}}_2$ and *trans*-double bonds, as seen in the maleated product oil. With a value of 32.7 ppm for the α -methylene relative to the double bond in the maleated product, the *trans*-configuration of the newly introduced double bond was evident.

Mass spectroscopy (MS) results MS spectra (ESI Q-TOF, see experimental) of maleated sunflower oil (MSOHO) as well as of the starting vegetable oil were recorded (Figure 4). The main signals are listed in Table 6 (SOHO and MSOHO). Unmodified triglycerides can be observed at approximately 895 m/z^1 in the mass spectra. Attachment of up to

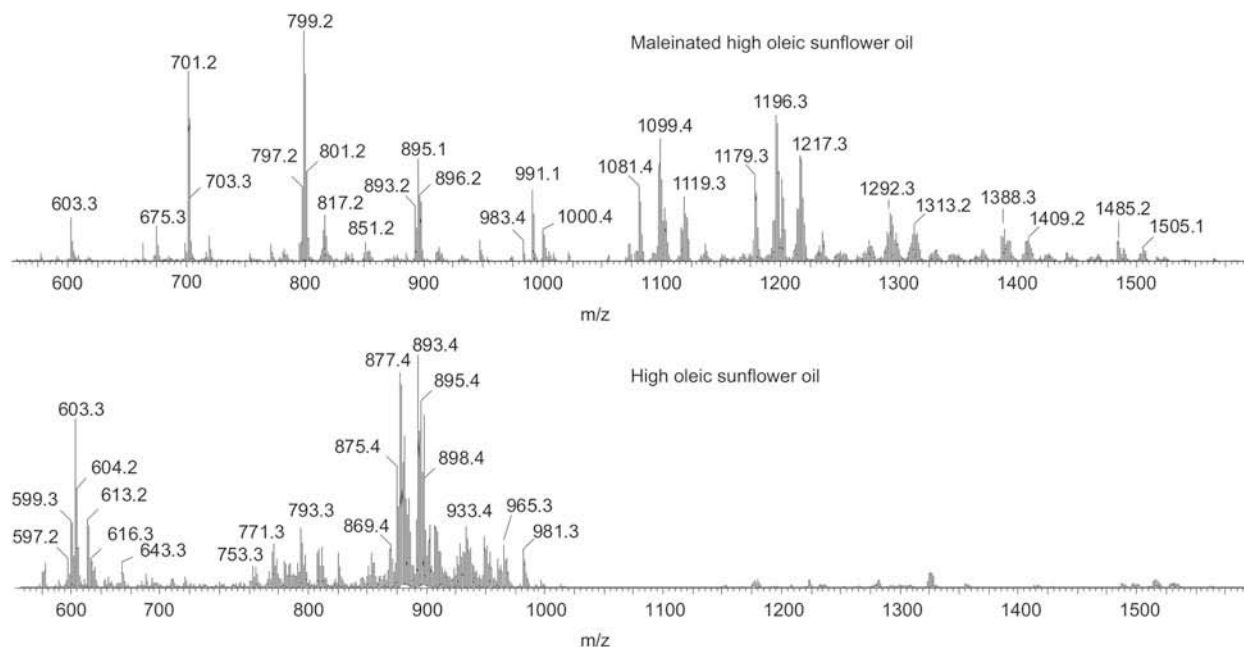
**Figure 4** Mass spectra of MSOHO and SOHO.

Table 6 MS data for high oleic sunflower oil (SOHO) and maleated high oleic sunflower oil (MSOHO).

Mass (m z ⁻¹)	Mass difference to di-/triglyceride (m z ⁻¹)	Structural assignment
603.3		Unmodified diglyceride
701.2	97.9	Diglyceride+1 MAA
799.2	195.9	Diglyceride+2 MAA
895.4		Unmodified triglyceride
991.1	95.7	Triglyceride+1 MAA
1099.4	204.0	Triglyceride+2 MAA
1196.3	300.9	Triglyceride+3 MAA
1292.3	396.9	Triglyceride+4 MAA
1388.3	492.9	Triglyceride+5 MAA
1485.2	589.8	Triglyceride+6 MAA

6 MAA residues to the triglycerides was reflected in the spectra. The increasing number of succinic residues in the product is represented in the approximate m z⁻¹ difference of 99 between the signal maxima. No quantification of the signals is possible in the applied MS mode.

Conclusions

The maleated oil products were characterized comprehensively with ATR-IR, NMR, and ESI MS. The *ene*-reaction mechanism for the attachment of the maleic acid – that becomes a succinic acid moiety upon the reaction – was confirmed, as was the conversion of the *cis*-double bonds in the starting oils to *trans*-structures upon maleation. In both NMR and ATR-IR spectra, the maleation is clearly reflected by the occurrence of characteristic resonances and bands, respectively. In the case of NMR, a full resonance assignment in both the ¹H and the ¹³C domain was achieved. The composition data retrieved from the NMR spectra are in superb agreement with the results from wet-chemical and chromatographic analysis presented in the previous part of this series (Part 1 in this issue: Lackinger et al. 2011). Also, in ATR-IR, an assignment of all major bands was possible. MS confirmed that up to six succinic residues per triglyceride can be attached.

The subsequent parts of this series will address the important points of hydrolytic stability and emulsion stability under different conditions, sizing effectiveness and charac-

teristics, an in-depth comparison to conventional sizes, and a report on practical applicability and usage.

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Novel paper sizing agents from renewables. Part 3: Emulsion stability and hydrolysis behavior compared to conventional sizes

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Abstract

The hydrolytic stability and sizing behavior of a new paper sizing agent based on renewable vegetable oils (maleated sunflower oil, high oleic: MSOHO) was compared to two conventional alkenyl succinic anhydride (ASA) specimens, a commercial sample, and a reagent-grade ASA sample. At various pH conditions as well as upon addition of Ca^{2+} ions, MSOHO was more stable than both ASA samples. This superior stability of MSOHO was also supported by zeta potential measurements over 1 week. Whereas for sizing of paper higher dosages of MSOHO were needed to gain certain water repellency as compared to the ASA samples, the addition of alum had a pronounced positive effect on the sizing efficiency of MSOHO. The higher stability of MSOHO made it possible to size with an MSOHO-starch emulsion that was aged for one day at room temperature, when conventional ASA-starch emulsion had long lost any sizing efficiency.

Keywords: alkenyl succinic anhydride (ASA); ASA sizing; emulsion stability; green chemistry; high oleic sunflower oil; hydrolysis; maleated oils; paper sizing; plant oils.

Introduction

During paper production, sizing chemicals are used to hydrophobize paper. These interact with cellulose in fibers with a polar part of the molecule, whereas the apolar parts are thought to “shield” the cellulose surface and hinder water

penetration. Paper sizing agents are applied as emulsions in an aqueous polymer solution, often cationic starch. Stability of the sizes in these emulsions and efficiency of the emulsified sizing agents are two crucial factors determining appropriateness and quality of a sizing agent.

A new sizing compound was developed, which is based on vegetable oils as renewable raw materials (Lackinger et al. 2009, 2011a,b). It is produced through maleation of unsaturated fatty acid moieties, mainly oleic acid residues, in the triglyceride according to an *ene*-reaction with maleic anhydride (MAA). The maleated vegetable oil can be applied in exactly the same way as conventional alkenyl succinic anhydride (ASA). High oleic sunflower oil (SOHO) was established to be superior to all other alternative sources. The production procedure of the maleated vegetable oil, high oleic (MSOHO) was comprehensively optimized. In comparison to ASA, MSOHO has several advantages. First of all, it is a “green” raw material. Moreover, the pure high oleic sunflower oil reacts directly with MAA without the need of previous or further modifications. This means considerably reduced production costs. For comparison, to produce ASA, α -olefins have to be isomerized to internal olefins prior to the maleation step, which is a highly energy-demanding step.

A major drawback of sizing agents with a reactive anhydride group is their quick hydrolysis in the presence of water. This hydrolysis behavior is the reason why conventional ASA emulsions have to be reacted with paper within 30 min of their preparation. Otherwise, ASA will be hydrolyzed which is unfavorable for an even distribution of the sizing chemical on the cellulose fibers (Nishiyama et al. 1996a,b), as will be explained below. Another drawback of hydrolyzed ASA is its tendency to form sticky deposits with calcium ions present in abundance in the most common filler calcium carbonate (Roberts 1996).

The new, renewable-based sizing agent also has a succinic anhydride moiety as reactive group, similar to conventional ASA sizes. In general, it will also be affected by the same hydrolysis mechanisms as ASA, but owing to its different molecular structure, the reaction rates can very well be different. Isogai and Morimoto (2004) have reported that sizing efficiency and hydrolysis behavior were different for various alkyl oleate succinic anhydrides and ASA, the ethyl derivative being clearly superior to ASA at pH values of 7 and 9.

A parameter that is able to indicate the stability and usability of sizing emulsions is the zeta potential. Cellulosic fibers in an aqueous matrix are negatively charged at their surface, so sizing emulsions are “equipped” with positively charged components to provide good retention: ASA emulsions, for example, are prepared with cationic starch solu-

tions. During hydrolysis, however, the cationic surface of the ASA/starch droplets becomes more and more amphoteric due to the formed ASA acids, and with progressing hydrolysis time big agglomerates can be formed which prevent a uniform distribution of ASA molecules over the formed sheet and thus are detrimental to the sizing effect (Isogai 2000). Zeta potential can thus be a secure indicator for hydrolysis of the sizing agent which means a reduced sizing efficiency.

For comparing the sizing efficiency of different chemicals, the Stöckigt sizing degree (JIS P 8122, JIS method 1979) is a simple, effective, and reliable method. Here, the time is measured that is needed for an aqueous solution of FeCl_3 to penetrate through the paper sheet. The retention of the sizing chemical provides the link between the sizing degree and the actual amount of sizing agent in the sheet (Isogai et al. 1996; Sato and Isogai 2003).

In the present paper, results will be presented concerning the hydrolytic stability, emulsion stability, and sizing efficiency of the newly developed MSOHO sizing agent. Its performance will be compared with that of conventional ASA sizes.

Experimental

Materials

Commercial hardwood bleached Kraft pulp was beaten to 510 ml of Canadian Standard Freeness in a PFI mill. The new sizing compound (MSOHO) was prepared according to Lackinger et al. (2011b). A commercial ASA (Hydroses AS 1000) was provided by Kemira Chemie GesmbH Austria. The standard ASA (reagent grade, r.g.) was isoctadecenyl succinic anhydride from Tokyo Chemical Industry Co., Japan. Aluminum sulfate, calcium hydroxide, iron(III)chloride, and ammonium thiocyanate (Wako Pure Chemicals Co., Japan) were not further purified. Emulsion preparation was done by cationic starch HICAT 132 with a DS of 0.04 (Roquette Co., France). Methylation agent for pyrolysis-GC (Py-GC) analysis: tetramethylammonium hydroxide (TMAH) solution (25 w% in methanol) from Sigma Aldrich.

Preparation of sizing emulsions 1% cationic starch solution was prepared by heating the starch in deionized water at 95°C for 12 min. After cooling to r.t., emulsions of the three sizing agents were prepared by adding 0.5% size to the starch solution and dispersing it at r.t. with a double-cylinder homogenizer for 2 min. The sizing emulsions were kept in an ice bath or at 4°C, and sheets were prepared within 30 min of emulsion preparation, if not stated otherwise.

Preparation of hand sheets The calculated amounts of sizing emulsion (see results section) were added to a 0.15% pulp slurry with a pH of 6.7–7 under stirring at 500 rpm; for some sheets, 0.5% (wt.) aluminum sulfate per dry weight of paper was added. The basis weight of the hand sheets was 60 g m⁻², prepared according to Tappi standard T 205 om-88 (Tappi standard 1995). No filler was used. After wet pressing, the sheets were dried in a rotary drum dryer at 120°C. All sheets were conditioned for 24 h at 23°C and 50% RH before measuring the sizing degree.

Sizing with aged emulsions 0.5% ASA r.g. and MSOHO emulsions, respectively, were aged at 4°C and 25°C, and their sizing

effect was investigated after production of unfilled hand sheets using these emulsions after different aging times. To all hand sheets 0.5% alum was added. ASA r.g. was tested at 0.2% and MSOHO at 0.8% addition levels.

Instrumental analysis

Hydrolytic stability Sizing emulsions with 0.1% size content were prepared by diluting 20 g of the 0.5% stock emulsions with 80 g of deionized water. To characterize hydrolysis stability of sizing emulsions, the consumption of 0.02 M NaOH was determined at a constant pH of 7 and 9 with a pH-stat device (Auto-Titrator AUT 501, DDK-TOA Co., Japan) at 25°C.

Stability against calcium ions The sensitivity of the two ASA samples and MSOHO towards calcium ions was studied at pH 9 by means of the pH-stat device and titrating the sizing emulsions with 0.017 M $\text{Ca}(\text{OH})_2$ at 25°C.

Zeta potential For zeta potential determination, 0.0125% sizing emulsions were prepared by dilution with deionized water and measured using a Laser-Doppler electrophoresis type zeta-meter (Zetasizer 3000, Malvern Instrument Ltd., UK). The quality of the emulsion droplets with regard to shape and size was controlled with an Olympus BX51 TF Microscope (Olympus Optical Co. Ltd.) equipped with a camera and docking station (Olympus DP 20).

Stöckigt sizing degree Sizing efficiency was measured as Stöckigt sizing degree (JIS P 8122, JIS method 1979). The three sizing agents were tested with and without addition of 0.5% alum (based on dry weight of paper) under various drying conditions. After drum drying, all sheets were conditioned at 23°C and 50% RH for 24 h. Then aliquots were cured at 105°C for 10 min and the sizing degree was measured immediately. The measurement was repeated after another 24 h of conditioning.

Retention determination by pyrolysis GC (Py-GC) The retention behavior of the new sizing component (MSOHO) was investigated on a Shimadzu PYR-4A and Shimadzu GC-14B Py-GC equipped with a TC-1 column (GL Sciences Inc.) and an FID detector as previously described for ASA analysis (Isogai et al. 1996; Sato and Isogai 2003). For analysis, approximately 0.3 mg of a hand sheet sample was placed in the pyrolysis platinum pot and 0.5 µl TMAH solution was added for on-line methylation. Injection and detection temperatures were set to 450°C. The column temperature was set to 150°C and was increased at 5°C min⁻¹ to 300°C.

Results and discussion

Hydrolysis of emulsions

All three sizing agents tested are susceptible to hydrolysis, which is evident owing to their reactive succinic anhydride residues. At pH 7, the commercial ASA and the MSOHO size were more stable against hydrolysis than ASA r.g. At increased pH (pH 9), the hydrolysis was accelerated for all sizing agents, but clear differences were observed. MSOHO proved to be the most stable compound, followed by commercial ASA and ASA r.g. Hydrolysis kinetics was measured between 2 and 14 h.

Mathematical analysis of the curves proved a zero-order rate law for the hydrolysis, i.e., an independence of the actual

concentration. This allowed the conclusion that the hydrolysis rate of the sizing agent in the starch emulsion is only influenced by the diffusion of water into the emulsion droplets, and is thus determined by shape and size of the micelles. The calculated hydrolysis rate constants are presented in Table 1, concerning the three sizes prepared at pH 7 and pH 9, and again at pH 9 in the presence of Ca^{2+} . All sizing agents responded to an increased pH of the aqueous medium with accelerated hydrolysis, e.g., a higher rate constant was observed. For both titration tests with NaOH, the MSOHO had the lowest rate, i.e., the highest stability against hydrolysis. In view of the fact that non-hydrolyzed and reactive sizing agents are needed, this characteristic is a benefit with regard to application in paper mills, which are run at neutral to slightly alkaline pH.

Sensitivity towards calcium ions

In conventional papermaking, the filler calcium carbonate is widely used. The bivalent calcium ions have a high disposition to form sticky deposits with ASA-like sizing agents. This process is comparable to the formation of precipitates from conventional soap solutions by the calcium ions present in water.

The hydrolysis behavior of the sizes was tested at pH 9 with 0.017 M $\text{Ca}(\text{OH})_2$ as titrant solution. Upon calcium addition, the concentration of r.g. ASA dropped rather fast, whereas ASA and especially MSOHO proved to be more stable (Figure 1). Also for this hydrolysis type, the reaction rate constants were calculated (reaction times: between 2 and 14 h for MSOHO and ASA, between 2 and 4 h for r.g. ASA). The data are displayed in Table 1.

Adding $\text{Ca}(\text{OH})_2$ solution to the 0.1% sizing emulsions at pH 9 further eroded the stability of the ASA sizing agents compared to hydrolysis solely with NaOH at the same pH. For the r.g. ASA, a ten-fold higher reaction constant was found when titrating at pH 9 with $\text{Ca}(\text{OH})_2$ instead of NaOH.

Table 1 Hydrolysis rate constants for ASA and MSOHO at pH 7 and 9.

Reaction conditions	Zero reaction order $c(t) = -k \cdot t + c_0$ k (mmol l ⁻¹ h ⁻¹)
pH 7	
ASA r.g.	0.017
ASA Hydrores AS 1000	0.009
MSOHO	0.006
0.02 mol l ⁻¹ NaOH consumption ^a	
pH 9	
ASA r.g.	0.074
ASA Hydrores AS 1000	0.068
MSOHO	0.049
0.02 mol l ⁻¹ NaOH consumption ^a	
pH 9+Ca(OH)₂	
ASA r.g.	0.742
ASA Hydrores AS 1000	0.135
MSOHO	0.035
0.017 mol l ⁻¹ Ca(OH) ₂ consumption ^a	

^aBasis for calculation.

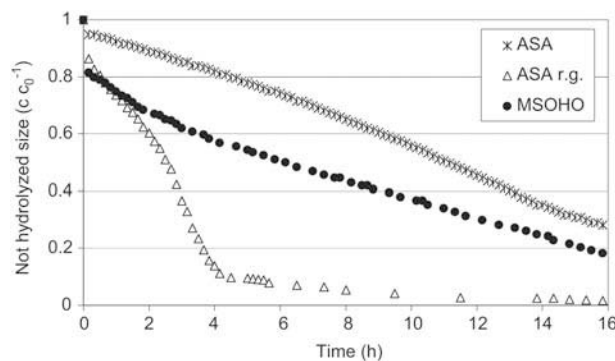


Figure 1 Hydrolysis at pH 9 titrated with $\text{Ca}(\text{OH})_2$ at 25°C. (Comment: the first drop within 10 min is due to setting the pH and thus not relevant for the hydrolysis behavior).

Also for commercial ASA, the rate constant doubled. For MSOHO, the reaction constants at pH 9 were in the same range independently of whether NaOH or $\text{Ca}(\text{OH})_2$ solution was used; the reaction constant for the $\text{Ca}(\text{OH})_2$ titration of MSOHO was even smaller than that for the NaOH titration. This behavior could be explained by the built-up of hydrophobic MSOHO calcium salts on the surface of emulsion droplets during titration. This effect additionally slows down the access of water molecules to non-hydrolyzed MSOHO in the interior of the droplets. The high hydrophobicity of ASA calcium salts has been proven (Wasser and Brinen 1998). Another explanation for the reduced hydrolysis rate in comparison to commercial ASA samples might be the higher viscosity of MSOHO. Whereas ASA has a viscosity from 100 to 250 mPas, the viscosity of the MSOHO sample amounts to 3400 mPas. In combination with the hydrophobic salt deposit on the droplet surface, the higher bulk viscosity further decreases the probability that water finds access to intact MSOHO molecules in the inner parts of the droplets.

These results clearly demonstrate the superiority of MSOHO against ASA with regard to hydrolytic stability. In particular, the insensitivity towards calcium ions is a clear advantage of the reagent with regard to practical application. As CaCO_3 is by far the most common filler in paper production, a sizing agent that is less sensitive to Ca^{2+} ions is of immense advantage, because it reduces the tendency of deposit formation and related problems in the paper machine.

Zeta potential measurements

Directly after production of sizing emulsions based on sizing agents and cationic starch, the zeta potentials of these emulsions were clearly positive (+35 mV), as expected. In the course of time, sizing compounds are progressively hydrolyzed, the surfaces of the emulsion droplets become more amphoteric, and the zeta potential decreases. When the samples were stored at 4°C, the zeta potentials stayed constant for at least 48 h, but clearly decreased after 1 week (Figure 2a). Storing the emulsions at 25°C caused an immediate and gradual decrease in potentials (Figure 2b). MSOHO was more stable than both ASA samples. The slower hydrolysis was thus reflected in the decelerated decrease in zeta poten-

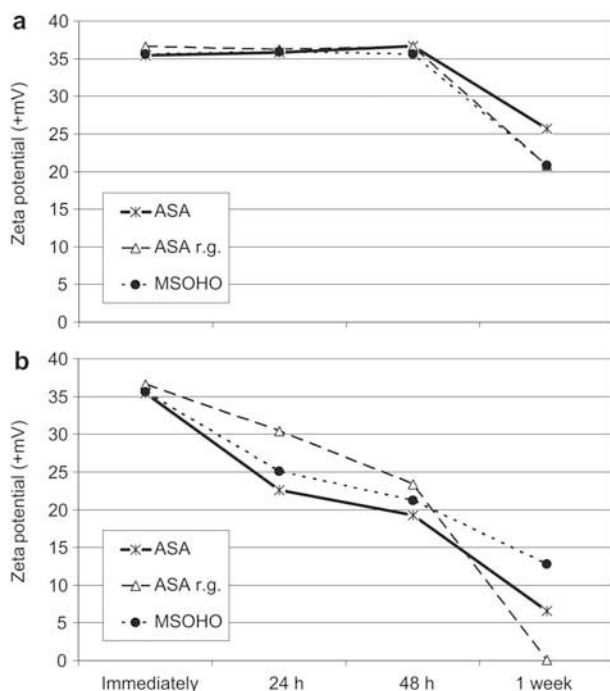


Figure 2 Zeta potentials of (a) 0.5% sizing emulsions stored at 4°C and (b) 0.013% sizing emulsions stored at 25°C.

tial. The slower formation of carboxylate groups within MSOHO emulsion droplets slowed down the formation of amphoteric (less positive) droplet surfaces.

Emulsion shape

The emulsion shapes were controlled by microscopic analysis. There was hardly any difference between the ASA and MSOHO emulsion that were freshly prepared or stored for 24 h (Figure 3a, a', b, and b'), and no significant difference in droplet size was detected. The formation of agglomerates in the presence of calcium ions was visible for both sizing agents, but it was much less pronounced for the novel MSOHO reagent (Figure 3c, c'), a finding, which is in line with the above results on stability in the presence of Ca^{2+} .

Sizing degree

All three sizing agents were tested for their sizing efficiency measured by the Stöckigt sizing method (JIS P 8122, JIS method 1979) under various conditions. The Stöckigt degree takes the time for a FeCl_3 solution to penetrate through the sheet as a gauge for sizing efficiency. The higher the Stöckigt sizing degree in seconds, the better is the paper sizing. With r.g. ASA, sizing was possible with the addition of only 0.2% ASA (see Figure 4a). The addition of alum clearly increased its sizing efficiency by approximately 10 s in the Stöckigt test, whereas curing did not have a significant influence. Commercial ASA sizing without alum and without curing was only observed at dosages of 0.4% ASA level or higher (Figure 4b). The addition of alum, however, enabled sizing already at degrees of 0.2%. Curing had no additional bene-

ficial effect when alum was added. Also, curing without alum addition was advantageous, but only at 0.4% level and above.

