

ASA Optimisation -

Control of Particle Size, Stability and Hydrolysis

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Summary

This work has shown that a reproducible ASA emulsification with optimal particle size is possible, and well controllable, in the laboratory. The most important factors for the adjustment of particle size are emulsification time, shear forces, ASA concentration and temperature. The protection colloid and the emulsifier used are also important factors for the particle size that can be achieved. Concerning the emulsification there is an optimum as regards particle size - which is mainly dependent on the starch or polymer to ASA ratio.

The stability and hydrolysis of ASA emulsions depend mainly on pH, temperature and water hardness (Ca^{2+} , Mg^{2+}). However, the tendency to build up agglomerates and deposits is only caused by calcium ions, due to the fact that the ASAcid calcium salts are of much lower solubility than the magnesium salts. Agglomeration and hydrolysis can be reduced by increased starch addition or by the introduction of long-chain polymers such as polyacrylamides. It is surprising that the cationic charge of the used protection colloid showed almost no or even a negative influence on the emulsion and hydrolysis stability of the ASA. Furthermore, particle size plays an important role during the evaluation of hydrolytic stability and deposition. Therefore, it is very important that emulsions and different protection colloids should only be compared at the same particle size. However, high cationic liquid starches or the new “particle stabilized ASA” (bentonite or colloidal silica) seem to be the best alternative solution, as compared to the standard cooking starches.

1 Introduction and Objective

In paper production, sizing is one of the most important parameters for further processing and for product quality of the paper (e.g. writing properties). The synthetic sizing agents used - such as AKD (alkyl ketene dimer) and ASA (alkenyl succinic anhydride) - are comparatively expensive and have to be added very accurately to avoid process disturbances such as deposits, and achieve the desired paper quality. This work is focussed on the sizing agent ASA which has several advantages compared to the still predominantly used AKD.

In paper sizing, it is essential that the sizing agent reacts with the cellulose fibre. The competing ASA hydrolysis affects the sizing properties and the runnability of the paper machine, due to the formation of sticky deposits - such as ASAcid calcium salts. Sizing agents, which are hydrolysed or not retained, do not contribute to the sizing performance to the desired extent, and get into the white water. There they can contribute to negative interactions with chemical additives or other substances.

The objective of the work presented in this report was to determine the most important factors which influence particle size, stability, and hydrolysis of ASA emulsions. In the experimental designs, factors such as temperature, pH, conductivity, starch to ASA ratio, starch concentration, or the types of protection colloids have been varied systematically, and particle-size measurements, as well as dynamic titration to investigate the stability of the emulsions were carried out. The results show possibilities regarding how ASA sizing agents can be used more effectively, process disturbances avoided, and costs reduced.

2 Alkenyl Succinic Anhydride (ASA)

2.1 Introduction and basics of ASA

Alkenyl Succinic Anhydride was patented for paper sizing in 1964 [1] and therefore is the newest of all currently used internal sizing agents. With the change to neutral papermaking, ASA has been established more and more as a cost-effective alternative to AKD. Furthermore, ASA has several advantages compared to AKD.

Table 1: Advantages of ASA sizing

- Immediate sizing (no curing time necessary)
- Effective in a wide range of pH (pH 5-9)
- Good paper convertibility (e.g. no slippery effect)
- Better adjustment of sizing compared to AKD
- No interference on paper quality due to hydrolysis products (compared to the ketones of AKD)
- Good sizing against hot water (gypsum board)
- Good sizing against hydrogen peroxide
- Lower overall sizing costs

Due to the clearly higher reactivity compared to the AKD, this sizing agent also has some disadvantages that are summarised in the following table.

Table 2: Disadvantages of ASA sizing

- In situ emulsification necessary
- Higher investment costs for the equipment
- Faster hydrolysis
- Higher risk of deposits
- Good fine and filler retention necessary

2.2 Structure and reactions of ASA

The anhydride ring is mainly responsible for the high reactivity of the ASA. A commonly used model is that ASA reacts with the hydroxyl group of the cellulose to form an ester bond. However, due to the higher reactivity the hydrolysis [2-7] also proceeds much faster compared to AKD. Thus, it is not possible to deliver ASA as a ready to use emulsion which can be stored; it has to be converted into an aqueous form just before the addition. This process is called emulsification and is normally done with cationic starch or synthetic polymers [7-11].

Hydrolysis cannot be avoided completely, but the speed and the effects on the paper making process can be minimized. This starts with the preparation of the ASA and goes on with process parameters such pH, temperature, and salt content [4, 5, 11, 12].