The MSOHO reagent alone showed less sizing efficiency (Figure 4c); sizing was impossible even at an addition level of 0.8%. By contrast, good results were obtained upon co-addition of alum. Curing the MSOHO sheets without alum had a far more positive effect than in the case of curing the sheets with ASA without alum and r.g. ASA without alum. It can thus be stated that utilization of the MSOHO reagent is best with alum addition and subsequent curing.

Testing sizing efficiency within 30 min after emulsion preparation yielded the following results: sizing with MSOHO and alum addition is necessary to achieve good sizing degrees within reasonable addition levels. This was not so urgently needed for ASA and has an even smaller effect on r.g. ASA. As stated by Isogai (2000), ASA-like sizing agents might need alum for a better distribution of sizing agent throughout the paper web. This seems to be of even higher importance for MSOHO. With a 10-times higher viscosity than ASA, MSOHO might be more dependent on a strong mediator between the amphoteric emulsion droplets and the negatively charged cellulose fibers. Orientation and spreading of MSOHO on the cellulose fibers might also be influenced by Al^{3+} ions.

The Stöckigt sizing degree (JIS P 8122, JIS method 1979) is a somewhat sensitive method. Small unsized spots on the sheet lead to far smaller sizing degrees. Thus, this method is also very responsive towards non-uniformly distributed sizing agent. For MSOHO sheets, it was observed that in the absence of alum weakly sized spots are scattered sometimes in well-sized areas. Evidently, an absolutely even spread on the paper is harder to realize for MSOHO than for ASA under the tested paper sheet forming conditions. This can be explained by the higher viscosity of MSOHO. The negative effect was completely overcome if sheets were cured or if alum was added, as demonstrated.

In a previous paper (Lackinger et al. 2011a), sheets sized with MSOHO and with maleated rapeseed oil (MRSO) already showed good sizing results for an addition between 0.6% and 0.8% without addition of alum. Quantification of the sizing degree was done according to the Cobb method (DIN 53 132, DIN standard 1990), which determines the water (in g m^{-2}) retained in the sheet after certain soaking time. The Cobb test is less sensitive to small structural differences in the sheet compared to the Stöckigt method. This is the reason why the sheets sized with MSOHO and MRSO yield satisfying Cobb values at lower addition levels and without alum, whereas satisfying Stöckigt values required higher sizing levels and alum addition.

Retention

The retention of the sizing agent on the paper was measured with Py-GC. When the addition level of MSOHO was increased from 0.4% to 0.6% and to 0.8%, the measured values by Py-GC for the relative retention were also higher. MSOHO (0.8% sizing) was retained on the sheet to the same extent, independently of whether alum had been added or

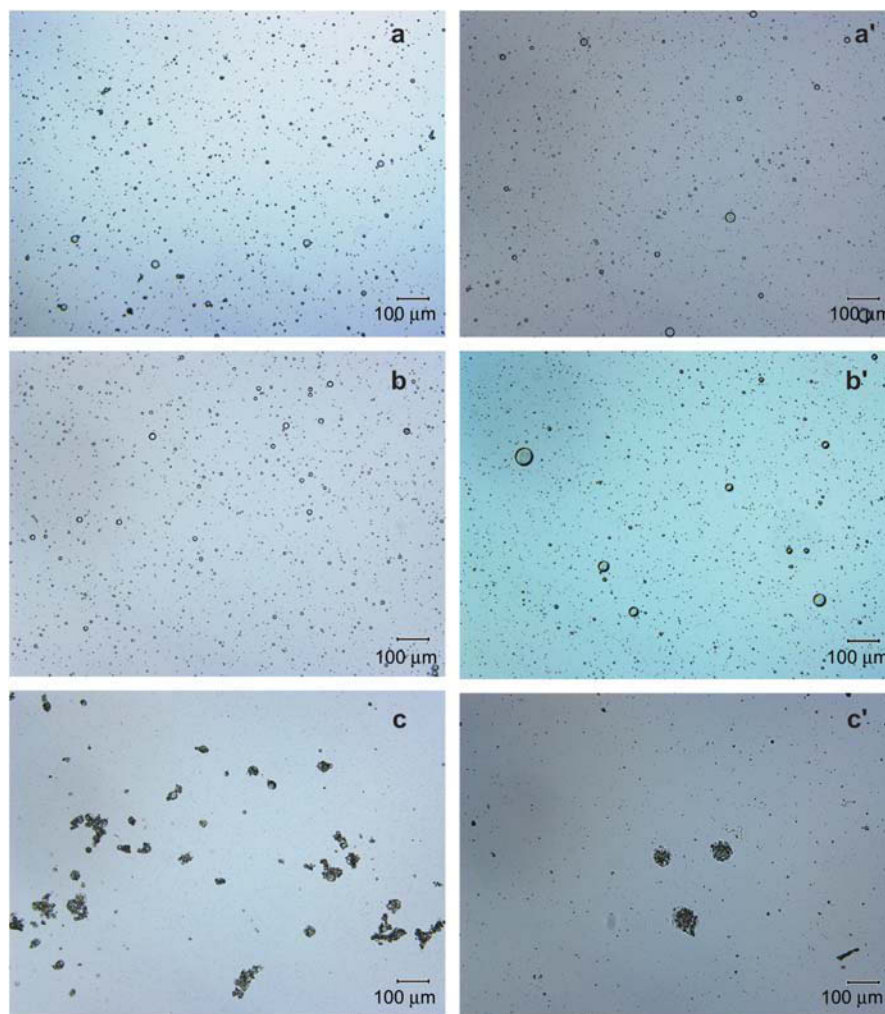


Figure 3 Sizing emulsions a, b, c (ASA) and a', b', c' (MSOHO) on day of preparation (a, a'), 24 h after preparation (b, b'), and after titration with $\text{Ca}(\text{OH})_2$ (c, c').

not. However, the increase in the retention went parallel with the increase in Stöckigt sizing degree only in the case of alum addition (Figure 5). Without alum or curing, sheets did show reagent retention, but they were not sized. Thus, it is not only necessary to provide MSOHO sizing molecules to the paper sheets. To prevent water from entering or penetrating through the sheet, a certain orientation or arrangement has to be adopted, which is brought about by the mediator alum and further improved by thermal curing.

Sizing with aged emulsions

The comparison of sizing efficiency of aged r.g. ASA and MSOHO emulsions once more proved the higher stability of MSOHO emulsions and pointed out a huge practical advantage of the MSOHO size: after storage for 1 day at 25°C no sizing at all was possible in the case of the r.g. ASA emulsion, whereas the MSOHO emulsion still was capable of providing some water repellency to the produced hand sheets (Figure 6). Upon storage at 4°C, the sizing efficiency for both emulsions was maintained over 1 day.

An interesting additional effect was seen for sizing with MSOHO emulsions. The sizing efficiency increases after storage for 2 h. It did not even matter at which temperature the emulsions were kept over this time range. For r.g. ASA nothing similar could be observed. This special MSOHO characteristic might originate in its higher resistance against hydrolysis. As was supposed by Isogai et al. (1996), an amphoteric surface of the sizing emulsion droplets is needed to provide sufficient retention and distribution of the size throughout the paper sheet. Whereas r.g. ASA hydrolyses rather fast and can build up this amphoteric surface during emulsion production or a few minutes later, MSOHO hydrolysis is significantly slower. Therefore, it takes a few hours until a sufficient amount of MSOHO molecules at the droplet surface is hydrolyzed to build up the amphoteric surface required for optimum retention and distribution.

The higher viscosity of MSOHO is advantageous when it comes to emulsion and hydrolytic stability. Sizing was still possible with an almost 30-h-old MSOHO emulsion, whereas no sizing effect was observed for an ASA sized sheet produced under the same conditions. Owing to the high vis-

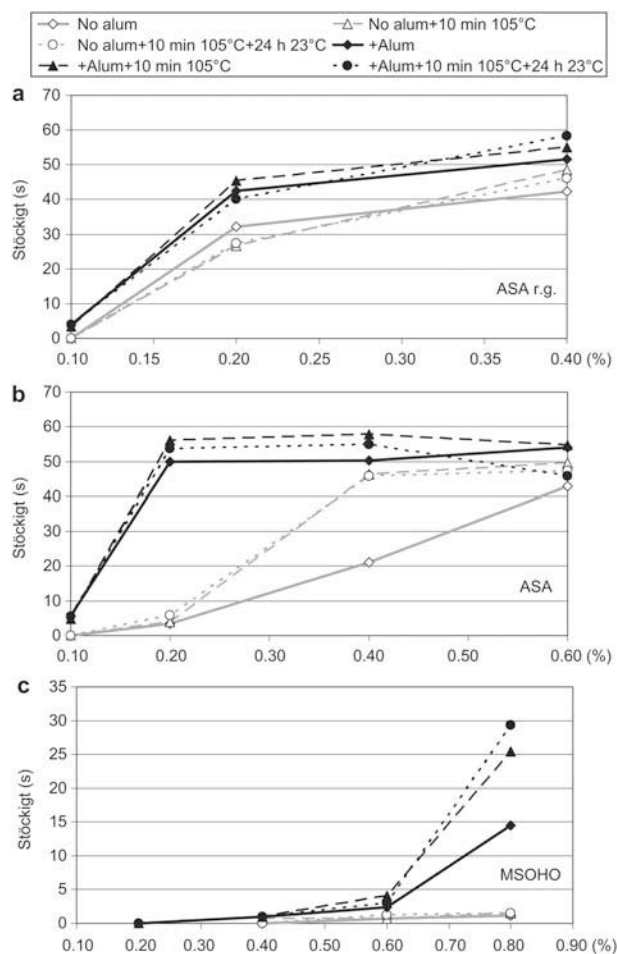


Figure 4 Influence of alum and different curing conditions on sizing efficiency of (a) ASA r.g., (b) ASA, and (c) MSOHO.

cosity, the MSOHO emulsion droplets are only slowly hydrolyzed from the surface. Inside the droplet, enough reactive MSOHO remains to provide hydrophobicity to the hand sheet.

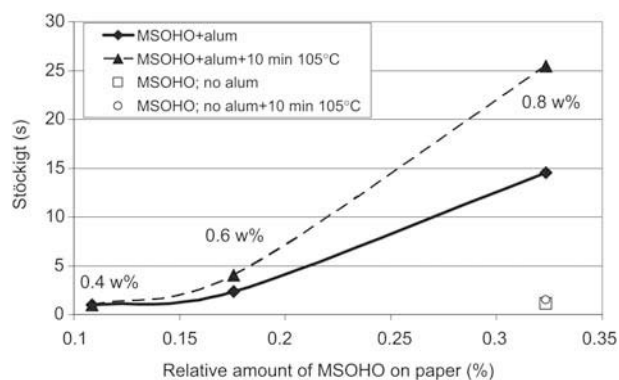


Figure 5 MSOHO: relative amount on paper (from Pyrolysis GC) vs. sizing degree for different sheet forming conditions.

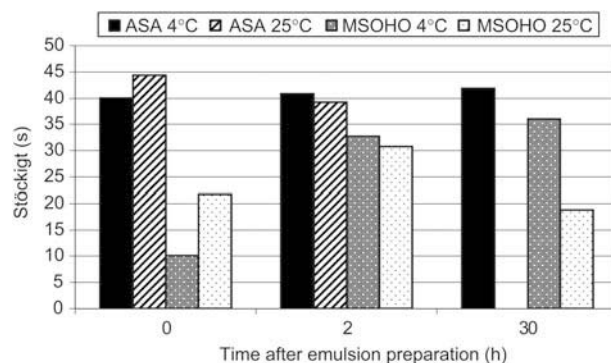


Figure 6 Development of the sizing efficiency of ASA and MSOHO emulsions stored at 4°C and 25°C with time.

Conclusions

The characteristics of a new sizing agent that is based on renewable raw materials were investigated in comparison to ASA. It is produced according to an *ene*-reaction mechanism by maleation of high oleic sunflower oil. MSOHO is a green alternative to conventional ASA for paper sizing. Production costs for MSOHO are lower than for ASA, because in the latter case a thermal isomerization step of α -olefins to internal olefins is required. High oleic sunflower oil can be maleated without such a treatment. Also, the local availability of the vegetable oil and the resulting low transportation costs contributes to its ability to compete.

Compared to ASA, the MSOHO size has a reduced sizing efficiency. This effect, however, is canceled out by adding alum, which acts as a mediator between the negatively charged cellulose fibers and the amphoteric sizing emulsion particles. Curing additionally helps spreading the sizing agent evenly and therefore increases its sizing efficiency.

This study proves that the sizing agent MSOHO has some interesting beneficial properties compared to commercial ASA and reaction grade ASA. Owing to its higher stability against hydrolysis, sizing is possible over a much longer time range than with ASA or r.g. ASA. MSOHO is also less affected by the presence of Ca^{2+} ions, which reduces the risk of deposit formation in the paper mill.

Hydrolysis behavior and emulsion stability of MSOHO, its practical application and its combination with other sizing agents will be topics of the upcoming parts in this series.

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Novel paper sizing agents based on renewables. Part 4: Application properties in comparison to conventional ASA sizes

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Abstract

Reactive paper sizing agents, such as alkenyl succinic anhydride (ASA), provide hydrophobicity to paper. The reactive anhydride group of these reagents is highly susceptible to reaction with water and thus resistance against hydrolysis is of primary importance for their practical application. This study describes different application-relevant properties of recently developed sizing agents that are based on renewable vegetable oils including hydrolysis behavior, time-dependent sizing efficiency, and tendency to form deposits or foam. The novel sizing agents – maleated high oleic sunflower oil (MSOHO) and maleated rapeseed oil (MRSO) – are compared to conventional ASA as the state-of-the-art sizing agent. Although the reactive group is the same in all reagents, there are pronounced differences between the three reagents, with MSOHO showing the best performance, i.e., the slowest hydrolysis. This oil has a higher ratio of hydrophobic side chains that impede the water attack at the anhydride group. Also, the higher viscosity of MSOHO plays an important role in performance, because diffusion of water molecules into a MSOHO emulsion droplet is much slower than in the case of conventional ASA.

Keywords: alkenyl succinic anhydride (ASA) sizing; green chemistry; hydrolysis; maleated oils; maleated high oleic sunflower oil (MSOHO) sizing; paper sizing; renewable resources; vegetable oils.

Introduction

To enhance the resistance of paper against water, sizing agents are added before sheet formation in paper production.

This process is referred to as internal sizing. For a long time, the most common internal sizing agents have been synthetic reactive sizing agents, such as alkenyl succinic anhydride (ASA) and alkylketene dimer (Roberts 1996). In many applications ASA is preferred because of its shorter curing time and higher cost efficiency. Recently, we reported the development of a new sizing agent that can replace ASA, since ASA is fully derived from petrochemicals. The driving force behind this research is the increasing demand for “greener” sizing agents based on renewable resources and the increased cost of petrochemicals in the long run. In previous accounts in this series (Lackinger et al. 2010a,b), we communicated the use of maleated rapeseed (MRSO) and maleated high-oleic sunflower oil (MSOHO) as novel, renewable-based ASA substitutes. The optimized production procedure for maleated fatty oils was reported. It was investigated which natural vegetable oils are best suited as starting materials and the obtained products were submitted to an in-depth characterization.

Based on their molecular structure containing the reactive anhydride moiety (Figure 1a), ASA, MRSO and MSOHO are prone to hydrolysis when in contact with water. In this process, the succinic anhydride group is converted into succinic acid (Figure 1b). In applications related to internal paper sizing, the reactive sizing agents are dispersed in a cationic polymer solution, e.g., cationic starch, prior to their addition to the paper stock. In the case of conventional ASA, it is well known that the resulting emulsions have to be used within minutes – otherwise the sizing efficiency will decrease significantly and eventually even be lost due to an increasing content of hydrolyzed sizing agent, which does not contribute to sizing (McCarthy and Stratton 1987; Nishiyama et al. 1996). Accordingly, ASA emulsions must be continuously prepared on-site and have to be added to the stock immediately after preparation. In a related account, Iso-gai and Morimoto (2004) reported sizing efficiency and hydrolysis behavior of different alkyl oleate succinic anhydrides to be enhanced compared with ASA.

Partly hydrolyzed ASA also has the tendency to form detrimental deposits. As paper machines do not retain fibers and chemical additives completely, some of the added ASAs will be released into the white water, where they circulate, hydrolyze completely, and accumulate. Then it forms sticky calcium salt deposits, with the cation calcium being derived from calcium carbonate as the most commonly used filler (Roberts 1996).

The present paper focuses on characteristics crucial for the practical application of these reactive sizing agents in paper mills: the deposit-forming behavior, long-term sizability

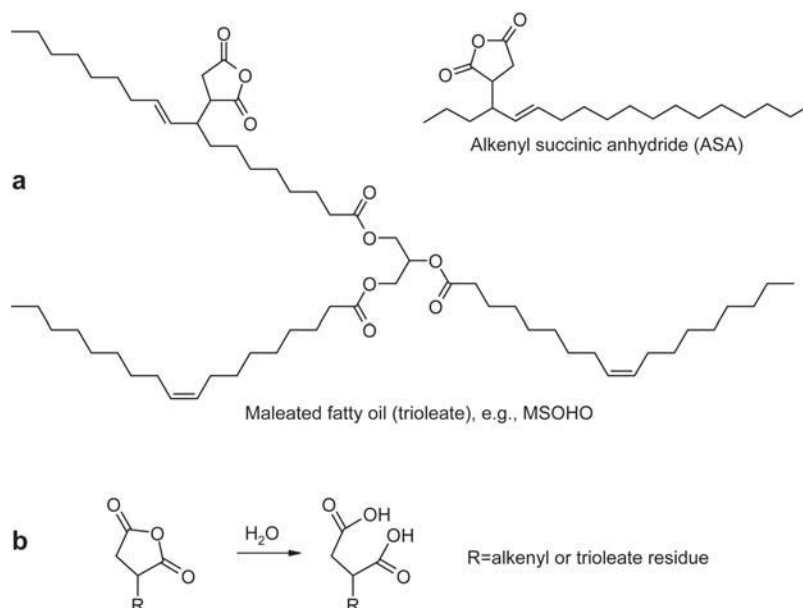


Figure 1 (a) Molecular structures of maleated fatty oil and alkenyl succinic anhydride. (b) Hydrolysis of the succinic anhydride group.

properties, and hydrolysis behavior. The new sizing agents MRSO and MSOHO will be compared with conventional ASA as a state-of-the-art sizing agent. The paper will show that there are surprising differences between these sizing agents, despite the identity of the reactive groups in all of them. The different performances will be discussed in terms of different molecular structures and viscosities of the reagents.

Material and methods

Source of chemicals

Commercial ASA samples (Hydrores AS 1000 and Hydrores AS 3000): Kemira GesmbH, Austria. Butylated hydroxytoluene (BHT, di-*tert*-butyl-hydroxytoluene), purity > 99%: Sigma Aldrich, Austria. Butylated hydroxyanisole (BHA, *tert*-butyl-hydroxyanisole), food grade: Eastman Chemical Company, USA. 4% Cationic starch HICAT 5103A from Roquette Co., France was used for emulsion preparation. Other chemicals: veratrylamine (3,4-dimethoxybenzylamine, 97%, Sigma Aldrich, Austria), *ortho*-phosphoric acid (p.a., Merck, Germany), sulfuric acid (95–97%, Merck, Germany), sodium sulfate (analytic reagent, VWR, Austria). Acetonitrile, diethyl ether, toluene, and tetrahydrofuran (all HPLC grade) were purchased from Fisher Scientific GmbH, Austria. Ethanol (abs.) was purchased from VWR, Austria and acetone (techn.) from Brenntag CEE GmbH, Austria.

Fatty oils (rapeseed and high oleic sunflower oil) were from C. Thywissen GmbH, Germany and maleic anhydride of synthesis grade was from Merck, Germany. The maleated oils were produced as described in Part 1 of this series (Lackinger et al. 2010a). The abbreviations MRSO and MSOHO are used for maleated rapeseed and maleated high oleic sunflower oil, respectively.

Preparation of hand sheets

A paper stock solution from commercial bleached kraft pulp with 2% dry content consisting of 30% short fiber and 70% long fiber

was beaten to 30°SR (ISO 5267-1; ISO 1999). The standard stock solution was prepared by diluting the 2% paper stock solution to 1% dry content. The solution contained 1% fibers and 0.25% ground calcium carbonate. MSOHO and MRSO for sizing tests contained 1% (wt) emulsifier (Imbentin-T/400 G, Dr. W. Kolb AG, Switzerland).

Sheet former: Rapid-Köthen (Type G8-E, Gockel & Co. GmbH, Germany). In a first step, 1% of the tested sizing agent was emulsified in a carrier polymer solution (4% cationic starch in water) with an Ultra-Turrax homogenizer (IKA Werke GmbH & Co. KG, Germany) for 2 min at 10 000 rpm at 70°C. This emulsion was diluted 1:10 with deionized water. The respective amounts of the diluted emulsion were added to approximately 190 g of standard stock solution to form sheets with a basis weight of 70 g m⁻². As retention aid 4.6 ml of Fennopol (0.01%, cationic polymer, K 3400R from Kemira Oyj) was used for each sheet.

The freshly prepared sheets were dried in the drum dryer at ~115°C at a speed of approximately 1 turn/40 s. After this treatment the Cobb₆₀ values were measured for ASA immediately, whereas the MSOHO and MRSO sheets were additionally cured at 125°C for 10 min.

Production of hydrolyzed sizing agents

Hydrolyzed sizing agents, required as standards for HPLC analysis as well as for the foam tests, were produced by dispersing 15–20 g of sizing agent in approximately 100 ml of deionized water with an Ultra-Turrax at 10 000 rpm for 2 min at 70°C. This emulsion was kept at 70°C for 2 h, cooled down to room temperature (r.t.) and acidified with 1 N H₂SO₄. The hydrolyzed size was extracted with diethyl ether, the organic phase dried over Na₂SO₄, and the solvent evaporated.

Progress and completion of the hydrolysis reaction can be readily controlled with ATR-IR. Characteristic IR bands for pure ASA (Hydrores AS 1000) are found at 1862 cm⁻¹ and 1781 cm⁻¹ for the asymmetric and symmetric vibration of the C=O in the succinic anhydride residue, whereas for hydrolyzed ASA the characteristic C=O vibration of the succinic acid residue is found at 1703 cm⁻¹.

Deposit testing

In a conventional kitchen mixer equipped with a heating system, 1.5 kg of standard stock solution (containing 1% fiber and 0.25% ground calcium carbonate) was stirred at 50°C for 3 h after the addition of 15 g of pure sizing agent. The stock solution was removed after the test and the bowl was carefully rinsed with water. The residues were analyzed with ATR-IR and photographs were taken.

Attenuated total reflection: IR spectroscopy

Instrument: AVATAR 370 FT-IR device with a Smart DuraSample IR probe head (Thermo Nicolet Corporation, USA). The spectra were analyzed by means of the Omnic 6.2 software package (Thermo Nicolet Corp., 1992–2001). One drop of the neat substance was placed on top of the probe head and the measurement was started immediately.