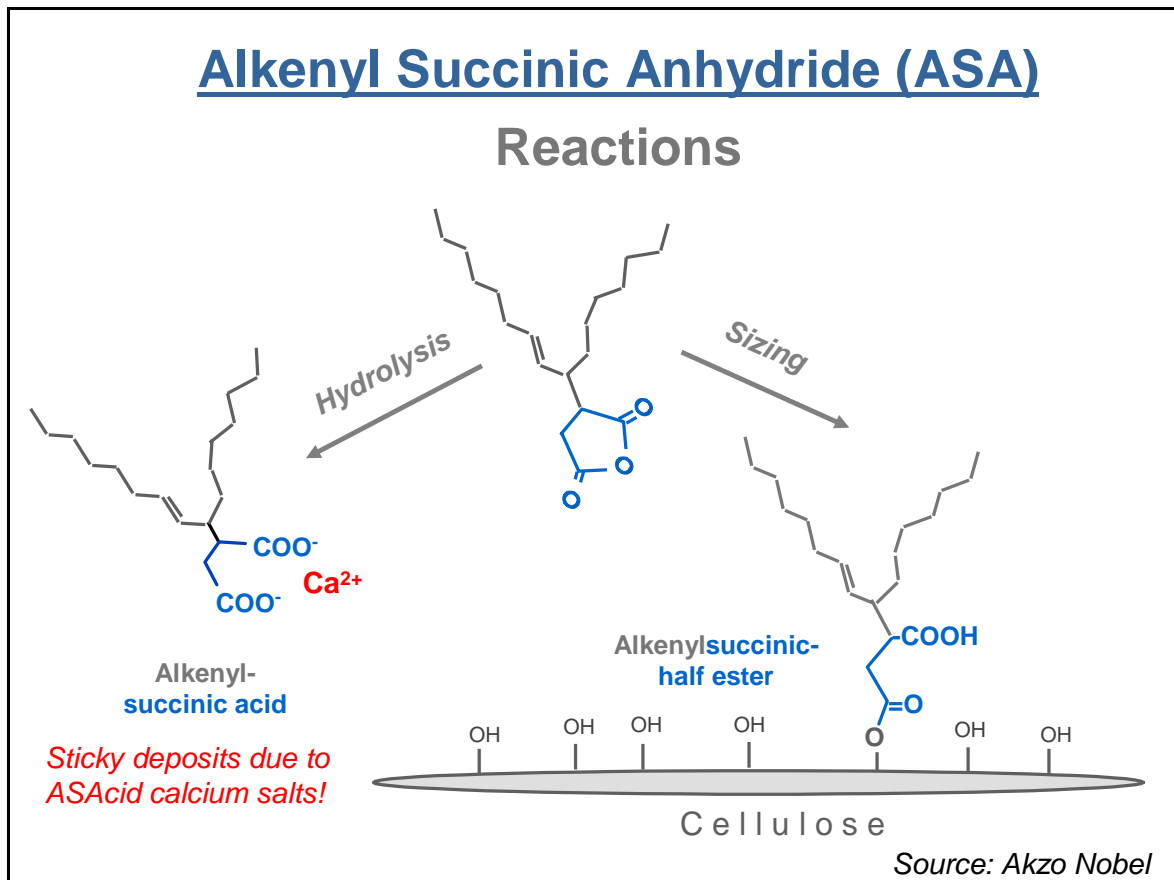


Figure 1: Reaction of ASA with cellulose (esterification) and water (hydrolysis)

An excellent - mainly theoretical - work about the mechanisms of ASA hydrolysis and sizing has been published by Boris Zhmud et al. in 2001 [13].

Besides the process parameters, it is also possible to stabilize the ASA with parameters and protection colloids during emulsification and therefore reduce hydrolysis and deposits. In this field, there have been investigations with polymers and modified natural products (starch, guar) [14, 15] as well as alternative ASA structures (AOSA) [16]. Many investigations related to the use of alternative protection colloids or other substances at the emulsification of ASA are patent-protected [17-21].

In addition to this arrangements, the utilisation of aluminium products (alum, PAC) is also recommended to reduce the formation of deposits. On one hand, these substances support the fixation of ASA, especially in combination with starch. On the other hand, they mask the ASA hydrolysis products and therefore reduce their stickiness [17, 22-26].

However, further studies about the ASA mechanism have indicated that even hydrolysed ASA, as well as its calcium salt, can contribute to sizing when these products are retained in the paper sheet [3, 27]. Furthermore, it has been observed that a big part of the ASA found in the paper is not linked to the cellulose by a covalent ester bond [28-30].

2.3 ASA emulsions

To achieve a good sizing effect, the most important quality parameters of ASA emulsions are particle size and stability. With increasing particle size, the specific surface area of the ASA particles decreases, resulting in a significant reduction of sizing levels.

The determination of the particle size is an important control factor of every ASA emulsification unit. This measurement is normally done according to the light

scattering principle. In practice, typical ASA emulsions have particle size distributions with 50 % of the particles below 1 μm and 90 % below 2.5 μm [23].

The second important criterion of an ASA emulsion is the stability. Stability can be understood as the stability of particle size (emulsion stability) as well as the stability as regards hydrolysis (hydrolysis stability). Hydrolysis stability goes very often parallel to the emulsion stability due to the fact that a faster hydrolysis also causes an agglomeration of the ASA particles, especially in combination with calcium ions. This can, for example, be seen at increasing pH or temperature values. Higher pH or temperature values increase the hydrolysis and contribute to faster agglomeration. However, it is important to look at both stability parameters together because hydrolysis must not cause higher agglomeration as a rule. This can, for example, be true for different ions.

3 Experimental

3.1 Preparation of ASA emulsions

For ASA emulsification, first the starch solution with the required concentration (1 - 10 w-%) was prepared. Afterwards, the ASA was poured together with the starch into the mixer (Waring Laboratory Blender) and has been emulsified for 1 - 3 minutes at speed level 2 (18500 rpm). As a top frame, a modified osterizer vessel (mini jar) has been used. The total volume of each emulsion was 200 ml so that the energy density does not change.