Quantification of foaming tendencies

For the preparation of the sizing agent emulsion, 3 g of sizing agent were mixed with 97 g of cationized starch (4% HiCat 5103A) at 70°C and 10 000 rpm for 2 min with an Ultra-Turrax. The emulsion was poured into a graduated cylinder (1 l) and nitrogen was flushed through at a rate of 10 l h⁻¹ with a glass frit at the bottom. After 1 and 2 min, the foam heights were measured. The frit was removed after 2 min and the foam height measured again after 3 min.

Particle size measurement

Particle size of emulsion droplets were measured with Sympatec Helos BA equipped with a Succell CL (both Sympatec GmbH, Germany), based on static light scattering. The reported D90 values mean: 90% of all measured particles are smaller than this value.

Water absorption, Cobb₆₀

The Cobb₆₀ value determination (DIN 53 132; DIN 1990) was described in Part 1 of this series (Lackinger et al. 2010a).

HPLC quantification of the additives and their hydrolysis products

HPLC system: Hitachi High Technologies Corporation (Tokyo, Japan) consisting of an L-2130 quaternary gradient pump, autosampler L-2200, UV-detector L-4250 at 230 nm, and degasser DG-2410 (Degasys, Uniflows CO., LTD., Tokyo, Japan). The aliquots from the hydrolysis experiments were extracted with 1 N H₂SO₄ and diethyl ether (v/v = 1:1). The organic phase was removed and dried over Na₂SO₄. After removal of the drying agent by filtration, the solvent was evaporated and the oily residue was prepared for HPLC measurement according to the OSHA method # 90 (OSHA 1991) as follows. A sample aliquot (150–300 mg) was weighed into a volumetric flask. Veratrylamine (approximately 150–250 mg) was added and the flask was filled up with the solvent (for ASA: acetonitrile; for maleated oil: diethyl ether/acetonitrile/ethanol, v/v/v = 2:2:1). A Supelcosil C₈ column (Supelco, Supelcosil LC-8 58297, 25 cm × 4.6 mm ID 5 μm) was used in combination with the following solvents and binary/ternary gradient systems at a flow rate of 2 ml min⁻¹: A: acetonitrile HPLC grade; B: deionized H₂O + 0.1% *ortho*-phosphoric acid; C: ethanol abs. Gradient program for ASA: start: 15% A, 85% B; during 7 min to: 30% A, 70% B; from 7.1 to 14 min: 80% A, 20% B. Gradient program for maleated vegetable

oils: start: 15% A, 85% B, 0% C; during 5 min to: 80% A, 20% B, 0% C; until 5.1 min to: 75% A, 5% B, 20% C; until 8.5 min to: 65% A, 5% B, 30% C; until 9.5 min to: 49% A, 5% B, 46% C; until 10.5 min to: 10% A, 5% B, 85% C; hold until 14.5 min; from 14.6 to 20 min: 15% A, 85% B, 0% C.

Hydrolysis of sizing agents in homogeneous phase

ASA (0.414 g) or MSOHO (0.873 g) were weighed into a 100 ml volumetric flask together with 16.4 g of water (800-fold excess). The mixture was filled up to the mark with tetrahydrofuran (THF). After mixing, the solution was transferred into a pressure reactor (452HC Parr Instrument Company, USA), heated up to 70°C, pressurized with Argon up to ~4 bar, and stirred for 300 min. Samples were taken: 1 ml of the THF solution (containing approximately 4.1 mg of ASA or 8.7 mg of maleated oil) was transferred to an Autosampler vial with 1 drop veratrylamine (50 mg), mixed, and analyzed by the described HPLC method.

Viscosity

Instrument: Rota viscosimeter (Rheometer MC1, Anton Paar GmbH, Austria) at 20°C and a shear rate of 50 s⁻¹.

Results and discussion

Deposit tests

Retention of fibers and additional chemicals in paper machines is never complete. In addition, an ASA starch emulsion is not completely discharged together with the produced paper. As pointed out in the Introduction, a part of it remains in the water circuit, hydrolyzes and reacts with Ca²⁺ ions that originate from ground CaCO₃, which is the most common filler in modern paper production. The Ca salts of ASA form sticky deposits can cause severe problems for various machines in the paper mill. To predict the tendency towards deposit formation for ASA and MSOHO, a heated mixer was used to simulate circulating sizing agent in contact with paper stock.

The yellowish precipitates formed looked rather similar and had a pasty consistency (Figure 2). ATR-IR analysis of the precipitates showed characteristic bands for the calcium salt of hydrolyzed ASA at 1552, 1640, 1707, 2852, and 2921 cm⁻¹ and at 1554, 1741, 1783, 2852, and 2921 cm⁻¹ for the calcium salt of hydrolyzed MSOHO. Whereas ASA was quantitatively hydrolyzed, only smaller amounts of hydrolyzed MSOHO were detected in addition to unchanged MSOHO in the bulk phase of the deposits. It was thus concluded that MSOHO hydrolyses slower than ASA, which is beneficial for a sizing agent.

Foam tests

The avoidance of foam in the paper machine is mandatory for highly efficient paper production. Thus, the foaming tendencies of ASA and MSOHO emulsions and their hydrolyzed forms were tested. Foam formation was induced by flushing with nitrogen through a glass frit and reached the maximum after approximately 2 min. After stopping the



Figure 2 Deposits from sizing agents. Left: from ASA, right: from MSOHO.

flushing, the foam height quickly decreased. Both additives behaved similarly in the foaming test (Table 1). Whereas hydrolyzed MSOHO emulsion behaved like the original MSOHO, it was remarkable that hydrolyzed ASA formed a gel when emulsified in starch solution. On the one hand, this gel-like emulsion did not foam, but on the other hand, it would have been impossible to use it as sizing emulsion due to its very high viscosity.

Hydrolysis in starch solution

As stated in the Introduction, ASA emulsions are generally prepared on-site and are continuously fed to the paper stock to provide sizing. The limited hydrolytic stability makes it impossible to store ASA emulsions, even for a few hours. To learn about the hydrolytical stability of MRSO and MSOHO, cationic starch-based sizing emulsions were prepared and stored at 70°C under stirring. Paper sheets were continuously formed using that size and the sizing characteristics were determined (Table 2).

In the case of ASA, sizing was only effective during the first 10 min, after which the sizing efficiency dropped dramatically resulting in uselessly high Cobb₆₀ values that exceeded 30 g m⁻². These results prove the very weak stability of ASA against hydrolysis. With MRSO as the sizing agent, sufficient sizing was still provided after 15 min, in the case of MSOHO even after 30 min (Table 2). The latter result is remarkable as sizing efficiency is retained three times longer than in the ASA case. These results are seen as an additional support for the fact that MSOHO has superior hydrolytic resistance compared to ASA (see also Lackinger

Table 2 Sizing with emulsions of different ages.

Time (min)	Water absorption as Cobb ₆₀ values		
	ASA (g m ⁻²)	MRSO (g m ⁻²)	MSOHO (g m ⁻²)
0	25 (2 min)	28	25
15	23 (10 min)	31	25
20	63		
30	78	110	29
60			87

et al. 2010c). The prepared emulsions have particle sizes of 2.98 μm (MRSO), 2.57 μm (MSOHO), and 4.49 μm (ASA). As a consequence, the higher hydrolytic stability of MSOHO cannot be attributed to a possible bigger size of its particles. The later discussed chemical and viscosity effects could explain its hydrolysis stability better.

Hydrolysis in water

To eliminate possible effects of the stabilizing agent (cationic starch), the hydrolysis rates of ASA, MRSO, and MSOHO were also determined in pure water in a 1:5 (w/w) ratio. These mixtures were emulsified at 70°C and then stirred at this temperature, while taking aliquots for HPLC analysis. The resulting hydrolysis curves are presented in Figure 3. In the range of 100 down to approximately 30% active sizing agent, an approximated zero-order rate was found for the reaction of all sizing agents. Thus, the hydrolysis was independent of the concentrations of either reactant (sizing agent or water), but was governed by another phenomenon. It can reasonably be assumed that the diffusion of water into the size droplet is decisive. As the reactants are immiscible, water molecules are only able to react with the anhydride groups after having diffused into the emulsion droplets. This could be increasingly hindered by higher viscosity and higher hydrophobicity. Whereas MRSO and MSOHO have rather high viscosities (approximately 7500 and 1000 mPas), ASA tends to have a rather low one (100–250 mPas).

The half-times of the hydrolysis reaction were calculated from the linear regression fits in the range of approximately

Table 1 Foam test of ASA and MSOHO emulsions.

Sizing agent	Foam height after 1, 2, and 3 min		
	1 min (ml)	2 min (ml)	3 min (ml)
ASA	30	50	30
Hydrolyzed ASA	Gel	Gel	Gel
MSOHO	40	50	40
Hydrolyzed MSOHO	40	50	30

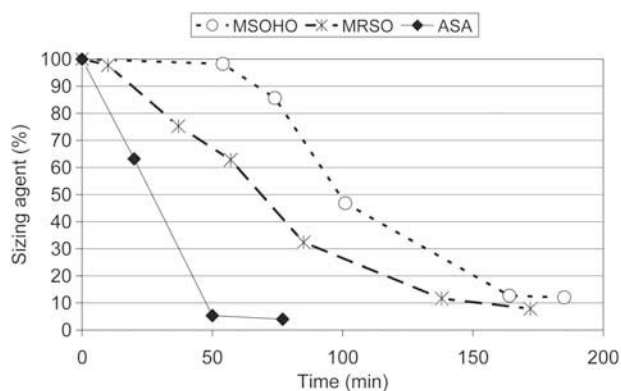


Figure 3 Hydrolysis of the sizing agents dispersed in water at 70°C; ○ MSOHO, ◆ ASA, *MRSO.

30–100% active size. They varied from 27 min for ASA over 67 min for MRSO and 100 min for MSOHO.

To cancel out all diffusion phenomena and other physical effects on the hydrolysis rate, the reaction was studied in organic solution. THF proved to be a good solvent, as THF and water are miscible and all sizing agents are properly soluble in a THF-water mixture. The concentration of sizing agents was set to give the same molar concentration (0.14 mmol l^{-1}) of reactive anhydride groups in solution. The succinic anhydride content per triglyceride is measured according to the analytical methods described in Part 1 of this series (Lackinger et al. 2010a).

The results of the hydrolysis tests in THF solution are presented in Figure 4 for MSOHO and ASA. As expected, the hydrolysis rates were of pseudo-first order, the reaction rate being only dependent on the concentration of the sizing agents. Also here, the half-times were calculated based on the linear regression of the $\ln(c/c_0)$ vs. t plot, and they were rather similar: 86 min for MSOHO and 80 min for ASA, with reaction constants being 0.486 h^{-1} and 0.522 h^{-1} for MSOHO and ASA, respectively. The reaction rate is now exclusively determined by the chemical reactivity of the reaction center, which is in all cases the succinic anhydride moiety. The influence of the molecule to which the succinic moiety is anchored will be rather small. Nevertheless, MRSO

showed two anhydride moieties of slightly different reactivities with similar half-times. The reason for the two different reactivities in the case of MRSO is currently under study.

Conclusions

In the deposit test, where the sizing agents were in contact with stock solution in the presence of calcium ions, the MSOHO showed an increased stability against hydrolysis as compared to conventional ASA. At prolonged times, MSOHO also formed sticky calcium salt deposits as did ASA. Concerning the little foaming tendencies of MSOHO and ASA starch emulsions, no differences were found. Hydrolyzed ASA formed a gel under the given conditions that did not allow further application due to high viscosity, whereas in the case of hydrolyzed MSOHO a neat emulsion was formed that had the same foaming characteristics as the original MSOHO emulsion.

With MSOHO emulsions that were aged at 70°C, well-sized papers could be produced even after 30 min, whereas for the aged ASA emulsion this was only possible until 10 min. This higher resistance of MSOHO against hydrolysis in an aqueous emulsion environment was confirmed by tests conducted in aqueous dispersions at 70°C, the half-life for MSOHO being four times that for ASA. In emulsions and dispersions, the crucial factor is the higher viscosity of MSOHO which impedes diffusion of water into the emulsion droplets and accounts for the higher hydrolytic stability. This difference was canceled when hydrolysis was carried out in THF solution and thus without the influence of viscosity and diffusion effects. Here, the rate is governed only by the reactive group (succinic anhydride), which is the same in both ASA and MSOHO.

Considering these results, maleated vegetable oils, such as MSOHO, have some definite application benefits over conventional ASA, apart from the generally positive fact that they are based on raw materials derived from green sources. In a water-based environment, as is the case in paper mills, the new MSOHO sizing agent is hydrolytically more stable than ASA and thus offers significantly larger time windows

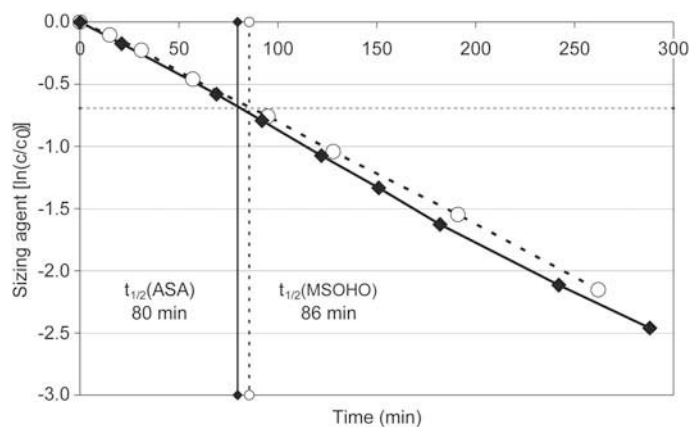


Figure 4 Hydrolysis of the sizing agents in THF at 70°C; ○ MSOHO, ◆ ASA.

for application of the aqueous size emulsions to the paper stock.

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Novel paper sizing agents based on renewables. Part 5:

Characterization of maleated oleates by ozonolysis

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1. Abstract

Maleated high oleic sunflower oil (maleated SOHO, MSOHO) has been shown to be a promising substitute for alkenyl succinic anhydrides (ASA) which are widely used as sizing agents for paper. The part of the MSOHO molecule that is believed to be responsible for adhesion of the molecule onto cellulose, i.e. the maleated oleic acid moiety, was separately prepared and analytically characterized. Structural analysis was completed by studies of the molecular fragments obtained upon ozonolysis. The interesting question whether there was a preferential reactivity during the ene-reaction of maleic anhydride with oleates was answered in a way that the newly formed double bond was placed to either side with no apparent selectivity.

2. Key words

Ene-reaction, maleated plant oils, maleated high oleic sunflower oil, sizing agents, maleated oleic acid, ozonolysis

3. Introduction

In previous work, the use of maleated high oleic sunflower oil (maleated SOHO, MSOHO) as paper sizing agent was introduced. The synthesis was based on an ene reaction between unsaturated fatty acid moieties in triglycerides and maleic anhydride, which was comprehensively optimized. The maleated products were thoroughly analytically characterized (IR, NMR, MS) and their application properties were studied with regard to sizing efficiency, hydrolysis behavior, retention behavior, and deposit formation among other factors (Lackner et al. 2009; 2011a-d).

An important factor for the quality of the product is the amount of fatty acids that were modified by maleic anhydride (MAA) during the ene-reaction of the natural triglyceride (e.g. high oleic sunflower oil) with MAA. So far, the amount of maleated fatty acids was quantified indirectly by comparing the amounts of non-modified fatty acids before and after the ene-reaction by GC analysis of the methyl esters, which were obtained by treatment with BF_3 in methanol (Lackinger et al. 2011a). This was based on the assumption that no side reactions consuming fatty acid residues occur during ene-reaction and the following analysis steps. Similarly, NMR analysis of the maleated SOHO was carried out and provided data on the overall maleation degree and the ratio of non-maleated, mono-maleated and multi-maleated (two or more MAA per molecule) triglycerides (Lackinger et al. 2011b). Analysis of the position of the resulting succinic anhydride moieties along the fatty acid chains was not possible.

Although these studies show that there have been quite some attempts to investigate the molecular structure of MSOHO, one question remained unanswered so far: is there a preferred side to which the double bond flips during the ene-reaction (see Figure 1)? Does the bond relocate in a way that it becomes more central or is it moving to the edge of the chain? This issue is especially important for molecular modeling approaches addressing the mechanism of sizing on cellulose surfaces, for which the exact structure

of the maleated oleates must be known. An obvious method to address the issue of localizing double bonds in a (mono)unsaturated hydrocarbon is ozonolysis, followed by quantification of the fragments (Becker 1976), which was also used in the present account.

4. Materials and Methods

4.1. Materials

The used maleated high oleic sunflower oil was produced in 90 kg batches from maleic anhydride and high oleic sunflower oil (C. Thywissen GmbH, Germany) at a molar ratio 2:1 with the addition of 0.02% BHT (*di-tert*-butyl-hydroxytoluene, >99%, Sigma Aldrich) at 215°C under nitrogen (1.4 bar) over 7 h. The following characteristics were found for the produced MSOHO: $R = 1.26$ (ratio of MAA to triglyceride); viscosity = 3396 mPas (measured at 20°C and 50 s⁻¹); 12.3% polymers (molecular weight beyond monomeric triglycerides) determined by GPC; 10.9% residual oil. For characterization methods, see Lackinger et al. (2011a).

For thin layer chromatography (TLC) a spraying agent consisting of ethanol (abs., VWR, Austria), anisaldehyde (4-methoxybenzaldehyde, 98%, Merck, Germany), concentrated sulfuric acid (p.a., Merck, Germany), and glacial acetic acid (Normapur, VWR, Austria) (90:5:5:1 by volume) was used. The methylation agent consisted of borontrifluoride-methanol complex (50 wt% in methanol) from Sigma-Aldrich, Austria, methanol, and toluene, both HPLC grade, from Fisher Scientific GmbH, Austria, (35:35:30 by volume).

The analytical methods used required following chemicals: veratrylamine (3,4-dimethoxybenzylamine, 97%), deuteriochloroform, methyl oleate (p.a.), palmitic acid (puriss.), stearic acid (puriss.), oleic acid (puriss.), linoleic acid (puriss.), 1-heptanol (puriss.), methyl 10-hydroxy-decanoate (tech. grade >90%), sodium borohydride, n-

hexane, ethyl acetate, and methanol (dry) from Sigma-Aldrich, Austria, margaric acid (heptadecanoic acid, puriss.), 1-octanol (puriss.), tetramethylammonium hydroxide (purum $\geq 95\%$) from Fluka Chemie GmbH, Austria, sodium chloride (rectapur), potassium iodide (Normapur) from VWR, Austria, methylene chloride (p.a.) from Merck, Germany, calcium sulfate (Drierite regular; Alfa Aesar GmbH & Co KG, Germany), pentane (analytical reagent, VWR, Austria), tetrahydrofuran (HPLC grade, Fisher Scientific GmbH, Austria) and acetone (techn., Brenntag CEE GmbH, Austria).

4.2. Instrumental Analysis

4.2.1. Attenuated total reflection – infrared spectroscopy (ATR-IR)

An AVATAR 370 FT-IR spectrometer with a Smart DuraSamplIR probe head (Thermo Nicolet Corporation, USA) was used. Spectra were analyzed by means of the Omnic 6.2 software package (Thermo Nicolet Corp., 1992-2001). One drop of neat substance was placed on top of the probe head and the measurement was started immediately.

4.2.2. Thin layer chromatography (TLC)

For thin layer chromatography pre-coated TLC plates (silica gel 60, F_{254} , Merck) were used. The mobile phase was a mixture of n-hexane and ethyl acetate (80:20 by volume). To visualize the separated compounds the thin layer plates were wetted with acidic anisaldehyde solution and the chromatogram developed on a hotplate.

4.2.3. Gel permeation chromatography (GPC)

Substances with high molecular weight, such as vegetable oil triglycerides and their oligomers, methyl oleate or maleated methyl oleate, were separated and analyzed on a GPC system of the following setup: auto sampler AS-2000, interface D-6000, pump L-2600 (all three Hitachi High Technologies Corporation, Tokyo, Japan), degasser DG-

2410 (Degasys, Uniflows Co. Ltd., Tokyo, Japan), column oven (Jetstream 2 Plus) held at 40°C, refractive index (RI) detector (RI 2414, Waters Corp.), and a set of 4 columns (250 mm x 7 mm x 5 µm, Hibar, Merck, Germany) packed with divinylbenzene-crosslinked polystyrene (PS 20 / PS 4 / PS 1 / PS 1). Tetrahydrofurane was used as solvent for samples and as the eluant.

4.2.4. Pyrolysis gas chromatography – mass spectrometry (PyGC-MS)

Characterization of maleated methyl oleate and its ozonolysis products were carried out on a Focus Gas Chromatograph (Thermo Finnigan) coupled with a Mass Spectrometer (MD800, Fisons Instruments). For separation a TR-MS column (Thermo Finnigan) and He as carrier gas were used. Samples were pyrolyzed without prior derivatisation unless stated otherwise. For pyrolysis a valved interface 1500 and a Pyroprobe 1000 (both CDS Analytical. Inc.) at 300°C were used.

Maleated methyl oleate was analyzed with following temperature program: Initial temperature 100°C with a hold time of 1 min, temperature increase at 10°C/min to 300°C, hold for 15 min. Temperature program for ozonolysis fragments: 40°C for 1 min, temperature increased at 15°C/min to 300°C, hold for 15 min. For both methods the split flow was set to 45 ml min⁻¹.

Some important molecular weights:

Maleated triglyceride, trioleat,	for R=1	MW = 983.5 g mol ⁻¹
	for R=2	MW = 1081.6 g mol ⁻¹

R=1.26 corresponds to an average molecular weight of 1009.0 g mol⁻¹. (for definition of R see Lackinger et al. 2011a).

Maleated methyl oleate	MW = 440.62 g mol ⁻¹
Methyl oleate	MW = 296.49 g mol ⁻¹

4.2.5 Nuclear magnetic resonance (NMR) spectroscopy

Spectra were recorded at 400.13 MHz for ^1H and at 100.41 MHz for ^{13}C at a Bruker Avance II instrument, with CDCl_3 as the solvent if not otherwise stated. Chemical shifts, relative to TMS as internal standard, are given in δ values, coupling constants in Hz. ^{13}C peaks were assigned by means of APT, HMQC and HMBC spectra. 30 mg of the sample were dissolved in 0.6 ml of CDCl_3 for NMR analysis.

4.2.6 Gas chromatographic analysis of maleated fatty acid methyl esters

Based on isolated and purified maleated methyl oleate (*c.f.* wet chemical analysis below), a method was established to quantify this component in maleated vegetable oils. The results were compared to a previous gas chromatographic analysis method, where maleated fatty acids were quantified indirectly by comparing the fatty acids present in starting materials and maleated products (Lackinger et al. 2011a). The fatty acid methyl esters and maleated fatty acid methyl esters of different maleated oil samples were prepared using transesterification in BF_3 -methanol. (*c.f.* 4.3.1 below). Separation was carried out on a Focus gas chromatograph (Thermo Electron Corporation, IT) with an FID detector, an RTX-1 column (dimethyl-polysiloxane, Restek GmbH) or equivalent, H_2 as carrier gas, split flow 100 ml/min. The sample (1 μl) was injected with an autosampler (AS 3000, Thermo Electron Corporation, IT). Temperature program: initial temperature 100 $^\circ\text{C}$, hold time 1 min, temperature increase at 10 $^\circ\text{C}/\text{min}$ to 300 $^\circ\text{C}$, hold for 15 min.