For a standard ASA emulsion, a liquid starch has been diluted with deionised water to a concentration of 3 w-%. Then 185 g of the 3 w-% starch solution was emulsified for 75 seconds together with 15 g of ASA. The starch to ASA ratio was 0.37 : 1 and the ASA concentration 7.5 w-% or 0.075 g ASA / g emulsion.

3.2 Determination of the particle size

The particle size of the ASA emulsion was measured with the Mastersizer 2000 (Malvern Instruments). Therefore, depending on the ASA concentration, 5-15 drops

were added into 1 liter of deionised water until a laser obscuration of approximately 15 % has been achieved. A refractive index of 1.52 and an absorption coefficient of 0.001 have been used for ASA. The refractive index of the dispersing agent (water) was accepted as 1.33. The analysis was carried out according to the mie theory, which gives the best general solution for particles that are smaller than 50 μm (DIN ISO 13320-1 [31])

3.3 Determination of the emulsion stability

The emulsion stability was measured at 2000 rpm. Therefore, the emulsion was pumped into a loop for 30 - 40 minutes and the particle size was measured every 2 minutes. As a value for emulsion stability, the percentile amount of the particles below 2 μm was evaluated. A standard model water for this measurement contained 350 ppm Ca^{2+} and had a pH value of 8. The calcium ions (added in the form of calcium chloride) resulted in a conductivity of approximately 1500 $\mu\text{S}/\text{cm}$. The pH-value was adjusted with a 0.025 M sodium hydroxide solution and was kept constant with the aid of a dosing pump.

3.4 Determination of the hydrolysis

The investigations of the hydrolysis were accomplished with the Titrando 836 from the company Metrohm. For the determination of the hydrolysis rate, the consumption of a 0.1 M sodium hydroxide solution was measured. Therefore, the pH-value of a 1 w-% ASA emulsion was raised to 8 with caustic soda solution and afterwards the consumption of NaOH was detected for 30 - 60 minutes. Since for the neutralization of 1 mole alkenyl succinic acid 2 mole of NaOH are necessary the proportion of hydrolysed ASA can be calculated out of the concentration and the volume of the consumed sodium hydroxide and the molecular weight of the ASA. For the investigations, a pure C18 ASA with a molecular weight of 350 g/mol was used. In order to ensure a good reproduction of the reaction kinetics a value was recorded every 5 seconds. Since the hydrolysis in deionised water runs relatively slow, Ca^{2+} ions in the form of calcium chloride were added to the emulsion here as well.

4 Investigations and results

4.1 Particle size

In this part the most important factors which influence the initial particle size are discussed. These are emulsifying time, ASA concentration, temperature, starch to ASA ratio, viscosity, and different ASA types. Besides this, comparisons with different starches, polymers and emulsifiers for ASA emulsification have been accomplished.

In Table 3, the additives used as emulsification additives for ASA are specified as regards their cationic charge and molecular weight.

Table 3: Used additives for the emulsification of ASA

Additives	Charge [meq/g]	MW [g/mol]
Powder starch (potato) 0.5 % N, DS 0.06	0.5	40x10 ⁶
Liquid starch (potato) 1.2 % N, DS 0.16	1.2	17x10 ⁶
Guar DS 0.03	0.5	700.000
CMC DS 0.8	anionic	120.000
PAM	1.4	6.000.000
PEI	10	800.000
PAm	9.4	100.000
PVAm	5.1	400.000
P-DADMAC	8.1	100.000
PAE	3.8	1.000.000
Dicyandiamide	2.7	< 1000
Bentonite	anionic	micro particle
Colloidal silica	anionic	nano particle

Figure 2 shows the comparison of the particle size when emulsifying with starches and polymers as a function of different emulsification times.

It can be seen that during emulsifying with the liquid starch, a substantially higher emulsification time is needed, as when emulsifying with the cooking starch. With the cooking starch, an average particle diameter (D50) of 0.5 μm is already achieved after an emulsifying time of 30 seconds. Whereas the particle size of the liquid starch lies around 1 μm for the same time. The reason for the smaller particle sizes when emulsifying with the cooking starch is probably the higher viscosity, since all other factors were kept constant. The viscosity of a 3 w-% starch solution is approx. 800 mPas, whereby a 3 w-% solution of the liquid starch only has a viscosity of approx. 80 mPas. Due to the higher viscosity, a higher energy density of the emulsion in the mixer can be reached. Also, at higher viscosities a "vibrating" of the entire mixer and slightly increased temperatures of the emulsion (due to a higher friction) could be noticed. From the polymers, the polyamide epichlorhydrin resin (PAE), as well as the polyamine, showed similar emulsification properties as the liquid starch. However, with the polymers P-DADMAC and PAM, it was clearly more difficult to emulsify the ASA properly and even with emulsifying times of 150 seconds, no particle sizes under 1 μm could be reached.

However, it has to be stated very clearly that the emulsification of ASA is normally not controlled with the protection colloid but with emulsifiers (surface-active substances). The protection colloid has the primary function to stabilise the ASA and support the fixation to the cellulose fibre. Furthermore, the chosen protection colloids are only a very small selection of a lot of further possible derivatives. Here the focus was on typical retention and fixing agents.