4.2.7 Gas chromatographic analysis of ozonolysis fragments

A method was developed to quantify the fragments gained after ozonolytic cleavage of methyl oleate or maleated methyl oleates. The same equipment and columns as described above were used. Response factors were measured for 1-octanol

($f_{\text{octanol}} = 1.0176$) and for methyl-10-hydroxy decanoate (MHD) ($f_{\text{MHD}} = 0.6808$). 50-60 mg of 1-heptanol as the internal standard and 100-140 mg of sample were dissolved in n-hexane (10 ml). 1 ml of this solution was transferred into an autosampler vial and analyzed. The sample (1 μl) was injected from an autosampler (AS 3000, Thermo Electron Corporation, IT), split flow 100 ml/min, initial temperature 50°C, hold time 1 min, then temperature increase at 10 °C/min to 300°C, hold 1 min.

4.3 Wet-chemical analysis

4.3.1. Fatty acid methyl esters

Vegetable oil or maleated vegetable oil (100 mg) and margaric acid (20 mg, internal standard) were dissolved in THF (1 ml) in a 10 ml vial. 3 ml of methylation agent was added, the mixture was mixed vigorously, and the closed vial was stored at 105°C for 40 min. After cooling to r.t., 2 ml of deionized water and 2 ml of pentane were added and the mixture was stirred for 1 min. After phase separation, 1 ml of the organic (upper) phase was transferred into a GC autosampler vial and analyzed as described above (4.2.6).

4.3.2. Isolation and purification of maleated methyl oleate

Based the analytical protocol described above (4.3.1), a larger amount of maleated oil was cleaved into the corresponding fatty acid methyl esters for isolation and purification of the maleated methyl oleates. Maleated high oleic sunflower oil (MSOHO, 20 g) was added to 150 ml of the methylation agent. At 80 °C, the mixture was stirred under nitrogen for 3 hours. After 1 hour mixing time, 20 ml of toluene were added. After additional 5 hours the mixture was heated to 100 °C and another 40 g of BF_3 complex (50% in methanol) were added under stirring. After cooling to r.t., residual BF_3 is

quenched by addition of water (50 ml), and the organic compounds were extracted with pentane.

The reaction was controlled with ATR-IR and TLC. By ATR-IR the end of the methylation of the succinic anhydride residues can be determined by the disappearance of their typical IR bands of succinic anhydride at 1862 and 1782 cm^{-1} , only the C=O band of the esters at 1744 cm^{-1} remain (cf. with data previously published in Lackinger et al. 2011b). Complete cleavage of the triglycerides was confirmed by GPC. While in the starting material 86% of triglycerides were found besides two fractions of smaller molecules (1.2 and 0.5%), in the BF_3 -cleaved sample no triglycerides were found at all, but fractions of smaller molecule amounted to 67.2 and 32.0% (at retention times of 19.40 and 20.01 min, respectively). Assuming the triglycerides be ideal trioleates, the signals originate from maleated methyl oleate and methyl oleate with a molecular weight difference of 144 g mol^{-1} . Consequently, approx. 2 out of the three oleic acid residues per triglyceride were maleated, based on a response factor of 1 for both maleated methyl oleate and methyl oleate.

Maleated methyl oleate was purified via fractionated distillation at 0.2 mbar. The fraction to be used for analysis and ozonolysis was collected between 190 and 205°C. The purity of the product was controlled with PyGC-MS (see Figure 2), which showed a neat product without unwanted byproducts.

4.3.3. Ozonolysis

A setup as described in Figure 3 was used. Ozone was generated with a lab ozone generator (Labo 76, Trailgaz Ozone, France) at a pressure of 1 bar and at a current of 1 A, using synthetic air dried over CaSO_4 . Methyl oleate (0.5964 g, 2.01 mmol) or maleated methyl oleate (0.5195 g, 1.18 mmol) were solved in 20 ml dry methanol or 25 ml dichloromethane / dry methanol (1:4 by volume), respectively. Ozonolysis was

conducted for 40 min at -10 °C for methyl oleate and at 0 °C for maleated methyl oleate. Residual ozone was removed by flushing with Ar. Sodium borohydride in 10 ml THF / water (7:3 by volume) was added drop wise: 0.4668 g (12.34 mmol) for methyl oleate and 0.2754 g (7.28 mmol) for maleated methyl oleate. After flushing with Ar, the reaction mixture was allowed to warm to r.t. The reaction mixture was washed with brine, and the products were extracted with n-hexane followed by analytical characterization.

5 Results and Discussion

5.1. Characterization of the maleated methyl oleate

Transesterification of the maleated oils to a mixture of fatty acid methyl esters proceeded cleanly under BF_3 -methanol complex catalysis, as expected. Due to the high ratio of oleic acid moieties in the starting material SOHO, of which a certain amount was maleated in MSOHO, the transesterification product mixture contained mainly methyl oleates, both maleated and non-maleated. The maleated oleates were of prime interest for analytical characterization (Figure 1).

The purified maleated methyl oleate was subject to PyGC-MS analysis. As seen from Figure 2 (left), the product was neat. Specific masses assigned to fragments of the product molecule were the molecular weight of 440.6 g mol^{-1} , and the masses that remain after the molecule loses methanol from the methyl ester groups consecutively (408.5 , 377.8 , 348.4 g mol^{-1}), see Figure 2 (right). A mass fragment at 145.9 m z^{-1} corresponds to a succinic dimethylester fragment, and the one at 113.9 m z^{-1} to an octane fragment.

Further structural characterization was done by NMR spectroscopy. The peak assignment in the ^1H and ^{13}C domain was supported by two-dimensional homonuclear (H,H-COSY) and heteronuclear (HSQC and HMBC) experiments. All peaks could be

assigned in agreement with the molecular formula according to Figure 1, see Table 1 for ^1H and Table 2 for ^{13}C . The presence of three singlets confirms the presence of a three methyl ester moieties, one from the oleic acid residue and two in the succinic moiety. In both the ^1H and the ^{13}C spectrum a clear indication of the existence of two different structural isomers according to the double bond location was provided: in the ^1H spectrum two triplets were found for the $\alpha\text{-CH}_2$ group of the fatty acid residue at 2.27-2.33 ppm (see Table 1 and 4, top). In the ^{13}C spectrum two signals at 31.98 and 32.77 ppm were found for the carbon atom located next to the double bond (see Table 2 and 4, bottom). The other chemical shifts along the aliphatic chains in the molecule were not influenced by the structural diversity of the two isomers. A reliable quantification of the ratio between the isomers was not possible from the integrals in the ^1H spectrum. To give a profound proof of the existence of the two isomers according to the double bond location in the molecule and to quantify their ratio required another approach, which is described below: analytical Ozonolysis for double bond cleavage and analysis of the fragments.

5.2. Comparison of quantization methods for maleated fatty acids in maleated vegetable oils

In a previous paper of this series (Lackinger et al. 2011a) the amount of maleated fatty acids after transesterification of maleated oils to their corresponding fatty acid methyl esters was calculated indirectly by comparison of the non-maleated fatty acid contents between starting material and the product after ene-reaction with maleic anhydride. To countercheck those values a new GC-based method was developed and calibrated. The response factors for the different fatty acid methyl esters (according to the analysis methods described in 4.3.1 and 4.2.6 of the experimental) were: $f_{\text{Palmitic acid}} = 0.9910$, $f_{\text{Stearic acid}} = 1.0028$, $f_{\text{Oleic acid}} = 0.9047$, $f_{\text{Linoleic acid}} = 0.8362$, and $f_{\text{Maleated oleic acid}} = 0.4842$.

The new response factors correspond favorable with those used in the earlier, indirect approach: $f_{\text{Palmitic acid}} = 1$, $f_{\text{Stearic acid}} = 1$, $f_{\text{Oleic acid}} = 0.9612$, $f_{\text{Linoleic acid}} = 0.8492$. Different vegetable oils (SOHO) and their maleated products (MSOHO) were analyzed and their fatty acid distribution was compared to results gained with the former used method (Lackinger et al. 2011a). The results presented in Table 3 show a very good agreement between the results of the direct determination and the previously used indirect method. In general, the indirect method is sufficient for a quick screening and may be applied when large sample numbers must be processed and when there is no chance to measure the response factor for maleated oleic acid. The direct method is more time-consuming and requires calibration beforehand, but it is also more reliable.

5.3. Ozonolytic analysis of methyl oleate

The experimental setup for the analysis was that of a classical ozonation as schematically shown in Figure 3. For the reaction of double bonds with ozone, as proceeding upon analytic ozonolysis, a three-step mechanism has been proposed by Criegee (1975). In a first step ozone is added to the double bond according a 1,3-dipolar reaction mechanism (also called [2+3]-cycloaddition), forming an 1,2,3-trioxolan, which however is not stable, not even at -78°C , the temperature conventionally used during ozonolysis. This so-called primary ozonide rearranges into a 1,2,4-trioxolan structure, the so-called secondary or final ozonide. For the mechanisms a cleavage of the primary ozonide into a carbonyl and a carbonyl oxide fragment followed by a second [2+3]-cycloaddition step was proposed. Several side reactions may limit the yield of the final ozonide, in particular the dimerization of the carbonyl oxide fragments. Those side pathways can be suppressed by choosing methanol or acetic acid as the solvents [6-8].

The secondary ozonide is decomposed into stable and analyzable products according to different procedures. Oxidative cleavage provides two carboxylic acids,

whereas the more common reductive cleavage affords aldehydes or alcohols in dependence on the reductants and conditions used. As an example, the oleic acid ozonide is cleaved into two aldehydes upon treatment with zinc and acetic acid (Pryde and Cowan 1962), while treatment with ozone-free oxygen at 70-110 °C gives pelargonic and azelaic acid (Cornils and Lappe, 2009).

In our case, the reductive pathway was used to gain the stable alcohols according to a protocol proposed by Torres-Sanchez et al. (2007). The ozonides were treated at r.t. with sodium borohydride in THF / H₂O (v/v = 7:3) to gain the alcohol in a clean reaction without noticeable side product formation.

To test the suitability of the ozonolysis and work-up method for the analysis of maleated methyl oleate, the precursor, non-maleated methyl oleate, was subject to the ozonolysis procedure. The reaction proceeded neatly according to the scheme in Figure 5. The products were characterized with PyGC-MS without further derivatisation and the two main components found at retention times of 7.5 and 10.4 min, respectively, were identified according to their MS fragmentation patterns as 1-nonanol and methyl 9-hydroxynonanoate. For measurement of the two cleavage products the GC method described under 4.2.7 was used. Using the response factor for methyl 10-hydroxy-decanoate for methyl 9-hydroxy-nonanoate and that of 1-octanol for 1-nonanol (methyl 10-hydroxy-decanoate and 1-octanol standards are commercially available), the obtained ratio for the two cleavage products was 1.078, i.e., quite close to the theoretical value of unity. The small deviation from the theoretical ratio 1:1 is a result of slightly different response factors for the used standards and the measured compounds. In summary, the cleavage path way as pictured in Figure 5 was fully confirmed, and the methodological approach was shown to be robust, and appeared appropriate to study structural isomers in maleated methyl oleate as well.

5.4. Ozonolytic analysis of maleated methyl oleate

Our approach to investigate the ene-reaction of trioleate with MAA, where trioleate is the idealized structure of natural high oleic sunflower oil triglycerides, started with cleavage of the glyceride ester bonds with BF_3 - methanol. This converts all maleated oleic acid residues to either trimethyl 3-[(*E*)-non-1-enyl]decane-1,2,10-tricarboxylate or trimethyl (*E*)-3-octylundec-4-ene-1,2,11-tricarboxylate (see Figure 1) depending on the direction the double bond of the oleic acid residues flipped during ene-reaction. Both isomers have the same molecular formula ($\text{C}_{25}\text{H}_{44}\text{O}_6$), and they cannot be distinguished in PyGC-MS. Assuming that no energetic preference for one or the other “side” of double bond placement exists, both compounds should be present in 1:1 ratio, and also the respective ozonolysis products should be present in equimolar ratio.

Ozonolysis of the maleated methyl oleates was followed by reductive processing as in the case of non-maleated methyl oleates, converting the ozonolysis fragments into the corresponding alcohols, which were qualitatively and quantitatively analyzed. (Figure 6) Trimethyl 3-[(*E*)-non-1-enyl]decane-1,2,10-tricarboxylate (**1**) provided the fragment pair octan-1-ol (**3**) / trimethyl 3-(hydroxymethyl)decane-1,2,10-tricarboxylate (**4**) and trimethyl (*E*)-3-octylundec-4-ene-1,2,11-tricarboxylate (**2**) the pair dimethyl 2-[1-(hydroxymethyl)nonyl]butanedioate (**5**) / methyl 8-hydroxyoctanoate (**6**). An 1:1 ratio between the pairs, e.g. between octan-1-ol (**3**) and methyl 8-hydroxyoctanoate (**6**) or between the diesters **4** and **5**, would indicate the same abundance of either double bond position and thus unselective placement of the double bond during the maleation (ene-reaction), with no preference for either side.

The major fragments in the ozonolysis mixture as determined by PyGC-MS were 1-octanol (**3**), methyl 8-hydroxyoctanoate (**6**), 5-(7-methoxycarbonyl-heptyl)-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester (**7**), and 5-octyl-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester (**8**), see Table 4. Another peak at 10.60 min retention

time was identified as di-*tert*-butyl-hydroxytoluene (BHT, 220.35 g mol⁻¹), which was used as stabilizer in the production of the maleated oil, and was evidently insufficiently removed by distillation upon purification of the maleated methyl oleates. Compounds **7** and **8** are formed from the precursors trimethyl 3-(hydroxymethyl)decane-1,2,10-tricarboxylate (**4**) and dimethyl 2-[1-(hydroxymethyl)nonyl]butanedioate (**5**), respectively, by elimination of methanol under δ -lactone formation as the driving thermodynamic force. They are not directly formed upon ozonolysis, but are indirect products formed in a subsequent lactonization step. Thus, ratio calculation was based on 1-octanol (**3**) and methyl 8-hydroxyoctanoate (**6**) as direct ozonation products to avoid related inaccuracies. To quantify compounds **3** and **6**, the product mixture was analyzed with PyGC-MS according to the protocol described above (4.2.7). Measurement was carried out on four independent samples (Table 5), giving an average ratio 1-octanol (**3**) / methyl 8-hydroxyoctanoate (**6**) of 1 : 1.27 \pm 0.12, corresponding to a ratio of 44% : 56% (\pm 5%) between the maleated oleates **1** and **2**. Due to the fact that the response factor for methyl 8-hydroxyoctanoate was not determined directly, but the response factor for methyl 10-hydroxydecanoate was used instead, the value of methyl 8-hydroxyoctanoate might be slightly overestimated so that the actual ratio would come even closer to unity.

According to the ozonolysis results, there is no clearly preferred regioselectivity for placement of the newly formed double bond in the ene-reaction during maleation of methyl oleate. A slight preference for the *endo* position (compound **2**) over the *exo* placement as in compound **1** was noted which, however, falls almost within the error limit. The double bond, after the ene-reaction, has flipped to either direction to nearly the same extent. In molecular modeling approaches, so far either compound **1** or compound **2** are used. Both compounds, however, differ quite significantly in their geometries and molecular shapes as well molecular parameters, such as dipole moment and volume. Also the region accessible to the molecule once the succinic

anhydride in maleated oleate – and thus also in MSOHO – has reacted with a (model) cellulose surface is quite different. For reliable modeling results, a mixture of both components, corresponding to averaged molecular parameters, must be used.

5. Conclusion

In this paper a method to characterize maleated fatty oils according the localization of the succinic anhydride residue along the carbon chain of the fatty acids is presented. The maleated fatty acids (oleic acid) were isolated from maleated high oleic sunflower oil (MSOHO) as their methyl esters, which were also used to develop a direct quantification method for maleated fatty acids based on GC (Lackinger et al. 2011a). This new direct method confirmed results of a previous indirect determination.

PyGC-MS and NMR analysis confirmed purity and general structure of the maleated methyl oleates. NMR also provided evidence for the existence of two different structural isomers of maleated oleic acid, in which the C_{9,10} double bond of oleic acid was shifted to either C_{8,9} or C_{10,11} position upon ene-reaction with maleic anhydride. This moiety, converted into a succinic anhydride in this process, becomes attached to C₁₀ or C₉, respectively. Cleavage of maleated methyl oleate at the double bond with ozone and subsequent analysis and quantification of the fragments by PyGC-MS of fragments proved this mechanism and provided clear evidence that neither double bond location was preferred. Thus, there is no preferred side to which the double bond switches during ene-reaction. Quantum-chemical modeling of ASA-type sizing agents produced from oleic acid residues thus have to consider both double bond locations to reliably reflect the experimental situation.

6. Acknowledgements

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8. Figure and Table Captions

Figure 1

Formation of maleated oleic acid moieties in triglycerides and transesterification into maleated methyl oleates (compounds **1** and **2**).

Figure 2

GCMS data for purified maleated methyl oleate, left: GC chromatogram, right: mass spectrum (EI, 70 eV).

Figure 3

Ozonolysis setup.

- 1 Gas-washing bottle filled with CaSO_4
- 2 Gas-washing bottle filled with KI solution
- 3 Empty gas-washing bottle
- 4 Empty gas-washing bottle
- 5 Gas-washing bottle filled with KI solution
- 6 Gas-washing bottle filled with KI solution

Figure 4

NMR spectra of maleated methyl oleate; top: ^1H spectrum, bottom: ^{13}C (APT) spectrum.

Figure 5

Ozonolysis reaction of methyl oleate with reductive work-up.

Figure 6

Reaction scheme for ozonolysis of maleated methyl oleate.

- Compound **1**: trimethyl 3-[(*E*)-non-1-enyl]decane-1,2,10-tricarboxylate
Compound **2**: trimethyl (*E*)-3-octylundec-4-ene-1,2,11-tricarboxylate
Compound **3**: octan-1-ol
Compound **4**: trimethyl 3-(hydroxymethyl)decane-1,2,10-tricarboxylate
Compound **5**: dimethyl 2-[1-(hydroxymethyl)nonyl]butanedioate
Compound **6**: methyl 8-hydroxyoctanoate
Compound **7**: 5-(7-methoxycarbonyl-heptyl)-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester
Compound **8**: 5-octyl-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester

Table 1

^1H NMR peak assignment of maleated methyl oleate.

Table 2

^{13}C NMR peak assignment of maleated methyl oleate.

Table 3

Percentage of fatty acid distribution in SOHO (starting materials) and MSOHO (maleated products) according to indirect and direct analysis approaches.

Table 4

Assignment of major GCMS peaks for maleated methyl oleate.

Table 5

Quantification of cleavage products of maleated methyl oleate.

9. Graphs and tables

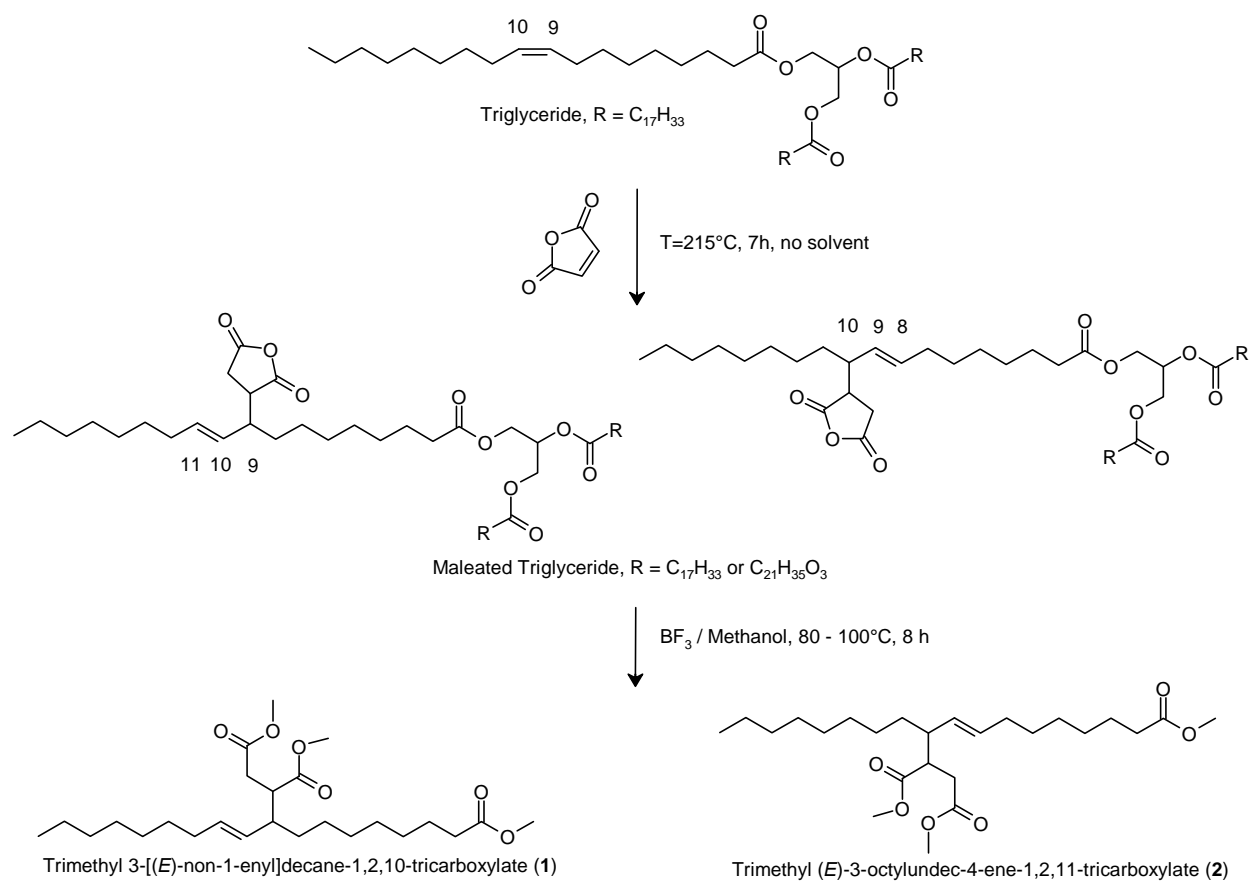


Figure 1 Formation of maleated oleic acid moieties in triglycerides and transesterification into maleated methyl oleates (compounds **1** and **2**).

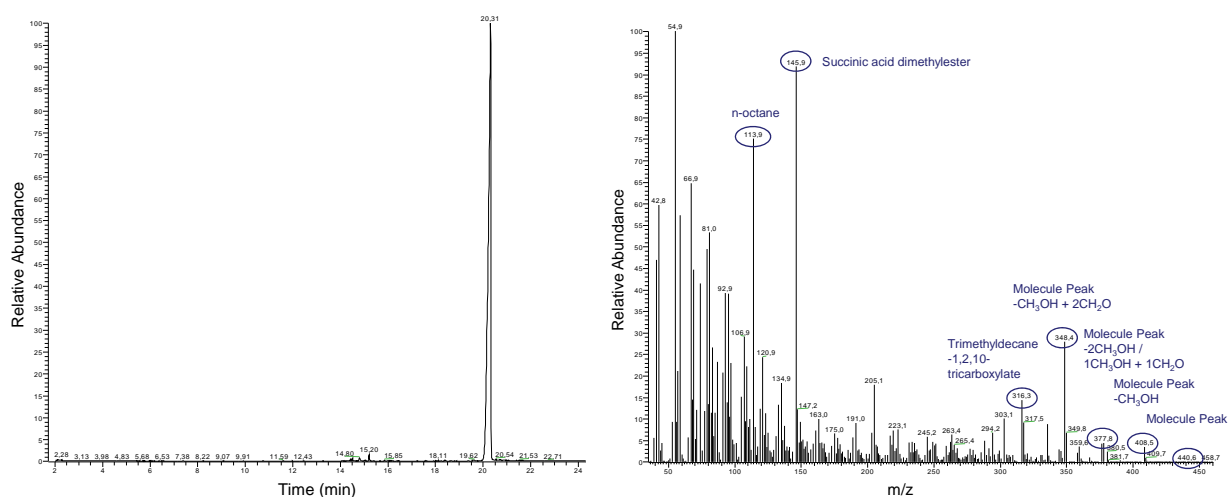


Figure 2 GCMS data for purified maleated methyl oleate, left: GC chromatogram, right: mass spectrum (EI, 70 eV).