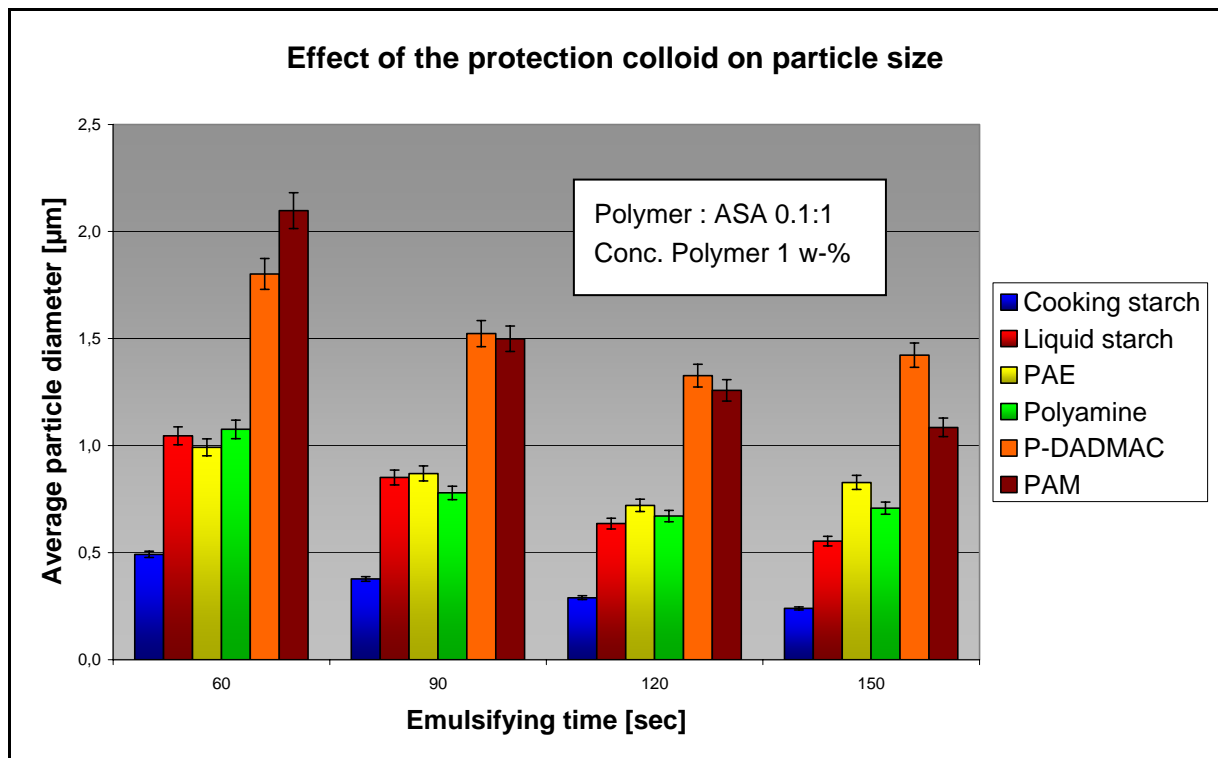


Figure 2: Effect of the protection colloid on particle size

Furthermore, the emulsification was investigated using alternative protection colloids. Only with the used guar gum it was not possible to produce an ASA emulsion with an adequate particle size. A new interesting option is the use of so called particle stabilized ASA emulsions. It can be seen that it is possible to emulsify ASA with bentonite as well as colloidal silica. This technology is a new trend in the paper industry and these trials indicate that it is possible to achieve very good particle sizes with considerably low energy input.

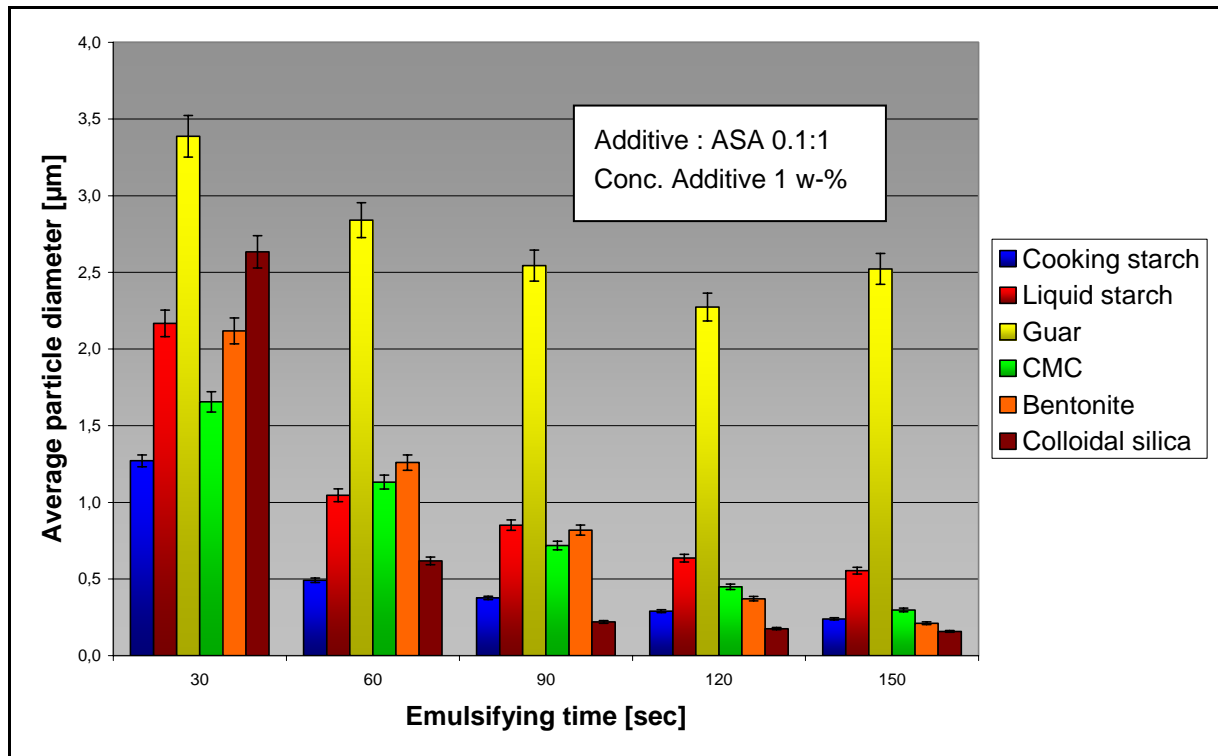


Figure 3: Effect of alternative protection colloids on particle size

In Figure 4 the effect of different emulsifiers - at a dosage of 0.5 % related to ASA - on the particle size is shown. It can be seen that especially ethoxylated alcohols seem to be good emulsifiers for ASA. The sulfonic acid and the PO/EO-Copolymer show almost no improvement of the ASA emulsification. Especially with the naphthalene sulfonic acid the same particle size as with no emulsifier is reached.

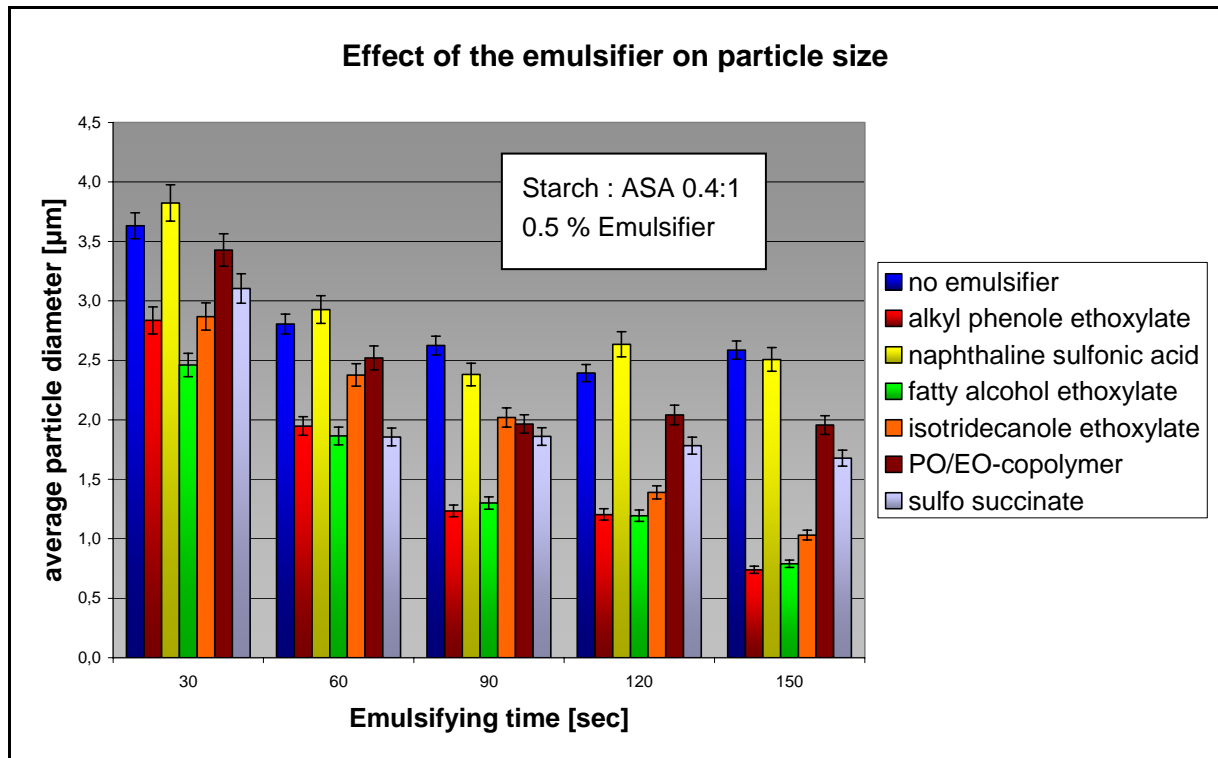


Figure 4: Effect of the emulsifier on particle size

All following investigations were done with the liquid starch, since this type showed some advantages even despite the higher emulsifying time in application in relation to the cooking starch. The comparison between cooking and liquid starch will be discussed in more detail in chapter 4.2.