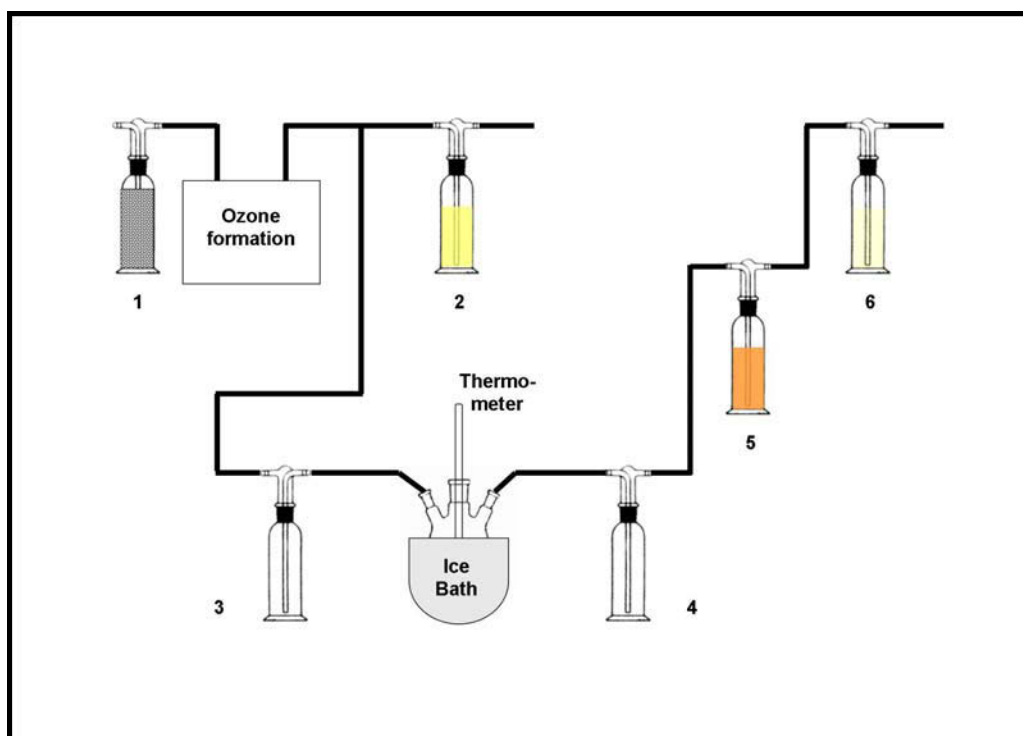


Figure 3 Ozonolysis setup.
 1 Gas-washing bottle filled with CaSO_4
 2 Gas-washing bottle filled with KI solution
 3 Empty gas-washing bottle
 4 Empty gas-washing bottle
 5 Gas-washing bottle filled with KI solution
 6 Gas-washing bottle filled with KI solution

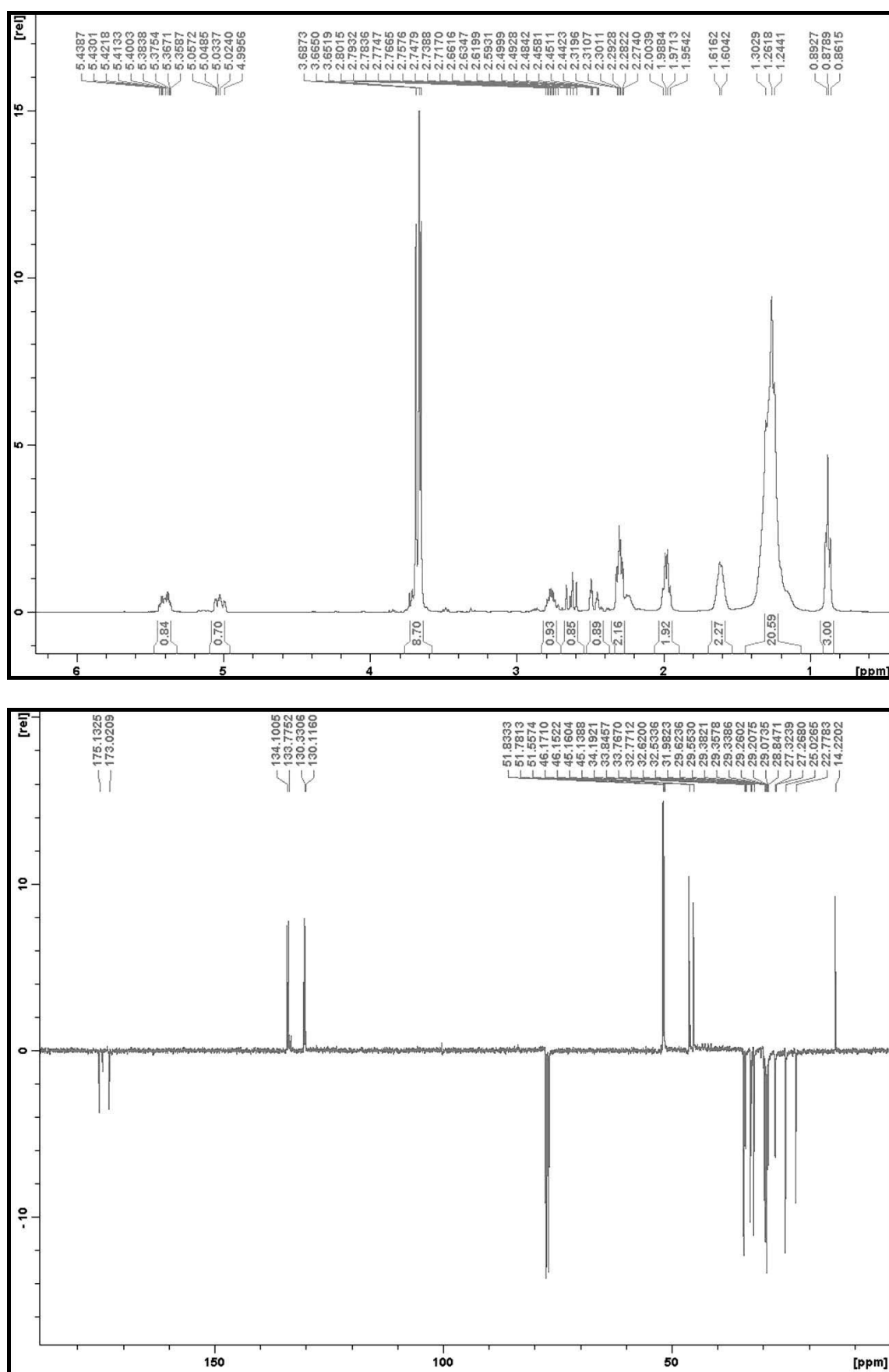


Figure 4 NMR spectra of maleated methyl oleate; top: ^1H spectrum, bottom: ^{13}C (APT) spectrum.

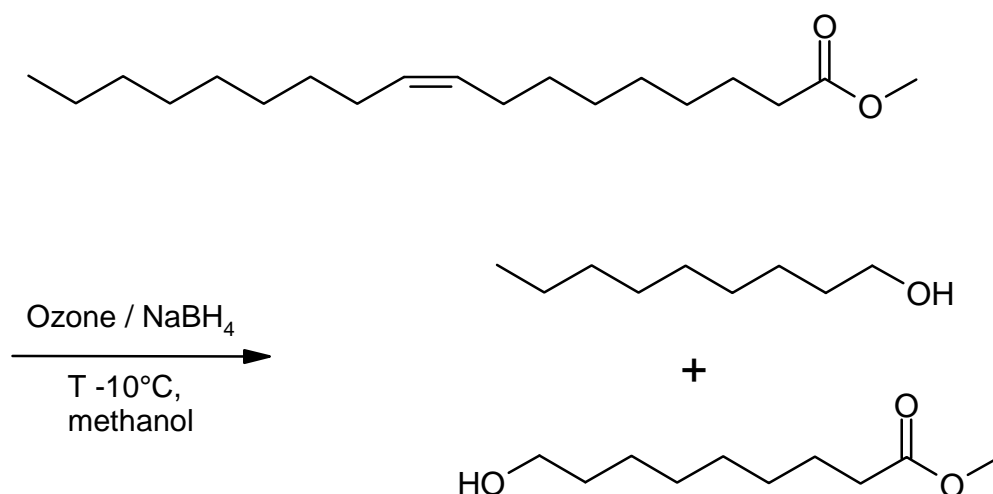


Figure 5 Ozonolysis reaction of methyl oleate with reductive work-up.

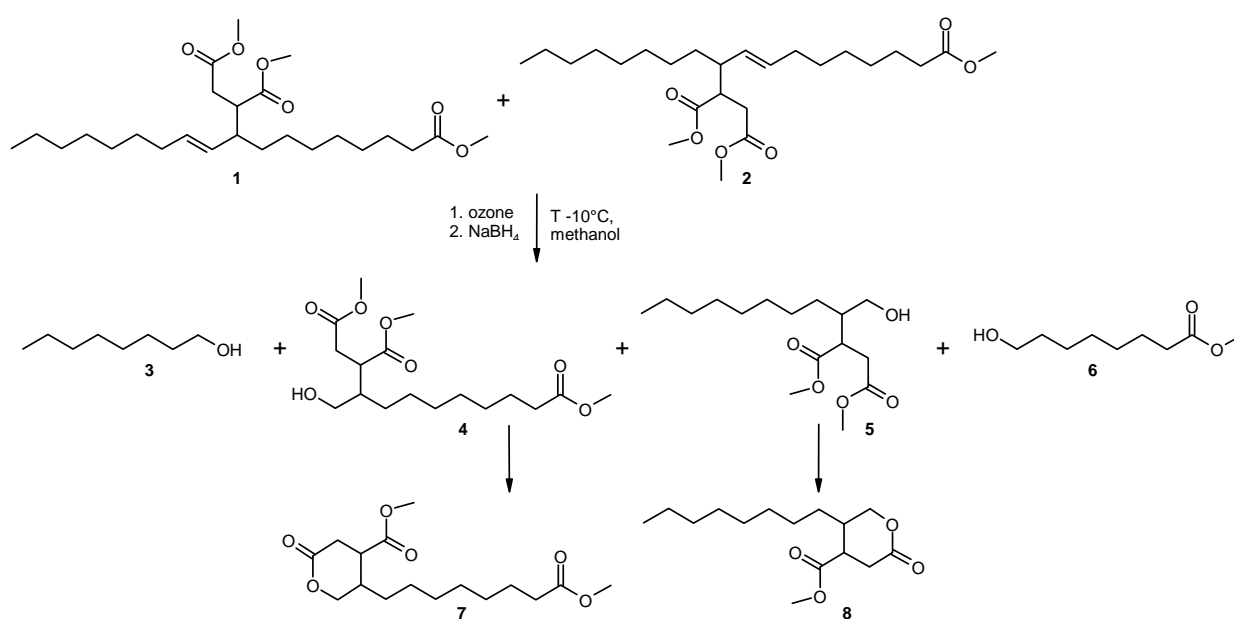


Figure 6 Reaction scheme for ozonolysis of maleated methyl oleate.

Compound **1**: trimethyl 3-[(*E*)-non-1-enyl]decane-1,2,10-tricarboxylate
 Compound **2**: trimethyl (*E*)-3-octylundec-4-ene-1,2,11-tricarboxylate
 Compound **3**: octan-1-ol
 Compound **4**: trimethyl 3-(hydroxymethyl)decane-1,2,10-tricarboxylate
 Compound **5**: dimethyl 2-[1-(hydroxymethyl)nonyl]butanedioate
 Compound **6**: methyl 8-hydroxyoctanoate
 Compound **7**: 5-(7-methoxycarbonyl-heptyl)-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester
 Compound **8**: 5-octyl-2-oxo-tetrahydro-pyran-4-carboxylic acid methyl ester

Table 1 ^1H NMR peak assignment of maleated methyl oleate.

Chemical Shift [ppm]	Peak Characteristics	Integration	Structural Element
0.88	t, $^3J = 6.2$ Hz	3 H	CH_3 of fatty acid residue
1.07 – 1.44	m	20 H	CH_2 other than below
1.53 – 1.70	m	2 H	$\text{OOC}-\text{CH}_2-\text{CH}_2$
1.89 – 2.07	q, $^3J = 6.6$ Hz	2 H	$\text{HC}=\text{CH}-\text{CH}_2-\text{CH}_2$
2.19 – 2.27	m	1 H	$\text{R}_2-\text{CH}-\text{HC}=\text{CH}$
2.27 – 2.33	2 * t, $^3J = 7.5$ Hz, $^3J = 7.3$ Hz	2 H	$\text{OOC}-\text{CH}_2-\text{CH}_2$
2.36 – 2.53	m, $^2J = 16.7$ Hz, $^3J_{\text{cis}} = 3.2$ Hz	1 H	Proton 1 of CH_2 in succinic methyl ester
2.55 – 2.70	m, $^2J = 16.7$ Hz, $^3J_{\text{trans}} = 10.7$ Hz	1 H	Proton 2 of CH_2 in succinic dimethyl ester
2.70 – 2.83	m, $^3J_{\text{cis}} = 3.2$ Hz, $^3J_{\text{trans}} = 10.7$ Hz	1 H	CH in succinic dimethyl ester
3.67	3 * s	9 H	$\text{COO}-\text{CH}_3$
4.96 – 5.1	m	1 H	$\text{CH}=\text{CH}-\text{CH}-\text{R}_2$
5.32 – 5.47	m	1 H	$\text{CH}=\text{CH}-\text{CH}_2$

Table 2 ¹³C NMR peak assignment of maleated methyl oleate.

Chemical Shift [ppm]	Peak Characteristics	Structural Element
14.22	s	CH ₃ of fatty acid residue
22.78	s	CH ₂ - <u>CH</u> ₂ -CH ₃
25.03	s	OOC-CH ₂ - <u>CH</u> ₂
28.85 – 29.62	m	CH ₂ other than below
31.98, 32.77	2 * s	CH=CH- <u>CH</u> ₂ -CH ₂
32.53 – 33.85	m	Proton 1+2 of CH ₂ in succinic methyl ester
34.19	s	OOC- <u>CH</u> ₂ -CH ₂
45.15	m	R ₂ - <u>CH</u> -HC=CH
46.16	m	CH in succinic dimethyl ester
51.56 – 51.83	3 * s	COO- <u>CH</u> ₃
130.12 – 130.33	m	CH= <u>CH</u> -CH-R ₂
133.78 – 134.10	m	CH= <u>CH</u> -CH ₂
173.02 – 175.13	3 * s	CH ₃ -OOC

Table 3 Percentage of fatty acid distribution in SOHO (starting materials) and MSOHO (maleated products) according to indirect and direct analysis approaches.

	16:0*	16:0°	18:0*	18:0°	18:1*	18:1°	18:2*	18:2°	maleated 18:1*	maleated 18:1°
SOHO 1	3	3	2	2	81	85	6.9	5.1	0	0
SOHO 2	4	4	3	3	76	80	10	9	0	0
MSOHO 1	3	3	2	2	30	33	0.2	0.5	59	60
MSOHO 2	3	3	2	2	31	33	0.2	0.2	59	60
MSOHO 3	3	3	2	2	32	34	0	0	57	52
MSOHO 4	3	3	2	2	33	33	0	0	57	54

* Conventional method using indirect quantification of maleated fatty acids (*c.f. Lackinger et al. 2011a*).

° Newly calibrated GC method for direct quantification of maleated fatty acids.

Table 4 Assignment of major GCMS peaks for maleated methyl oleate.

	Retention Time [min]	Molecular Mass [g/mol]	Molecule	Molecular Formula	Origin
1	6.56	128.91	Octanol (3)	C ₈ H ₁₈ O (MW 130)	
2	9.70	172.71	Methyl 8-hydroxyoctanoat (6)	C ₉ H ₁₈ O ₃ (MW 174)	
3	14.56	270.86	Ester lactone 8	C ₁₅ H ₂₆ O ₄ (MW 270.37)	5 , C ₁₆ H ₃₀ O ₅ (MW 302.41)
4	15.86	314.01	Diester lactone 7	C ₁₆ H ₂₆ O ₆ (MW 314.38)	4 , C ₁₇ H ₃₀ O ₇ (MW 346.42)

Table 5 Quantification of cleavage products of maleated methyl oleate.

Sample	1-Octanol [%]	Methyl 8-hydroxyoctanoat [%]	Ratio (methyl 8-hydroxyoctanoat / 1-octanol)
Sample 1	12.13	14.98	1.23
Sample 2	12.17	15.76	1.29
Sample 3	12.33	15.63	1.27
Sample 4	12.34	15.95	1.29
Average	12.24	15.58	1.27

Novel paper sizing agents based on renewables. Part 6:

Sizing properties of maleated high oleic sunflower oil

1. Abstract

The sizing efficiency of maleated high oleic sunflower oil (MSOHO), a green reactive sizing agent, was studied in various sizing tests. MSOHO can be applied in the papermaking process according to protocols conventionally used for alkenyl succinic anhydride (ASA) sizing. While good sizing degrees were reached with pure MSOHO, even better results coming close to ASA-sizing efficiency were obtained with blends of MSOHO and fatty acid anhydride (FAA), another green sizing agent. Although both pure sizing agents - FAA as well as MSOHO - lack some efficiency when compared to ASA, blending those two sizing agents at optimum ratio closes this gap towards ASA. This synergistic effect between MSOHO and FAA was not simply caused by decreasing viscosity of MSOHO. In another set of experiments sizing efficiency of ASA-MSOHO and ASA-MSOHO-FAA blends was investigated to propose mixtures to be used in full scale mill trials.

2. Key words

Alkenyl succinic anhydride (ASA), fatty acid anhydride (FAA), maleated high oleic sunflower oil (MSOHO), paper sizing, viscosity.

3. Introduction

For the production of various paper grades the addition of sizing agents is essential for providing the readymade sheets with some hydrophobicity. This water repellence is needed for durability and other desired paper characteristics like printability. It is achieved by a modification of the fiber properties in the paper. Amphiphilic sizing agent molecules - which are able to

attach to the fiber with the hydrophilic side and hinder penetration of water with the hydrophobic one - are added in the wet-end of the papermaking process. Treating paper this way is called internal sizing. For this procedure the sizing agent is emulsified in a polymer solution (cationic starch) and subsequently added to the paper stock prior to sheet formation. The dispersion is needed for two reasons: first, the small size of the dispersed fine droplets provides a good distribution of the sizing compound throughout the paper web. Second, the sizing agent gets in better contact with the fiber due to electrostatic attraction forces between the anionic fibers and the cationic or amphoteric emulsion droplets.⁽¹⁾

In modern paper machines, which are run at neutral or slightly alkaline pH under addition of up to 20% ground calcium carbonate as filler auxiliary, the common sizing agents are alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD). They are usually denoted as reactive sizes, since it was believed that they act by covalent bonding to cellulose fibers in the produced paper.⁽²⁾ In many internal sizing applications ASA is preferred over AKD, because it is more cost efficient and has a shorter curing time. Although ASA sizing seems to be the best current choice in many applications, there is always the demand for better sizing agents regarding efficiency, hydrolysis behavior, environmental compatibility and sustainability.

Our vision was to develop a new sizing chemical based on renewable resources that is able to substitute ASA in internal sizing, different aspects of this endeavor being reported in the current series on green ASA substitutes. The newly developed sizing agent, maleated high oleic sunflower oil (MSOHO), employs natural plant oils as raw material rather than crude oil-based olefins, as it is the case in ASA production.^(3,4) This way, production becomes independent of fluctuating oil prices, and additionally makes use of regionally available, renewable raw materials. In the preceding parts of this series, the focus was on the analytical characterization as well as practical aspects, such as hydrolysis behavior and deposit formation.^(5,6,7) It was shown that maleated oils are more stable against hydrolysis than ASA sizes and thus have superior application properties that could easily make up for their somewhat reduced sizing efficiency. MSOHO carries the same functional group as ASA and can be applied the same way.

In this paper, the influence of calcium carbonate (CaCO_3), the most prominent filler used in paper production, and alum ($\text{Al}_2(\text{SO}_4)_3$) on MSOHO and ASA was studied. Similarly the effect of curing – storing of sized papers for some time to boost the sizing result – was studied. This is especially known in alkyl ketene dimer (AKD) sizing; also for ASA even short curing times might positively affect sizing efficiency. Here, the curing characteristics of MSOHO and ASA were compared. In another series of tests ways to reduce MSOHO's high viscosity were investigated: Blends of MSOHO either with tall oil fatty acid anhydride (FAA), another green sizing agent applicable in the same way as ASA⁽⁸⁾, and hexadecane, an inert dilutant that does not contribute to sizing at all, were used in sizing tests. The most promising blends were then compared to ASA. For application tests of new sizing agents, especially if conducted at a paper mill, it is always useful to begin with blends of the new sizing chemical together with an established one. If the tests are indicating no loss of sizing efficiency or even increased performance, the content of the new sizing agent in the blend can then be increased step by step. To predict the characteristics of ASA blended with MSOHO and ASA blended with MSOHO and FAA, the sizing efficiency was measured and the ternary system was modeled with Minitab.

4. Experimental

4.1. Materials

For hand sheet production, a paper stock solution made from commercial bleached Kraft pulp with 2% dry content consisting of 30% short fibre and 70% long fibre was beaten to 30°SR. The standard stock solution was prepared diluting the 2% paper stock solution to 1% dry content; containing 1% fibers and 0.25% ground calcium carbonate (GCC), if not stated otherwise. Thus, the GCC content related to the dry substance in the standard stock solution was 20%. The stock solution had a pH of 8.

For sheet preparation, Fennopol (cationic polymer, K 3400R from Kemira Oyj, Finland) and alum (aluminum sulfate) was used as additives in some cases. 4 % cationic starch HICAT 5103A (Roquette Co., France) was used for emulsion preparation.

Samples of the maleated oils were produced in 90 kg batches of maleic anhydride and high oleic sunflower oil (C. Thywissen GmbH, Germany) at a molar ratio 2:1. The reaction was conducted at 180-220°C under inert gas at a pressure of 1.0-3.3 bar during 6-9 h. Small amounts (0.01-0.02%) of phenolic antioxidants were added, such as Anox 330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-4-hydroxybenzyl)benzene, Great Lakes Manufact. Italy S.r.l., Italy), BHT (di-*tert*-butyl hydroxytoluene, >99 %, Sigma Aldrich, Austria), BHA (*tert*-butyl hydroxyanisole, >99%, food grade, Eastman Chemical Company).