Figure 5 shows the relationship between starch to ASA ratio and particle size. In order to be able to accomplish the trials with a constant ASA concentration and with a constant emulsifying volume, the starch concentration had to be changed. It can be seen that with 30 - 50 % liquid starch with a starch concentration of 3 - 5 % the best results can be obtained as regards the particle size. With 30 - 50 % starch related to ASA, D_{50} and D_{90} values of 1 µm and 2,3 µm could be reached, whereas the values with 10 % or 100 % starch are 1,8 µm and 3,8 µm respectively. At starch concentrations of smaller than 3 %, it is assumed that the viscosity of the starch solution is not high enough, in order to ensure a sufficient application of energy into the emulsion. Conversely with regards to high starch quantities, the portion of the protection colloid is too high, and the ASA again becomes more difficult to emulsify.

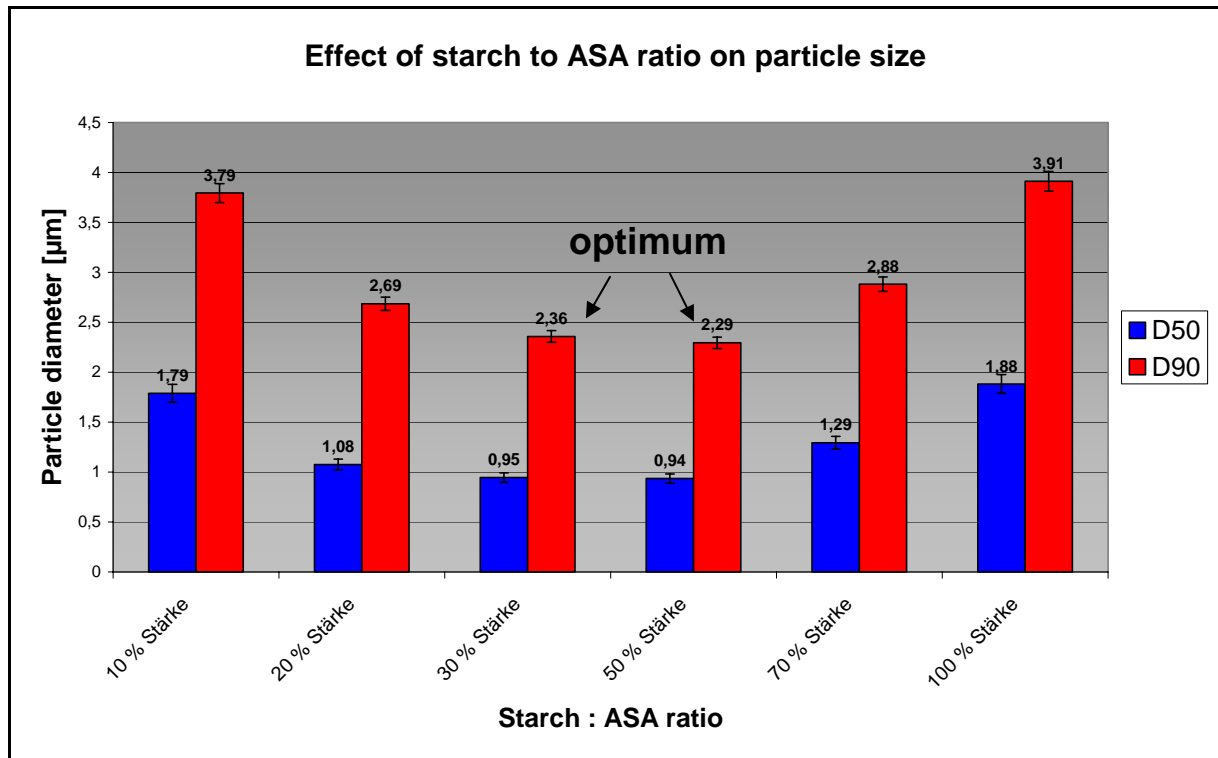


Figure 5: Effect of starch to ASA ratio on particle size

In Figure 6, the influence of ASA concentration on particle size is represented. According to this, an increase of the ASA concentration has a very negative effect on the resulting particle size. Especially with high ASA concentrations, almost no reasonable emulsification is possible. This effect is also dominant at higher emulsifying times. Thus, the ASA concentration is one of the factors with the biggest influence on the particle size besides the emulsification time.

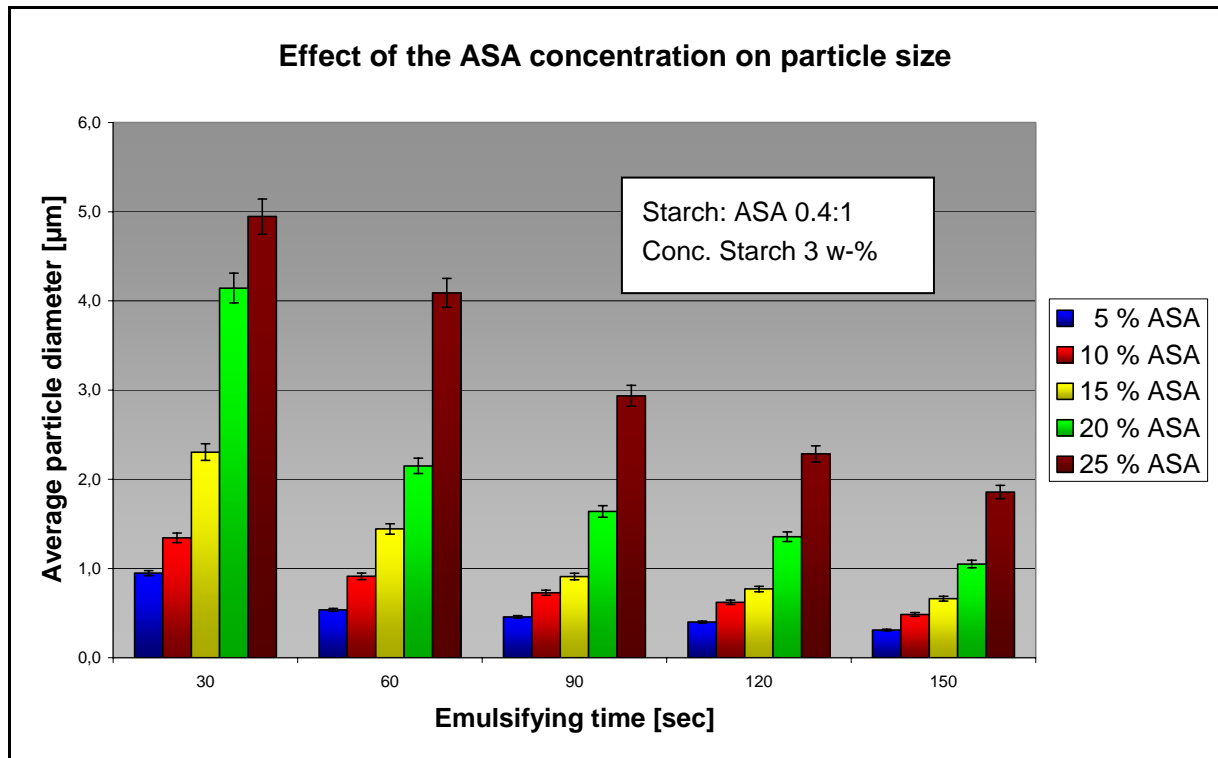


Figure 6: Effect of the ASA concentration on particle size

Figure 7 shows the influence of the temperature on the particle size. Therefore, the starch solution was heated on a magnet stirrer and afterwards poured into the mixing container together with the ASA. It could also be determined that the temperature is a factor, which can be used to adjust or optimise the particle size. An increase in temperature leads to smaller ASA particles.

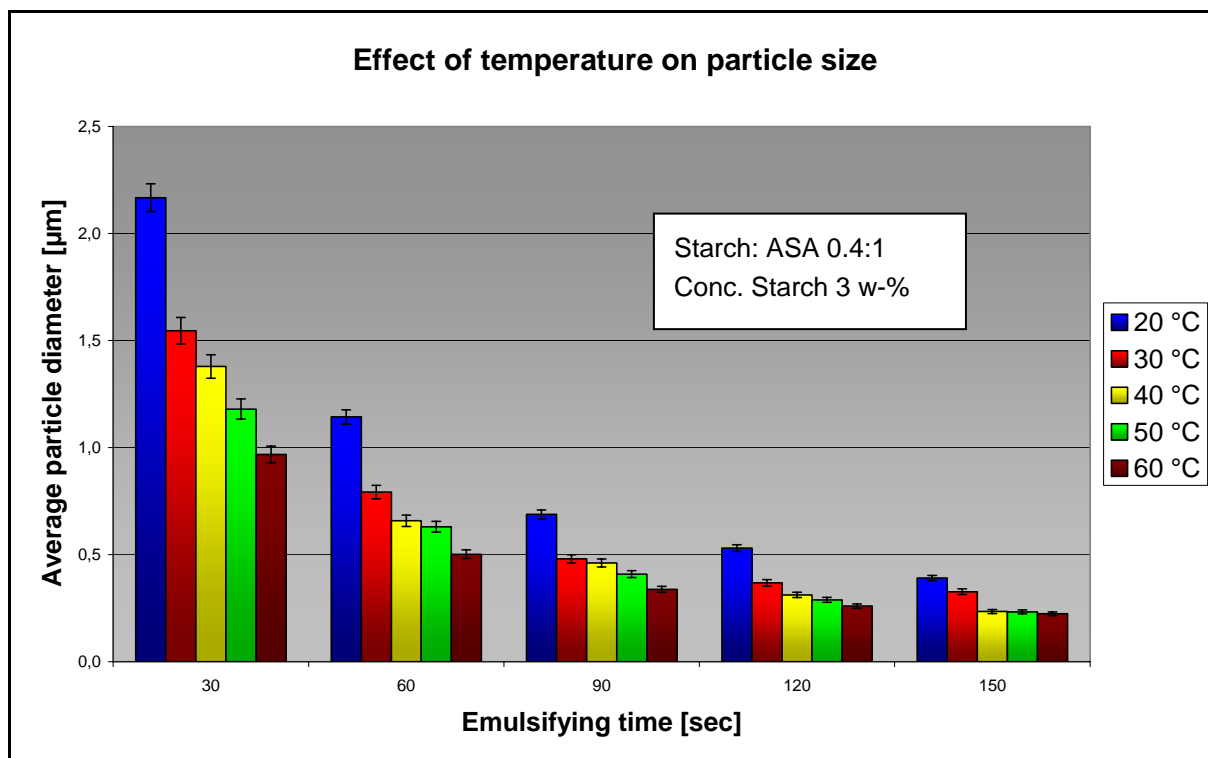


Figure 7: Effect of temperature on particle size

It could not to be excluded that due to the high shearing forces during emulsifying, a further heating took place by friction. The indicated temperatures, therefore, refer to the beginning of emulsifying. After emulsifying the temperatures were around 10-15 °C higher.