The commercial sizing agents ASA (Hydrores AS 1000) and FAA (Sacacid FAA 1000) were provided by Kemira Chemie GesmbH, Austria. For all tests 1% anionic sulfosuccinate emulsifier (Na-DOSS, sodium di-octyl sulfosuccinate, Cytec Industries, The Netherlands) was added to the MSOHO sizing agents. Due to high viscosity of MSOHO all blends prepared for the below mentioned experiments were mixed after gentle heating. Hexadecane (anhydrous, 99+%) was purchased from Sigma-Aldrich, Austria.

4.2. Methods and Analysis

4.2.1. Preparation of hand sheets

Sheets were formed on a Rapid-Köthen sheet former at 45°C from ground cellulose (standard stock solution). In a first step 1% of the tested sizing agent was emulsified in cationic starch with a double cylinder Ultra Turrax homogenizer (IKA Werke GmbH & Co. KG, Germany) for 2 min at 10 000 rpm and 70°C. This emulsion was then diluted 1:10 with deionized water (= 0.1% sizing emulsion). Calculated amounts of this sizing emulsion (see text) were added to approx. 190 g of standard stock solution to form sheets with a basis weight of 70-80 gm⁻². As retention aid 4.6 ml Fennopol (0.01%) was used for each sheet. Alum was added as a 1% solution where stated.

The freshly prepared paper sheets were dried in the drum dryer at 115°C at a speed of approx. 1 turn in 40 s. The air-conditioned sheet was then used for further analysis (Cobb₆₀ tests). Alternatively, the sheets were stored in a conditioning room at 22.0°C and 60% relative humidity for 30 min before measuring the Cobb₆₀ values. .

4.2.2. Cobb₆₀ test

The sizing efficiency of the different agents is measured as Cobb₆₀ value.⁽⁹⁾ This value is an expression of the water absorption over the time period of 60 s given in g/m². It is calculated according to equation 1 as follows:

$$Cobb[g/m^2] = \frac{(m_2 - m_1)[g]}{0.01[m^2]} \quad (1)$$

m₁ mass of the sample before Cobb determination (g)

m₂ mass of the sample after Cobb determination (g)

4.2.3. Viscosity

For the production of sizing emulsions in starch solution, as well as for pumping and dosing, the viscosity of the sizing agent, which should be as low as possible, is of major importance. The viscosity of the investigated sizing agents was determined on a rota-viscosimeter (Rheometer MC1, Anton Paar GmbH, Austria) at 25°C and 500 s⁻¹.

4.2.4. Minitab

The Minitab 15 programme (Minitab Inc. 2006) was used for displaying sizing results of ternary mixtures of the sizing agents MSOHO, FAA and ASA.

5. Results and Discussion

5.1. Influence of chalk

In standard paper production the use of ground calcium carbonate (GCC) added up to 20% is quite common. Due to the raw material costs of cellulose, the aim of paper producers is to even further increase the filler content. Therefore, the dependency of sizing efficiency of new sizing agents on the GCC content is an important issue. The sizing of various MSOHO - ASA blends was investigated with a standard stock solution containing amounts of ground calcium carbonate (GCC) ranging from 0 to 30% relative to dry substance of the standard stock solution.

Sheets were produced with 0.91 kg/t sizing agent and 6.8 kg/t alum per dry weight of paper. For each sheet the same weight of stock solution was used. The tested blends were: 0% MSOHO (=100% ASA); 50% MSOHO + 50% ASA; 75% MSOHO + 25% ASA; 100% MSOHO (=0% ASA).

The addition of GCC constantly increased the measured $Cobb_{60}$ values for all tested sizing agents, no matter if pure agents or blends (Figure 1). The agents with 0% and 50% MSOHO were less influenced by increasing amounts of GCC than the blends with 75% or 100% MSOHO. While there is no difference between 0% MSOHO and 50% MSOHO in the range of 0 – 20% GCC, a gap of around 20 gm^{-2} was detected at 30% GCC added.

For all sheets the same amount of stock solution was used, therefore the sheet weight increased from 2.0 g to 2.6 g when the GCC content was increased from 0 to 30%. This implies that also the amount of sizing agent per gram of dry paper changes, if for each sheet the same amount of sizing emulsion is used. While for sheets without GCC 1 kgt^{-1} sizing agent is used, for the sheets containing 20 and 30% GCC only 0.8 kgt^{-1} are used. So the rise in $Cobb_{60}$ values for sheets with higher amounts of GCC is a combination of 2 different factors: first, GCC can consume sizing agent so that less sizing agent is left to react with cellulose and to hydrophobize the paper sheet. Second, due to the higher sheet weight less sizing agent per ton of paper is added, which results in decreased sizing efficiency.

5.2. Influence of alum

It is well known that the addition of alum during sheet formation helps boosting the sizing efficiency of ASA. This influence was tested on ASA and on MSOHO with the standard stock solution, in a first test without any filler and in a second series with the standard amount of 20% GCC. The tested blends were again 0% MSOHO (=100% ASA); 50% MSOHO + 50% ASA; 75% MSOHO + 25% ASA; 100% MSOHO (=0% ASA). In the first series of sizing tests, where no GCC was contained, the pure sizing agents 0% MSOHO (=100% ASA) and 100% MSOHO (=0% ASA) were compared at an addition level of 0.62 kgt^{-1} , while for the 50% and 75% MSOHO blends 0.52 kgt^{-1} were used. The optimum alum amount for MSOHO was 1.52 kgt^{-1}

(Figure 2). It was evident that alum has a larger influence on MSOHO or MSOHO/ASA blends than on pure ASA.

For the tests with the standard stock solution containing 20% GCC, sizing agents and blends were used at an addition level of 0.88 kg t^{-1} , except pure MSOHO which was used at 1.08 kg t^{-1} . The results are presented in Figure 3. The optimum alum concentration for the tested MSOHO and ASA is 6.51 kg t^{-1} . As in previous tests, almost no difference in sizing degrees and affinity to alum was found between pure ASA and a 50% MSOHO/ASA blend. The difference in sizing efficiency between the 50% MSOHO and 75% MSOHO blends at optimum alum addition was 15 gm^{-2} . When additional 20% of sizing agent was added, the sizing degree for pure MSOHO was the same as for the 50% MSOHO/ASA blend.

5.3. Curing of MSOHO and ASA

ASA is a preferred internal sizing agent, because it does not need long curing times to give maximum sizing. To prove that MSOHO behaves similar to ASA both sizing agents were tested for their curing characteristics. For MSOHO sheets 1.05 kg t^{-1} and for ASA 0.73 kg t^{-1} sizing agent was used. To all sheets 6.5 kg t^{-1} alum was added.

The hand sheets they were treated as follows before measuring Cobb_{60} :

- a) No further treatment
- b) Storage for 30 min at 22°C and 60% RH
- c) Storage for 10 min at 125°C
- d) Sheets are put under water for 1 min and are dried at 125°C for 30 min afterwards.

The sizing degrees presented in Figure 4 where the average values of 2 measurements. Evidently, MSOHO and ASA behaved quite similarly under the tested curing conditions. While different ways of conditioning (storing at 22°C and 60% RH for 30 min or in the oven at 125°C for 10 min) result in lower Cobb_{60} values (which means better sizing), the sizing efficiency after wetting and drying the paper is the same as for the papers measured directly after preparation.

5.4. Relationship between sizing efficiency and viscosity for MSOHO / FAA blends

The following MSOHO/FAA blends were investigated: 100% MSOHO, MSOHO with 10, 20, 30, 40, 50, 60, 80% FAA, and pure FAA. Around 6 kg/t alum was used for each sheet.

For blends with up to 30% FAA the $Cobb_{60}$ values along with the viscosities decreased linearly with the ratio of FAA added to MSOHO. For addition levels of 40-100% FAA sizing efficiency deteriorated although viscosity decreased further (Figure 5). $Cobb_{60}$ values increased to $> 50 \text{ gm}^{-2}$ for viscosities below 250 mPas. This effect can be explained with the weaker sizing efficiency of pure FAA in comparison to MSOHO. So there is an optimum for the sizing efficiency of MSOHO/FAA blends at around 10-30% FAA in MSOHO. As these blends have viscosities in the range of ASA (100-250 mPas) – apart from the 10% FAA blend which still has a rather high viscosity (1201 mPas – they seem to be well suited for full scale trials in paper mills as both sizing efficiency as well as processing (pumping and dosing) will not be significantly different from ASA. For the exact $Cobb_{60}$ values see Table 1.

5.5. Reducing MSOHO viscosity with a sizing-neutral chemical

To reduce its viscosity without influencing sizing efficiency, MSOHO was blended with different amounts of hexadecane. This alkane has a very low viscosity – 3 mPas at $25^{\circ}\text{C}^{(10)}$ – and does not provide sizing to paper, even at an addition level of 12 kg/t. Following blends were prepared: 100% MSOHO; 90% MSOHO + 10% hexadecane; 80% MSOHO + 20% hexadecane; 70% MSOHO + 30% hexadecane; 60% MSOHO + 40% hexadecane; 50% MSOHO + 50% hexadecane. The 50/50m blend showed phase separation overnight at room temperature; it was not used for further tests. All other blends were stable, only some turbidity was noticed, and after viscosity determination they were used to prepare sheets with the addition of around 6 kg/t alum. For each blend two sheets were prepared. The addition level of MSOHO was kept constant throughout all sheets, and consequently the amount of blend per ton of paper increased when blends contained less MSOHO.

The results of the viscosity and sizing efficiency tests are presented in Figure 6. Decreasing blend viscosity below 500 mPas had a beneficial effect on sizing efficiency when the concentration of the inert auxiliary was 10% or 20%. At 30% hexadecane addition to the blend, viscosity increased further, but sizing was less effective. Considering that hexadecane does not contribute to sizing and the dosage of MSOHO was kept constant, reducing viscosity of MSOHO increased its sizing efficiency by up to 5 Cobb₆₀ points. In Figure 6, numbers above the Cobb₆₀ values give the actual dosage of the MSOHO-hexadecane blend. It becomes clear that a considerable amount (1.2 kg/t) of a sizing agent blend containing 20% hexadecane is needed to reach a target Cobb₆₀ value of 30 gm⁻².

5.6. Sizing efficiency of MSOHO blends versus pure MSOHO, FAA, and ASA

To conclude from the application tests, the sizing efficiency of all optimized MSOHO blends was compared to the pure sizing agents MSOHO, FAA and ASA in one test series. For all the blends viscosity was measured as well. Thus, following sizes were tested: MSOHO, FAA, ASA, 75% MSOHO + 25% FAA, and 75% MSOHO + 25% hexadecane. To all sheets 6 kg/t Alum were added.

Clearly; the synergy of MSOHO and FAA can be seen (Figure 7). The blend of MSOHO with 25% FAA had a better sizing performance than both pure MSOHO and pure FAA. Furthermore sizing efficiency of the MSOHO-FAA blend came quite close to that of ASA. As the sizing efficiency of the MSOHO-hexadecane blends is worse than for pure MSOHO there is no benefit in using those blends. They were just introduced in the present study to work out the viscosity effects.

5.7. Sizing with binary and ternary MSOHO blends

Blends with 25%, 30%, and 50% MSOHO in ASA were prepared and tested for their sizing efficiency. All sheets were produced with the use of 6.5 kg/t alum. No difference was detected in the sizing efficiency of the investigated blends (Figure 8). Thus, it is well possible to run first mill trials with a 1/1 blend of ASA/MSOHO, which provides sufficient sizing to paper at low dosage.

Blending three different sizing agents, the influence of ASA on MSOHO – FAA blends and on the synergistic effect between MSOHO and FAA was studied. The mixtures represent ternary systems of three sizing agents. Ten different ternary blends were produced (Table 2). The used MSOHO was produced in lab scale using a ratio maleic anhydride per triglyceride of 4:1, and all the precautions described earlier to optimize product quality were observed.⁽⁴⁾ All sheets were produced with the use of 6.5 kg/t alum and at a size dosage of 0.9 kg/t.

Area results for the ternary system were calculated with Minitab 15 (Figure 9) based on the measured Cobb₆₀ values for all blends. The synergy between MSOHO and FAA regarding sizing efficiency can easily be seen: While pure MSOHO has a Cobb₆₀ value around 60 gm⁻² the 50/50 blend MSOHO/FAA ranges between 30 and 40 gm⁻². Neat FAA and neat MSOHO lack some sizing efficiency as compared to ASA, but reasonable Cobb₆₀ values ranging from 30-40 gm⁻² at the rather low dosage of 0.9 kgt⁻¹ were reached with 1/1 mixtures of MSOHO and FAA.

6. Conclusions

Within this study, the sizing efficiency of a newly developed, renewables-based sizing agent, maleated high oleic sunflower oil (MSOHO) was investigated. To be able to readily compare the results, ASA was used as reference, because it is a well known sizing agent commonly used in internal sizing, honoring its high efficiency and quick curing characteristics. The new sizing agent MSOHO has the same reactive group as ASA and thus similar characteristics regarding its hydrolysis behavior and application protocol. Therefore the new sizing agent will have to compete against ASA if it is going to be introduced into the market. The most notable advantage of MSOHO is that it is based on renewable resources. In addition, it is more stable against hydrolysis than ASA. But all these advantages would be worthless if not a good sizing efficiency could be reached that would well compare to ASA. This study demonstrated that this good sizing efficiency can indeed be easily reached. The aim of this paper was in addition to find out what modifications in the application of MSOHO were needed to maximize this sizing efficiency.

The sizing efficiency of both pure MSOHO and pure ASA as well as of all MSOHO / ASA blends decreased with increasing amounts of ground calcium carbonate (GCC). The addition of alum however significantly improved the sizing efficiency at a constant size dosage. The alum addition had a larger influence on MSOHO than on ASA. As in ASA sizing alum is traditionally used as additive to keep the sizing degree at a constant level, it will be possible in most applications to add alum as well when sizing with MSOHO. For both MSOHO and ASA sizing degrees improved significantly after short storage of the already finished paper sheets at room temperature or elevated temperature (curing). The comparable curing characteristics for MSOHO and ASA proved their similar sizing mechanisms.

As mentioned in previous papers one characteristic of MSOHO in comparison to ASA is its high viscosity. While that high viscosity positively influences the hydrolytic stability of MSOHO in an aqueous environment, it is negative to sizing, because it makes even spreading onto the cellulose fibers more difficult. Within this paper a very convenient way was presented to overcome this problem: Another green sizing chemical with a very low viscosity, fatty acid anhydride (FAA), was blended with MSOHO. In addition to the desired effect of lowered viscosity, the mixtures had a much better sizing efficiency than both neat sizing agents, and even the sizing efficiency of ASA sizing could almost be reached. The positive influence of FAA was also seen when using ternary mixtures of MSOHO, FAA, and ASA. The results obtained are currently being used as the data basis for mill trials using binary and ternary mixtures of MSOHO, FAA and ASA.

7. Acknowledgements

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Figures and tables

Figure 1: Sizing with MSOHO - ASA blends at different calcium carbonate (GCC) levels.

Figure 2: Influence of alum on sizing without GCC.

Figure 3: Influence of alum on sizing with 20% GCC.

Figure 4: Influence of different curing treatments on MSOHO and ASA sizing.

Figure 5: Viscosities and Cobb₆₀ values for MSOHO - FAA blends.

Figure 6: Relationship of Cobb₆₀ and viscosity for MSOHO - hexadecane blends.

Figure 7: Sizing curves for optimized MSOHO blends, MSOHO, FAA, and ASA.

Figure 8: Sizing for MSOHO - ASA blends.

Figure 9: Ternary mixtures with MSOHO, FAA, and ASA.

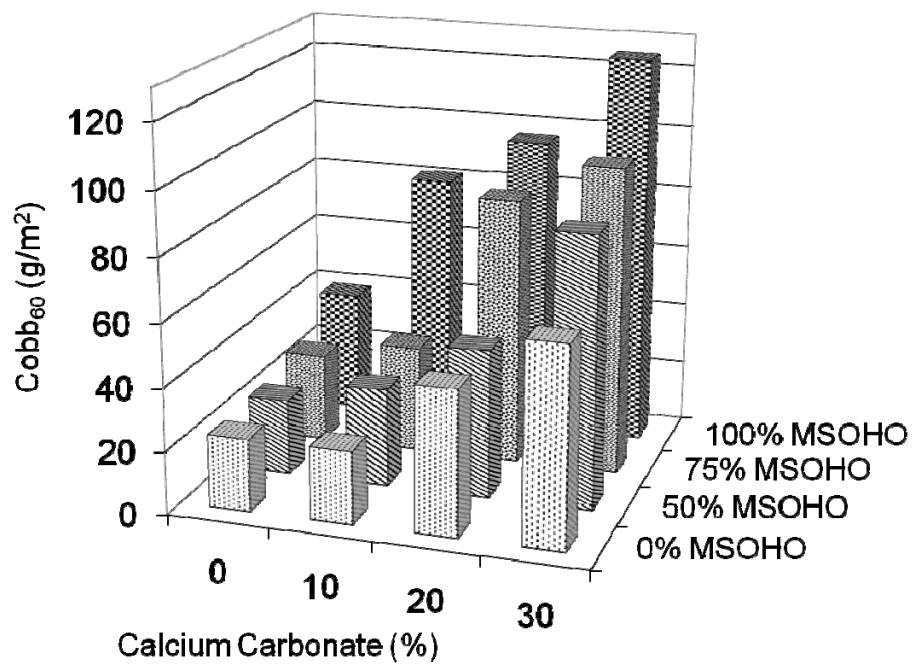


Figure 1: Sizing with MSOHO - ASA blends at different calcium carbonate (GCC) levels.

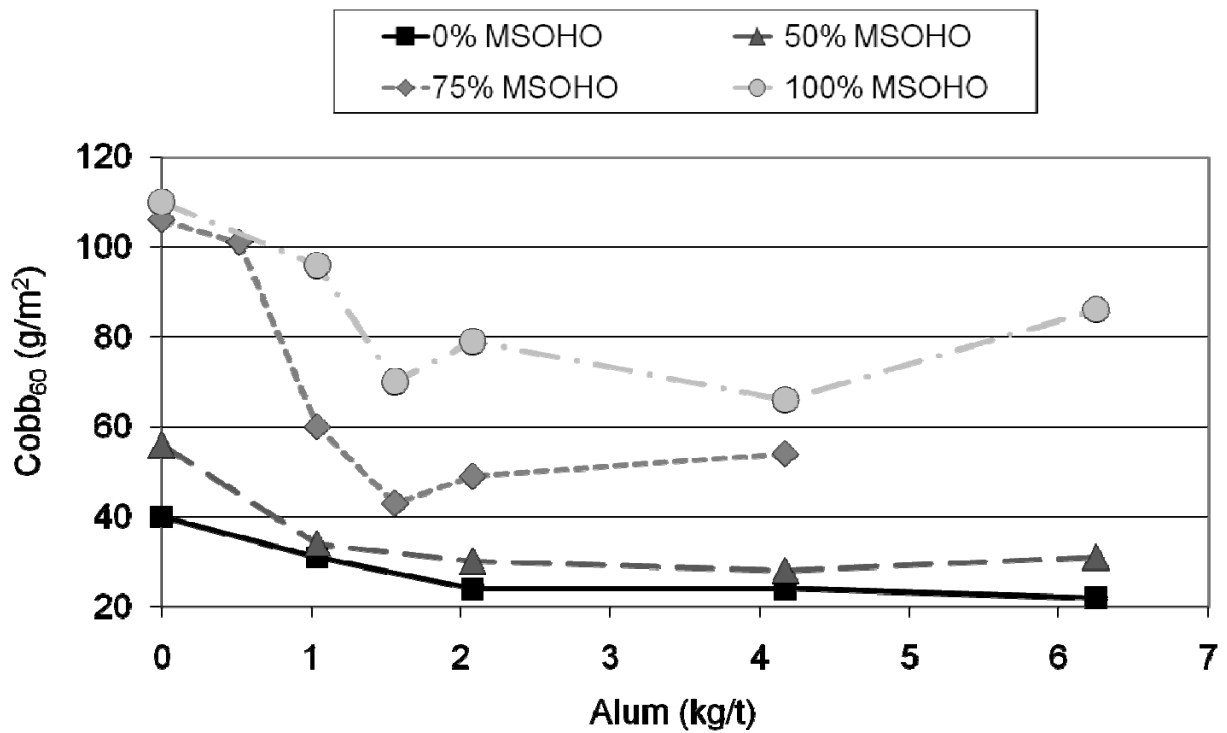


Figure 2: Influence of alum on sizing without GCC.

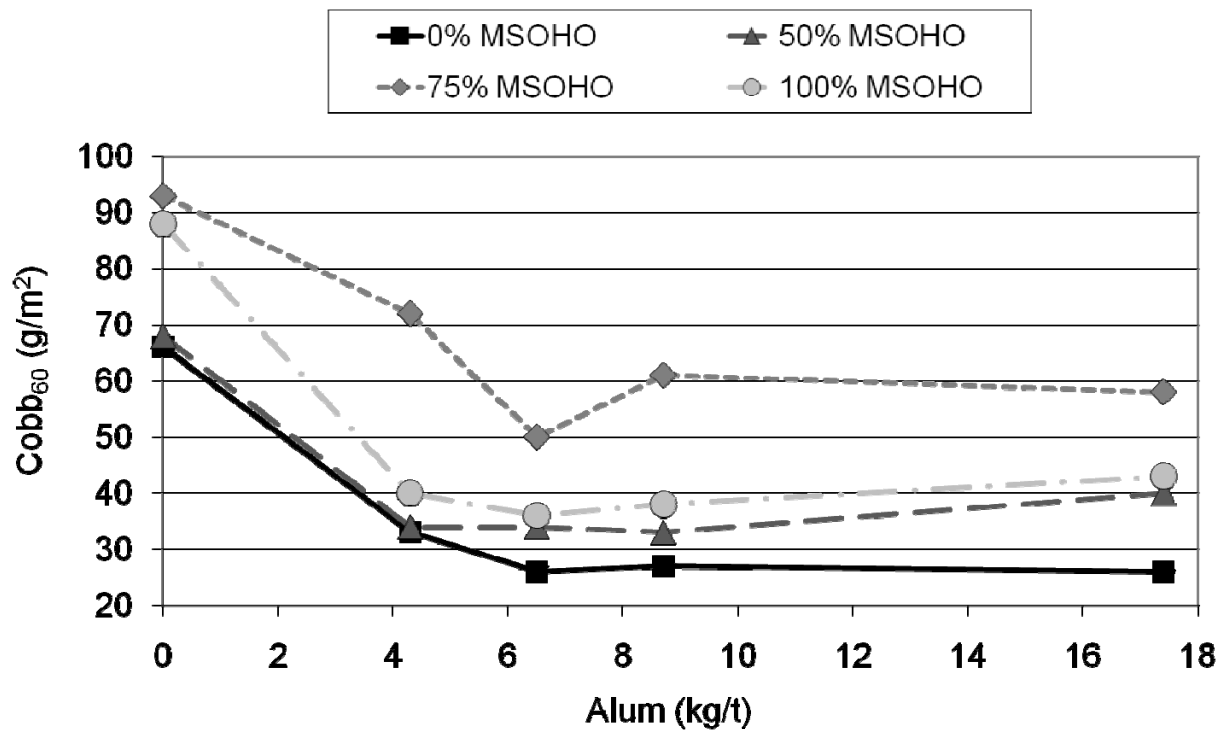


Figure 3: Influence of alum on sizing with 20% GCC.

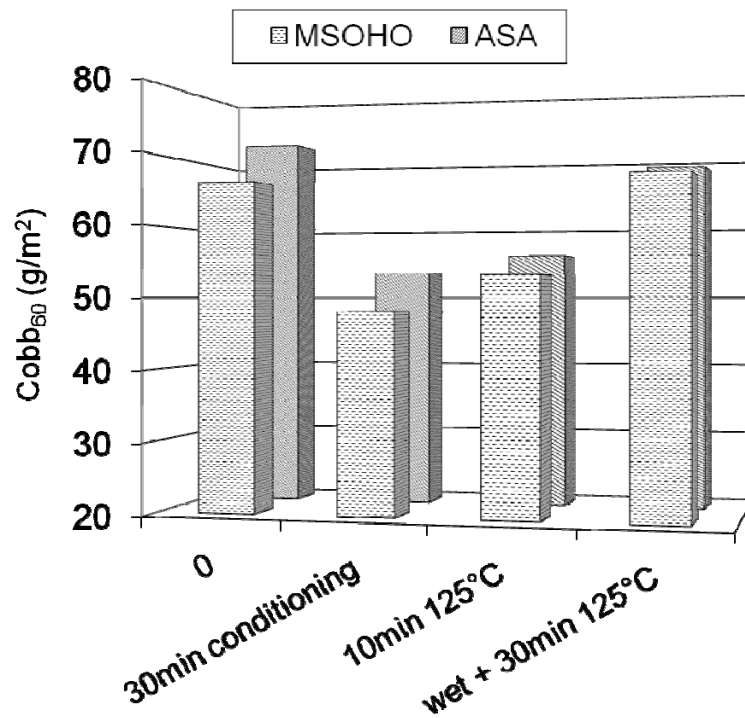


Figure 4: Influence of different curing treatments on MSOHO and ASA sizing.

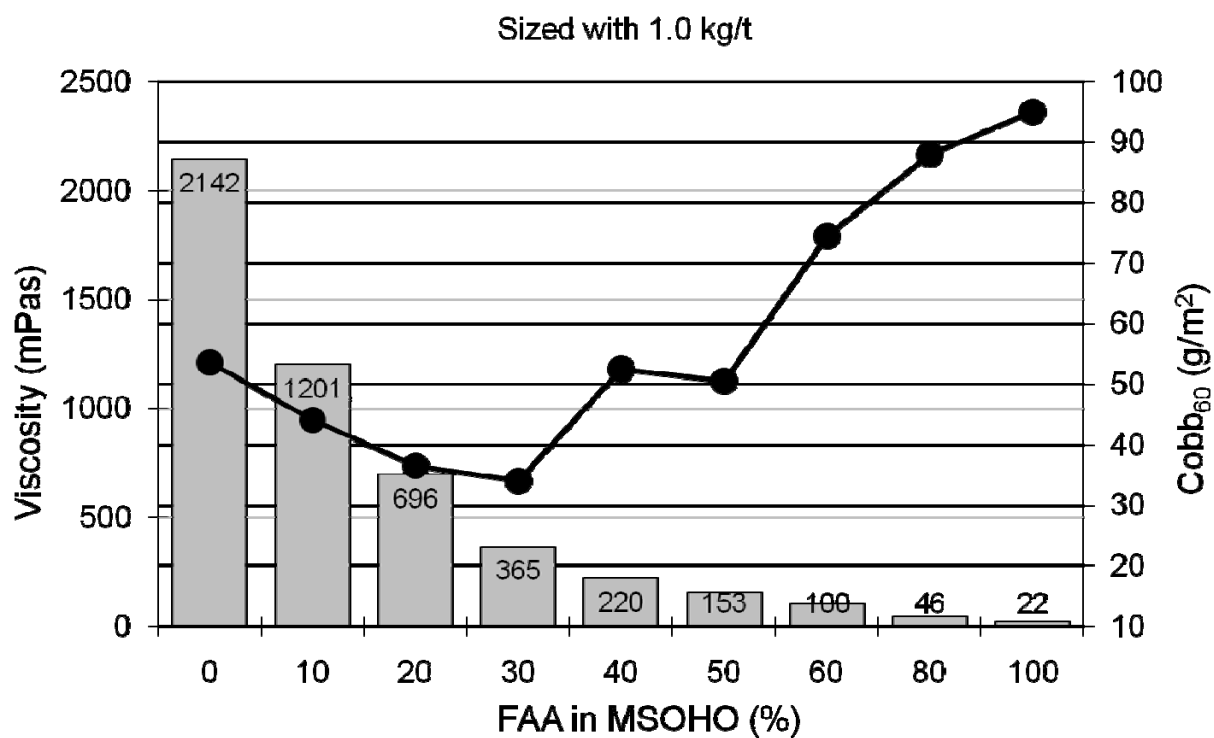


Figure 5: Viscosities and Cobb₆₀ values for MSOHO - FAA blends.

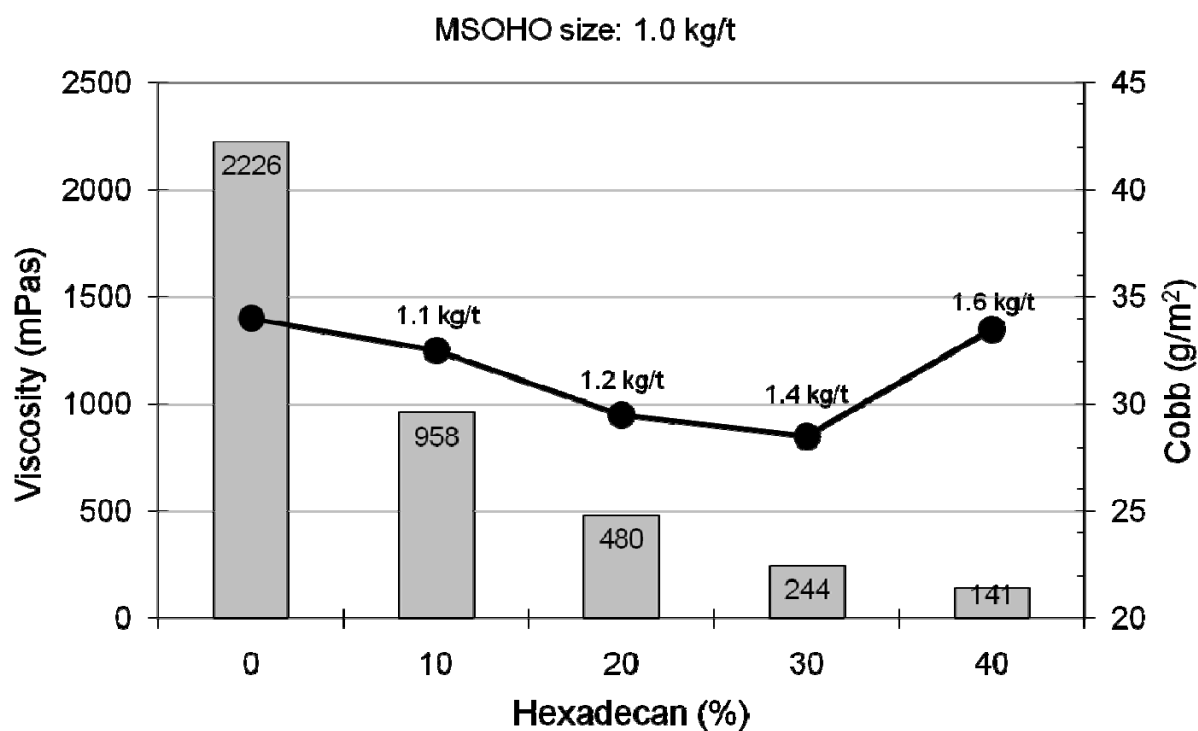


Figure 6: Relationship of Cobb₆₀ and viscosity for MSOHO - hexadecane blends.

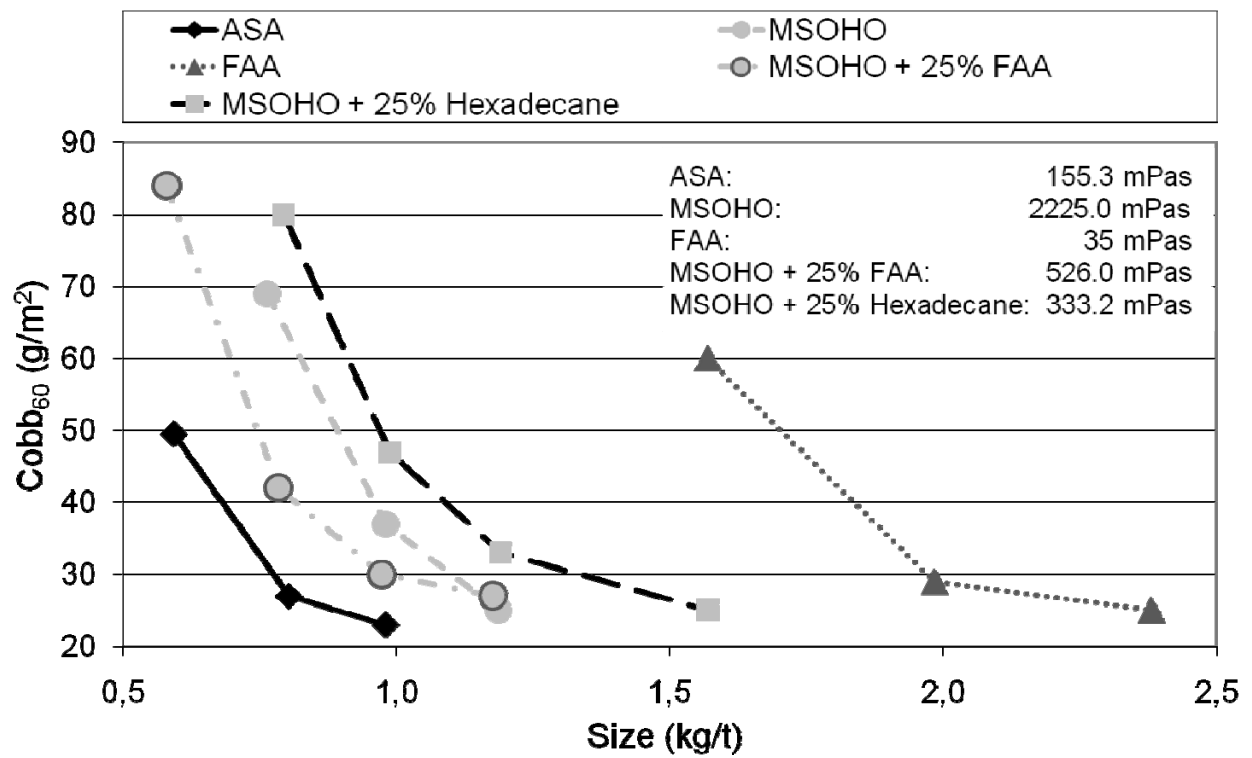


Figure 7: Sizing curves for optimized MSOHO blends, MSOHO, FAA, and ASA.

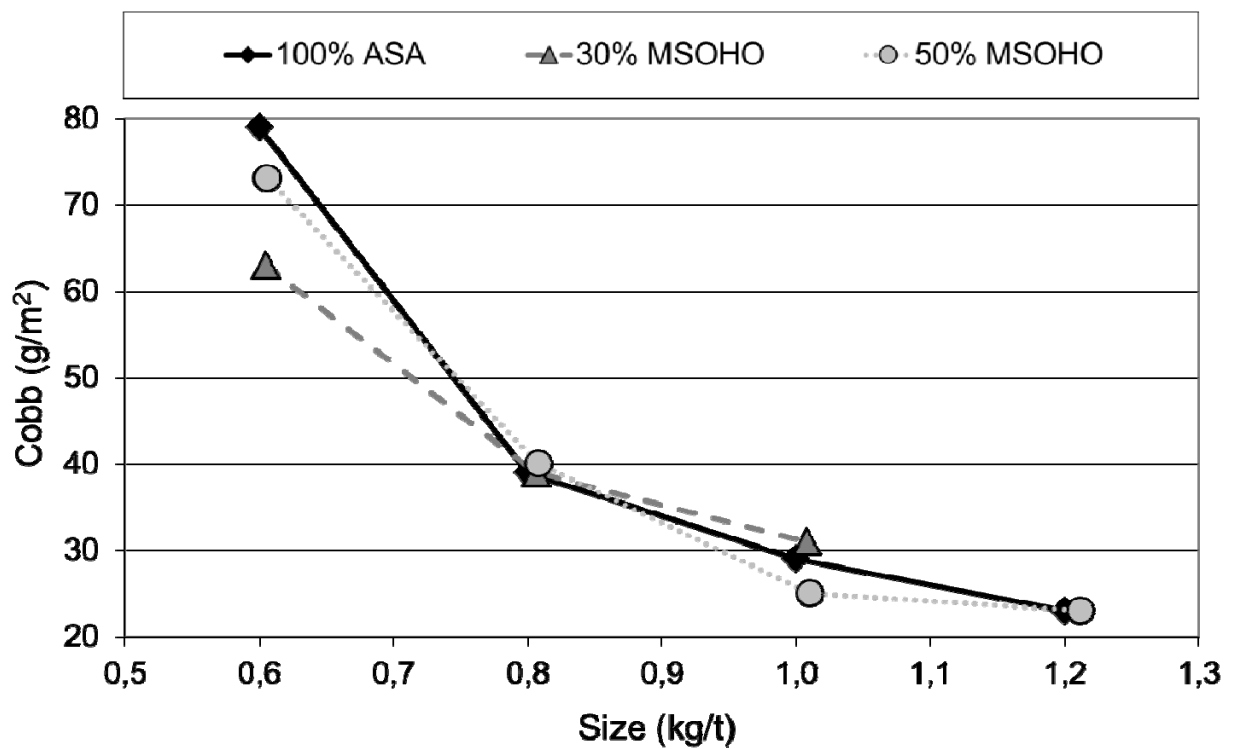


Figure 8: Sizing for MSOHO - ASA blends.

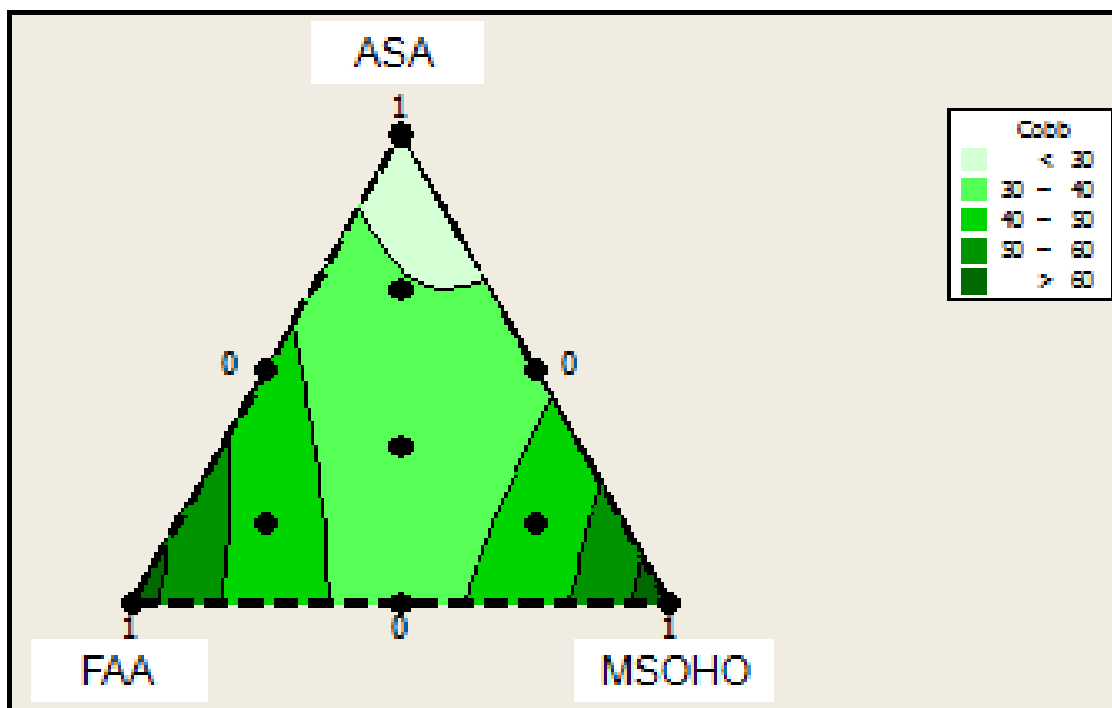


Figure 9: Ternary mixtures with MSOHO, FAA, and ASA.

Table 1: Viscosities and Cobb₆₀ results for MSOHO-FAA blends (cf. Figure 5).

MSOHO (%)	FAA (%)	Viscosity (mPas)	Cobb ₆₀ (g/m ²)
		T = 25°C	for 1.0 kg/t
100	0	2142	63 / 44
90	10	1201	50 / 38
80	20	696	33 / 40
70	30	365	32 / 36
60	40	220	52 / 53
50	50	153	47 / 54
40	60	100	79 / 70
20	80	46	89 / 87
0	100	22	95

Table 2: Ratios of sizing agents used in ternary blot (*cf.* Figure 9).

ASA	FAA	MSOHO
[%]	[%]	[%]
100.0	-	-
16.7	66.7	16.7
16.7	16.7	66.7
33.3	33.3	33.3
-	-	100.0
50.0	50.0	-
66.7	16.7	16.7
-	100.0	-
-	50.0	50.0
50.0	-	50.0

MODIFIED FATTY OILS IN PAPER SIZING AS GREEN ALTERNATIVE TO CONVENTIONAL SIZING AGENTS BASED ON CRUDE OIL

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ABSTRACT

Vegetable oils derived from different sources have been modified with maleic anhydride to produce a new, green paper sizing agent, which is a promising substitute of petrochemical-based ASA sizes. For a better understanding of their important characteristics including sizing efficiency and viscosity they were comprehensively characterized analytically including attenuated total reflection infrared spectroscopy (ATR-IR), ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy with full resonance assignment, and mass spectrometry. Furthermore, their hydrolysis behavior, sizing efficiency, and curing characteristics were studied in comparison to alkenyl succinic anhydride (ASA), which is the most prominent, fast curing sizing agent in neutral to alkaline paper sizing.

Keywords: Alkenyl succinic anhydride (ASA), high oleic sunflower oil, hydrolysis, maleated oils, paper sizing

INTRODUCTION

Sizing of paper is an important step in paper production. It hinders penetration of water into the sheet. This repellence is needed for durability and other desired paper characteristics, such as printability. For this purpose, amphiphilic molecules are used which are able to attach to the cellulosic fiber surface with their hydrophilic, polar side, whereas their hydrophobic, apolar side is directed away from the surface and repels water and thus hinders water penetration into the paper sheet. If the sizing chemicals are added to the paper stock before sheet formation it is called internal sizing. Today, alkenyl

succinic anhydrides (ASA) and alkyl ketene dimers (AKD) are the most common chemicals used for this purpose in neutral to slightly alkaline paper production [1]. Frequently, ASA is the preferred option, especially when a short curing time is required.

ASA is based on internal alkenes that react with maleic anhydride (MAA) at high temperatures around 200°C in an *ene*-reaction. The internal olefins have to be prepared by thermal isomerization from alpha-olefins in crude oil. So far the conventionally used C_{16/18} olefin mixtures for ASA production have been exclusively provided by the petrochemical industry, but the demand for “green” sizing agents has increased considerably. This demand was also the central impetus for our research toward a suitable ASA-substitute based on renewable raw materials, such as natural vegetable oils.

Interesting developments on the field of renewables based sizing agents have been going on. Pure fatty acids were used in a sizing dispersion as well as un-saturated fatty acid methyl esters that were modified with maleic anhydride [2-5]. Another proposal focused on liquid fatty acid anhydrides derived from mixtures of saturated and unsaturated fatty acid mixtures with chain lengths from C₁₂-C₂₄ [6]. Highly unsaturated vegetable oils (soy bean, cotton seed, corn, safflower, linseed, or peanut oil) or fish oil can also be applied. These oils are combined (by low-shear mixing) with emulsifying agents, trialkylamines and ammonium hydroxide as sizing agents [7]. Maleated oils for purposes different from paper sizing have been described in the literature as well: They can be used as additives for electro deposition of metals, components of hair care products, emulsifiers, or as components in latexes, coatings and textile finishes [8-11].

In our approach, a novel paper sizing agent was developed based on natural plant oils. Their unsaturated fatty acids, as part of triglycerides, were the co-reacting moieties in the *ene*-reaction with MAA [12]. The use of vegetable oil as raw material eliminates the additional energy-demanding isomerization step needed in the case of olefins, and it gives additional benefit by reducing logistic efforts and transportation costs, but above all it meets the general demand for greener products.

EXPERIMENTAL

Materials

Samples of the new sizing agent were produced from fatty oils: linseed, rapeseed, soybean, and high oleic sunflower oil (SOHO) from C. Thywissen GmbH, Germany, and maleic anhydride (MAA) of synthesis grade from Merck, Germany. The abbreviations MLSO, MRSO, MSBO, and MSOHO are used for maleated linseed, rapeseed, soybean, and high oleic sunflower oil, respectively. Standard ASA (reagent grade, r. g.) was isoctadecenyl succinic anhydride from Tokyo Chemical Industry Co. Japan.

Following antioxidants were tested during production of the maleated oils: Anox 330 (1,3,5-trimethyl-2,4,6-tris (3,5-di-*tert*-4-hydroxybenzyl)benzene, Great Lakes Manufacturing Italy S.r.l., Italy; butylated hydroxytoluene (BHT, di-*tert*-butyl-hydroxy-toluene), purity >99%, Sigma Aldrich, Austria; butylated hydroxyanisole (BHA, *tert*-butyl- hydroxy-anisole), food grade, Eastman Chemical Company, USA; and vitamin E acetate (alpha-tocopheryl acetate), 98%, Haupt Chemicals Trading GmbH, Austria.

Chemicals for characterization of the new sizing agents: hexatriacontane, and margaric acid (heptadecanoic acid), puriss., from Fluka Chemie GmbH, Austria; deuteriochloroform from Sigma-Aldrich, Austria.

Further used chemicals were tetrahydrofuran (HPLC grade) purchased from Fisher Scientific GmbH, Austria; Ethanol (abs.) and n-pentane (analytical reagent) from VWR, Austria; acetone (techn.) from Brenntag CEE GmbH, Austria; aluminum sulfate, iron(III)chloride, and ammonium thiocyanate from Wako Pure Chemicals Co., Japan.

BF₃-methylation agent

For the methylation agent boron trifluoride-methanol complex (50 wt% in methanol) from Sigma-Aldrich, Austria, methanol and toluene, both HPLC grade, from Fisher Scientific GmbH, Austria (35:35:30 by volume) were used.

Preparation of maleated natural oil

Vegetable oil 150 g (0.17 mol) was charged into a reactor in an inert gas atmosphere and then heated to 180 – 220°C under stirring. MAA was added in one step, the amount of the anhydride was varied between 16.61 – 66.45 g (0.17 mol - 0.68 mol). The reaction was performed under inert gas at a pressure of 1.0 - 3.3 bar for 6-8 h. The reaction mixture was cooled to r.t., the pressure was released, and excess MAA was distilled off at a reduced pressure of 10 mbar at 120 - 140°C. Antioxidants can be added in the range of 0.01 - 0.4 w% related to weight of the reaction mixture.

Preparation of sizing emulsions

1% cationic starch solution (HICAT 132 with a DS of 0.04 from Roquette Co., France) was prepared by heating the starch in deionized water at 95°C for 12 min. After cooling to r.t., emulsions of the sizing agents were prepared by adding 0.5% size to the starch solution and dispersing it at r. t. with a double-cylinder homogenizer for 2 min.

Preparation of hand sheets

Commercial hardwood bleached Kraft pulp was beaten to 510 ml of Canadian Standard Freeness in a PFI mill. The calculated amounts of sizing emulsion were added to a 0.15% pulp slurry with a pH of 6.7-7 under stirring at 500 rpm. The basis weight of the hand sheets was 60 g m⁻², prepared according to Tappi standard [13]. No filler was used. After wet pressing, the sheets were dried in a rotary

drum dryer at 120°C. All sheets were conditioned for 24 h at 23°C and 50 % RH before measuring the sizing degree.

Sizing with aged emulsions

All %-data are b. o. dry weight of paper. 0.5% ASA r. g. and MSOHO emulsions, respectively, were aged at 4°C and 25°C and their sizing effect was investigated after production of unfilled hand sheets using these emulsions after different aging times. To all hand sheets 0.5% alum was added. ASA r. g. was tested at 0.2% and MSOHO at 0.8% addition levels.

Instrumental Analysis

Gel permeation chromatography (GPC)

Substances with high molecular weight, such as polymeric material formed during maleation of natural oils, were separated and analyzed on a GPC system of the following setup: auto sampler AS-2000, interface D-6000, pump L-2600 (all three Hitachi High Technologies Corporation, Tokyo, Japan), degasser DG-2410 (Degasys, Uniflows Co. Ltd., Tokyo, Japan), column oven (Jetstream 2 Plus) held at 40°C, refractive index (RI) detector (RI 2414, Waters Corp.), and a set of 4 columns (250 mm x 7 mm x 5 µm, Hibar, Merck, Germany) packed with divinylbenzene-crosslinked poly-styrene (PS 20 / PS 4 / PS 1 / PS 1). Eluant: THF.

Gas chromatographic (GC) analysis of fatty acid methyl esters

To find a relationship between the fatty acid composition of the vegetable oils and the characteristics of the corresponding maleated products, the starting oils and the maleated product oils were transesterified into the corresponding methyl esters by treatment with BF₃-methylation agent. Vegetable oil or maleated oil (100 mg) and margaric acid (20 mg, internal standard) were dissolved in THF (1 ml) in a 10 ml vial. 3 ml methylation agent were added and the mixture was mixed vigorously. After stirring the closed vial it is stored at 105°C for 40 min. Then it is cooled to r.t. and the fatty acid methyl esters are extracted with pentane. 1 µl of the pentane solution was injected for GC (Thermo Electron Corporation instrument (Italy) with FID detection). GC setup: DB-1 column (100% dimethyl polysiloxane, J&W Scientific, USA), H₂ as carrier gas, auto sampler AS 3000 (Thermo Electron Corporation, Italy), split flow 150 ml min⁻¹, temperature program 170°C to 215°C at 2°C min⁻¹, further to 245°C at 4°C min⁻¹, and to 300°C with 15°C min⁻¹ with a hold time of 5 min.

Gas chromatographic (GC) quantitation of residual oil

Focus instruments (Thermo Electron Corp.) with autosampler and FID detection as described above. Thermo TR5 column (5% phenyl/methyl polysiloxane column, Thermo Electron Corporation, Italy) with H₂ as the carrier gas at a split flow of 400 ml min⁻¹. Temperature

program: 200°C, ramped to 350°C at 20°C min⁻¹ and a final hold time of 5 min. The injected volume: 1 µl. For sample preparation, hexatriacontane (20 mg, internal standard) and either 70 mg of not modified oil or 250 mg of maleated oil were dissolved in toluene (7 ml). 1 ml of this solution was put into the autosampler vial and subjected to GC analysis. The amount of unchanged triglycerides in the sample was quantified by comparison of the triglyceride peak area with that of the internal standard.

Viscosity

The viscosity was determined on a rota – viscosimeter (Rheometer MC1, Anton Paar GmbH, Austria) at 20°C and a shear rate of 50 s⁻¹.

Nuclear magnetic resonance (NMR) spectroscopy

Spectra were recorded at 400.13 MHz for ¹H and at 100.41 MHz for ¹³C at a Bruker Avance II instrument, with CDCl₃ as solvent, if not otherwise stated. Chemical shifts, relative to TMS as internal standard, are given in δ values; coupling constants in Hz. ¹³C peaks were assigned by means of APT, HMQC and HMBC spectra. 30 mg of the sample were dissolved in 0.6 ml of CDCl₃ for NMR analysis.

Wet-chemical Analysis

Soap number [14]

Soap numbers were determined. From these values, the amount of maleic anhydride equivalents on the triglycerides (R) was calculated according to equation 1, using the approximation of 885.5 g mol⁻¹ for the molecular weight of the oils and thus the assumption that the oil consisted solely of glyceryl trioleate:

$$R = \frac{MW_{(Oil)}}{\left(\frac{2000 * MW_{(KOH)}}{(SN_{(Maleated\ Oil)} - SN_{(Oil)})} - MW_{(MAA)} \right)} \quad (1)$$

MW_(Oil) 885.5 g mol⁻¹ (with the above assumption); MW_(KOH) 56.1 g mol⁻¹; MW_(MAA) 98.1 g mol⁻¹; SN [mg KOH per g of sample]

Stöckigt sizing degree

Sizing efficiency was measured as Stöckigt sizing degree [15]. The three sizing agents were tested with and without addition of 0.5% alum (based on dry weight of paper) under various drying conditions. After drum drying, all sheets were conditioned at 23°C and 50% RH for 24 h. Then aliquots were cured at 105°C for 10 min and the sizing degree was measured immediately. The measurement was repeated after another 24 h in the conditioning room.

RESULTS AND DISCUSSION

Raw Material Selection

Plant oil raw materials with a broad range of fatty acid compositions were screened according their qualification for the production of maleated oils usable in paper sizing and thus as ASA substitutes. The most suitable candidates were: linseed oil (LSO), soybean oil (SBO), rapeseed oil (RSO), and high oleic sunflower oil (SOHO). The oils were maleated in a reaction procedure similar to conventional ASA production, but having one important benefit: there is no need to modify (isomerize) the raw material before the maleation step, as the double bonds in plant oils are already present in central position along the chain. The conversion is a so called *ene*-reaction upon which the anhydride moiety is transformed from maleic to succinic under the loss of the double bond. [16]

For finding the oil with the most appropriate fatty acid composition the four vegetable oils were reacted with different ratios of MAA per triglyceride. Afterwards the anhydride to triglyceride ratio (R) was calculated according Eq. (1) using the soap numbers of the unmodified and modified vegetable oils. The more double and triple unsaturated fatty acids are present in the starting oil, the higher was R, when using the same ratio MAA per triglyceride during the maleation reaction. While for SOHO that was reacted with 3 equivalents of MAA an R value of 1.2 was found, for LSO being treated with the same ratio of MAA an R value of 2.0 was calculated.

Oils with high amounts of polyunsaturated fatty acid residues, such as linseed or soybean oil, tend to give overly viscous products when maleated, and are thus less qualified. Promising results were obtained with rapeseed and high oleic sunflower oil (SOHO), because less polymeric by-products are formed and higher yields can be reached. Further optimization of the reaction parameters included, temperature, pressure, addition of antioxidants and maleic anhydride-to-triglyceride ratio [17].

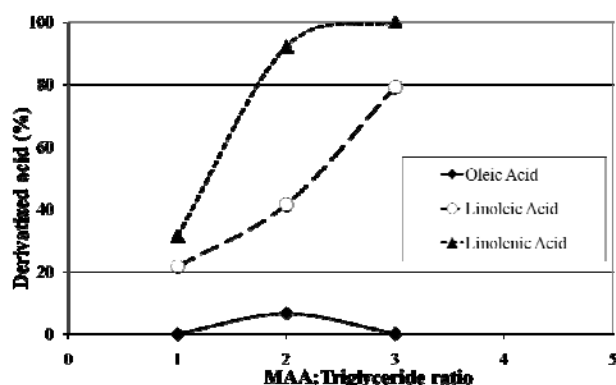


Fig. 1. Preferential maleation of polyunsaturated fatty acids in maleated soybean oil (GC analysis after transesterification into the fatty acid methyl esters, percentages of “Derivatized acid” are relative values).

Through subsequent analysis of the fatty acid composition via transesterification of the triglycerides to the fatty acid

methyl esters and GC analysis before and after the *ene*-reaction a clear preference of MAA for double and triple unsaturated fatty acids (linoleic and linolenic acid) was found. This general trend was confirmed with all starting materials, but is especially illustrative with SBO as can be seen in **Fig. 1**.

Increasing the MAA:triglyceride ratio during maleation the oleic acid part remains unchanged, while around 80% of the linoleic and 100% of the linolenic residues were converted at a MAA:triglyceride ratio of 3:1. Thus MAA is not evenly distributed over all triglycerides, and a large part of triglycerides might remain without maleation. In an attempt to anchor at least one MAA per triglyceride and to avoid a large amount of not reacted oil, which does not contribute to paper sizing, the content of polyunsaturated fatty acids in the raw material should be as low as possible. SOHO whose triglycerides are based on over 70% oleic acid, and 10% linoleic acid residues above others and which contains no triple unsaturated fatty acids is therefore the preferred raw material for our new sizing agent. It is closely followed by RSO with 56% oleic acid, 21% linoleic, and 6% linolenic acid residues, which also might be used.

Optimizing Reaction Parameters

Comparing products based on RSO and SOHO that were produced at the same MAA per triglyceride ratio the first mentioned were of considerably higher viscosity. This is caused by a higher content of polymeric by-products as was confirmed with GPC. The values are presented in **Table 1**. In terms of applying these maleated oils as paper sizing agent viscosity plays an important factor when it comes to emulsifying these oils in polymer solutions (e.g. cationic starch), as it is the standard procedure for ASA. Thus the further focus in optimizing the reaction parameters lay on MSOHO.

Table 1. Analysis results for different maleated oils. RSO: rapeseed oil; MRSO: maleated RSO; SOHO: sun flower oil high oleic; MSOHO: maleated SOHO.

Oil resp. MAA:Trigl. ratio ^a	Residual oil by GC [%]	R	Viscosity [mPas]	Polymers by GPC [%]
RSO	98	-	71	0.5
MRSO 2:1	21	1.1	8530	22.5
SOHO	99	-	78	0.1
MSOHO 2:1	20	1.1	2085	14.2

^a Numbers give the ratio between maleic anhydride and triglyceride during *ene*-reaction.

R Maleic anhydride equivalents on the triglycerides.

The aim was to reduce the content of residual oil and raise R to improve sizing reactivity, while keeping viscosity and the content of polymers as low as possible. To reach this goal the ratio MAA per triglyceride was raised from 2:1 to 4:1, which resulted in a reduction of

residual oil and an increase in R, as expected. See **Table 2**.

Furthermore the use of various antioxidants was tested. It was found that the addition of 0.02% of BHT/BHA (1:1) related to the mass of the reaction mixture worked best besides the sole use of BHT or Vitamin E acetate.

Table 2. Comparison of two maleated high oleic sunflower oil (MSOHO) products. Upper sample standard procedure, lower sample optimized procedure.

Oil resp. MAA:Trigl. ratio ^a	Residual oil by GC [%]	R	Viscosity [mPas]	Polymers by GPC [%]
MSOHO 2:1	20	1.1	2085	14.2
MSOHO 4:1	10	1.4	5775	8.8

^a Numbers give the ratio between maleic anhydride and triglyceride during *ene*-reaction.

R Maleic anhydride equivalents on the triglycerides.

Analytical Characterization with NMR

For a better understanding of paper sizing in general and the characteristics of the new sizing agent in particular its chemical structure was investigated using NMR. A signal assignment was possible for all relevant resonances in the ¹H and ¹³C domains due to the use of 2D techniques. Peak assignment for SOHO: ¹H NMR (400 MHz, CDCl₃): δ = 5.34-5.22 (m, 6 H; -HC=CH-), 5.21-5.17 (m, 1 H; O-CH_AH_B-CH(OR)), 4.22 (dd, ²J = 12 Hz, ³J = 4.4 Hz, 2 H; O-CH_AH_B-CH(OR)-), 4.07 (dd, ²J = 12 Hz, ³J = 6 Hz, 2 H; O-CH_AH_B-CH(OR)-), 2.70 (m, <1 H; HC=CH-CH₂-CH=CH), 2.27-2.22 (m (dt), ³J = 7.6 Hz, 6 H; OOC-CH₂-CH₂), 2.02-1.91 (m, 12 H; HC=CH-CH₂), 1.58-1.50 (m, 6 H; OOC-CH₂-CH₂), 1.30-1.12 (m, 60 H; -CH₂-), 0.81 (t, ³J = 6.8 Hz, 9 H; -CH₃); ¹³C NMR (100 MHz, CDCl₃, APT): δ = 173.2 and 172.8 (-COO-), 130.5-129.8 (HC=CH-CH₂-CH=CH and -CH=CH-), 127.8 (HC=CH-CH₂-CH=CH), 68.8 (O-CH₂-CH(OR)-), 62.1 (O-CH₂-CH(OR)-), 34.1 (OOC-CH₂), 31.9 (CH₃-CH₂-CH₂), 29.8-29.1 (-CH₂-), 27.2 (HC=CH-CH₂), 25.6 (HC=CH-CH₂-CH=CH), 24.8 (OOC-CH₂-CH₂), 22.6 (CH₃-CH₂), 14.1 (CH₃).

Following new signals were found in MSOHO after the *ene*-reaction with MAA: ¹H NMR (400 MHz, CDCl₃): δ = 5.57-5.47 (m; -CH(succ.)-CH=CH-), 5.10-5.00 (m; -CH(succ.)-CH=CH-), 3.12-3.05 (m; CH_AH_B-CH in succ.), 2.82 (ddd, ²J = 19.2 Hz, ³J = 9.8 Hz, ⁴J = 1.2 Hz; CH_AH_B-CH in succ.), 2.68 (dd, ²J = 19.2 Hz, ³J = 5.4 Hz; CH_AH_B-CH in succ.), 2.62-2.53 (m; -CH-CH(succ.)), 1.38-1.29 (m; -CH=CH-CH(succ.)-CH₂); ¹³C NMR (100 MHz, CDCl₃, APT): δ = 170.3 (C(=O)-O-C(=O) in succ.), 136.8 and 136.5 (-HC=CH-CH=CH-), 130.0-129.7 (HC=CH- and -CH(succ.)-CH=CH-), 126.4 and 126.2 (-HC=CH-CH=CH-), 45.5 (CH in succ.), 42.6 (-CH-CH(succ.)), 32.7-32.6 (CH(succ.)-CH=CH-CH₂), 30.2 (CH₂ in succ.).

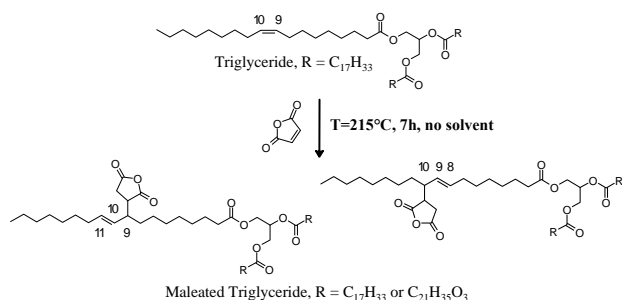


Fig. 2. *Ene*-reaction mechanism of vegetable oil with maleic anhydride.

Investigating the NMR results more closely following reaction mechanism for the *ene*-reaction of MAA and vegetable oil was confirmed: The *cis*-double bond of the unsaturated fatty acid residues on the triglycerides reacts with MAA to form a *trans*-double bond on the fatty acid residue that is shifted for one position; see **Fig 2**. This cannot be deduced from the ¹³C shifts of the double bond carbons themselves, as they are insensitive towards possible configuration change. However, the methylene carbons next to the double bond experience typical changes depending on the configuration of the double bonds. While methylene carbons remote from double bond systems in fatty acids resonate around 30 ppm, this value is shifted up-field to around 27 ppm for RCH=CH-CH₂ with *cis*-configuration as it is encountered in the starting SOHO oil, and down-field to about 33 ppm for RCH=CH-CH₂ and *trans*-double bonds, as seen in the maleated product oil. With a value of 32.7 ppm for the α -methylene relative to the double bond in the maleated product, the *trans*-configuration of the newly introduced double bond was evident. [18]

Hydrolytic Stability, Sizing with Aged Emulsions

A major drawback of sizing agents with a reactive anhydride group, like ASA or maleated oils, is their quick hydrolysis in the presence of water. This hydrolysis behavior is the reason why conventional ASA emulsions have to be reacted with paper within 30 min of their preparation. Otherwise, ASA will be hydrolyzed which is unfavorable for an even distribution of the sizing chemical on the cellulose fibers [19]. For a successful application of maleated oils they have to be at least as stable as ASA. In various tests these characteristics of the new sizing agent were investigated in comparison to conventional sizes [20]. It was found that with maleated high oleic sunflower oil (MSOHO) paper sizing is possible over a significantly longer time range than with ASA. Furthermore MSHO is less affected by the presence of Ca²⁺ ions, which is beneficial to limit deposit formation in paper mills.

Above other tests that tested the stability of MSHO against hydrolysis especially representative were results gained from the comparison of sizing efficiency of aged r. g. ASA and MSHO emulsions. After storage for one

day at 25°C no sizing at all was possible in the case of the r. g. ASA emulsion, whereas the MSHO emulsion still was capable of providing some water repellency to produced hand sheets (**Fig. 3**). Storing both emulsions at 4°C sizing efficiency was maintained over 1 day.

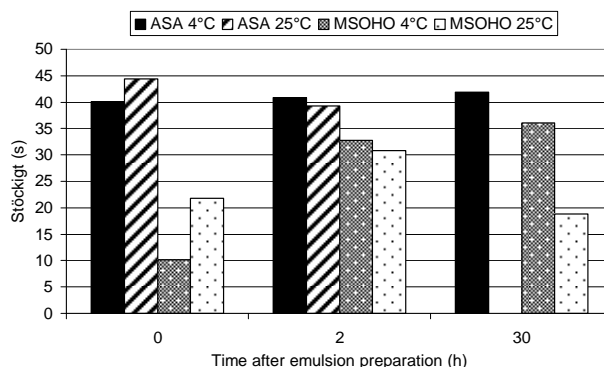


Fig. 3. Development of the sizing efficiency of ASA and MSHO emulsions stored at 4°C and 25°C with time.

An interesting additional effect was seen for sizing with MSHO emulsions. The sizing efficiency increases after storage for 2 h. It did not even matter at which temperature the emulsions were kept over this time range. For r. g. ASA nothing similar could be observed. This special MSHO characteristic might originate in its higher resistance against hydrolysis. As was supposed by Isogai et al. [21], an amphoteric surface of the sizing emulsion droplets is needed to provide sufficient retention and distribution of the size throughout the paper sheet. While r. g. ASA hydrolyses quite fast and can build up this amphoteric surface during emulsion production or few minutes later, MSHO hydrolysis is significantly slower as was revealed earlier [20, 22]. Therefore, it takes a few hours until a sufficient amount of MSHO molecules at the droplet surface is hydrolyzed to build up the amphoteric surface required for optimum retention and distribution.

The higher viscosity of MSHO is advantageous when it comes to emulsion and hydrolytic stability. Sizing was still possible with an almost 30 h old MSHO emulsion, while no sizing effect was seen for an ASA sized sheet produced under the same conditions. Due to the high viscosity, the MSHO emulsion droplets are only slowly hydrolyzed from the surface. Inside the droplet, enough reactive MSHO remains to provide hydrophobicity to the hand sheet.

CONCLUSIONS

Sizing agents based on renewable raw materials were developed as alternative to crude oil based alkenyl succinic anhydride (ASA). They were produced using an *ene*-reaction mechanism for the maleation of natural vegetable oils. It was found that vegetable oils with a high content of oleic acid residues on their triglycerides were

most suitable. Thus especially the use of high oleic sunflower and rapeseed oil is favored. In further studies the reaction parameters for the maleation were adjusted to limit the formation of polymeric by-products and the viscosity while increasing the yield of maleated triglycerides. The optimized reaction procedure comprises the use of BHT/BHA (1:1) as antioxidative and a maleic anhydride to triglyceride ratio of 4:1. The maleated high oleic sunflower oil (MSOHO) was characterized with NMR, which helped in confirming the proposed *ene*-reaction mechanism. When testing the emulsion stability of MSOHO in comparison to ASA an increased stability against hydrolysis was found and it was shown that MSOHO can be used to make paper sheets water repellent.

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Curriculum Vitae

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Personal details

Date of Birth: June 21st 1981
Place of Birth: Vienna
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Current position

Since 10/2008 PhD – student at the Christian Doppler Laboratory for Advanced Cellulose Chemistry and Analytics, University of Natural Resources and Life Sciences, 1190 Vienna, Austria
Topic: “Novel ASA-substitutes in paper sizing based on renewable raw materials”

Previous positions

03/2007 - 09/2008	Research Scientist R & D, full time, Kemira Chemie GesmbH, Krems, Austria
06/2004 - 03/2007	Technical Assistant, part time (10 h / week), “Measurement of air pollutants with passive samplers”, Institute of Chemical Technologies and Analytics, Technical University Vienna, Austria
07/2005 - 09/2005	Industrial trainee, full time, Heraklith AG, Fürnitz, Austria
08/2003 - 04/2004	Technical Assistant, part time (10 h / week), Institute of Applied Microbiology, University of Natural Resources and Life Sciences, Vienna, Austria
02/2003	Trainee, full time, Institute of Chemical Technologies and Analytics, Technical University Vienna, Austria
11/2001 - 10/2002	Technical Assistant, part time (20 h / week), Institute of Cancer Research, Vienna, Austria
7/2001	Trainee, full time, Institute of Cancer Research, Vienna, Austria
8/2000	Trainee, full time, Lebensmittelversuchsanstalt, Vienna, Austria

Education

11/2006	Master's degree in Technical Chemistry (Technical Biochemistry and Technology of Natural Raw Materials), Diploma thesis: "Analytical Determination of Urea in Atmospheric Aerosol", Supervisor: Ao. Univ. Prof. Dr. techn. Dipl.-Ing. Kasper-Giebl, Institute of Chemical Technologies and Analytics, Technical University Vienna, Austria
10/2001 - 11/2006	Study of Technical Chemistry at Technical University Vienna, Austria
1999 - 2001	HBLUVA for Chemical Industry, Vienna, Austria (College)
1991 - 1999	GRG 3 Vienna, Austria (Secondary School)
1987 - 1991	Schwestern v. a. Kinde Jesu, Vienna, Austria (Elementary School)

Awards and Fellowships

3/2009 - 5/2009	Short time - fellowship (KUWI) for Research at The University of Tokyo, Japan
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Language Skills

Native Speaker:	German
Fluent:	English
Basic:	Spanish, Russian, Japanese

Interests

Western riding
Dancing