During the investigations of different protection colloids already first hints as regards the effect of the molecular weight and the cationicity could be observed. However, the trials we not done at one defined product class. Therefore, in the following results are shown that are obtained using five defined polyacrylamides. During synthesis of the products it was tried to obtain three different levels for the molecular weight and the cationicity (“low”, “medium” and “high”). In Figure 8 the influence of the different polyacrylamides as regards emulsification is shown. Especially at low emulsification times it can be seen that higher molecular weights make the emulsification more difficult. This effect becomes more and more leveled at higher emulsifying times. For the cationicity of the used polyacrylamides no effect on the resulting particle size could be observed.

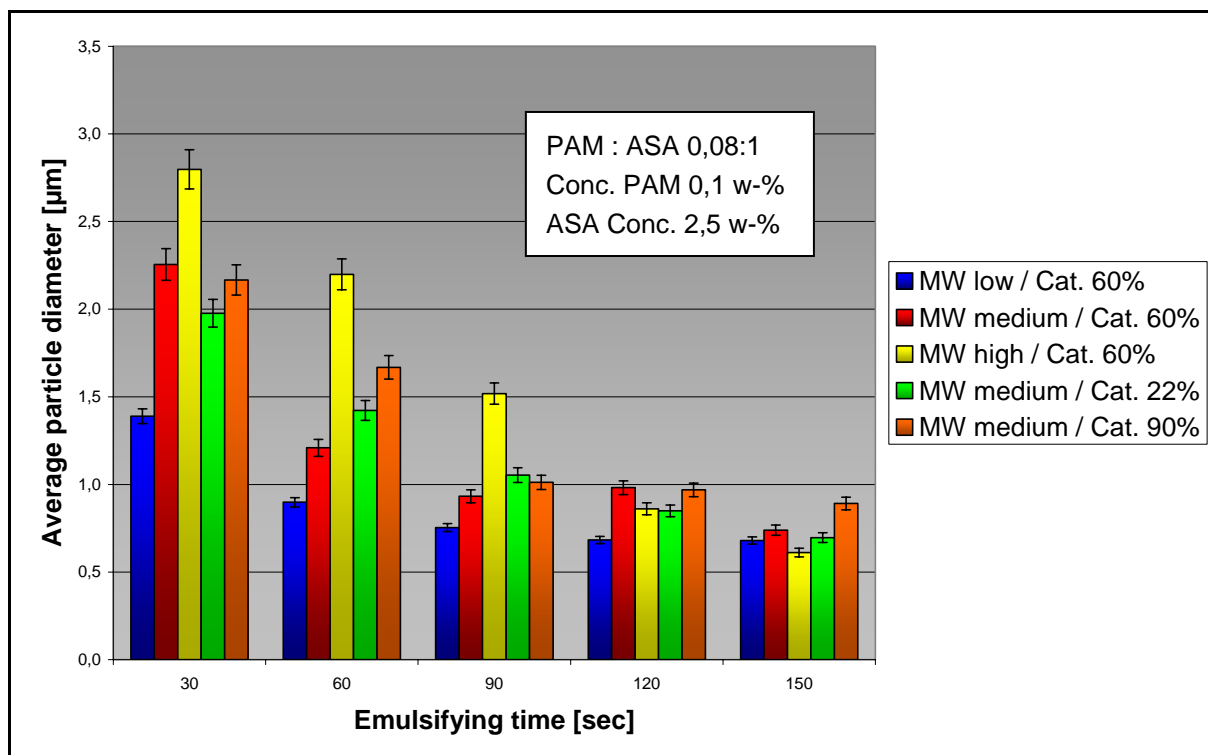


Figure 8: Effect of molecular weight and cationicity on particle size

In Figure 9, the comparison of different ASA types is represented. There are significant differences between the different ASA types. The two products without emulsifying agent can be emulsified only very difficult and even with emulsifying times of 2.5 minutes, average particle sizes of only 1.5 µm can be reached. The pure C18 product is even more difficult to emulsify than the C16/C18 mixture, which is probably due to the more hydrophobic character. The two products with emulsifying agent are clearly simpler to emulsify, and after 1.5 minutes, a particle diameter of under 1 µm is reached. However, here there is no difference between the C18 type and the C16/C18 mixture. As expected, the Instant ASA can be emulsified very easily. Here the minimum particle diameter of 0.5 is already achieved after an emulsifying time of 30 seconds. Even by further increase of the emulsifying time, the middle particle diameter improves only insignificantly.

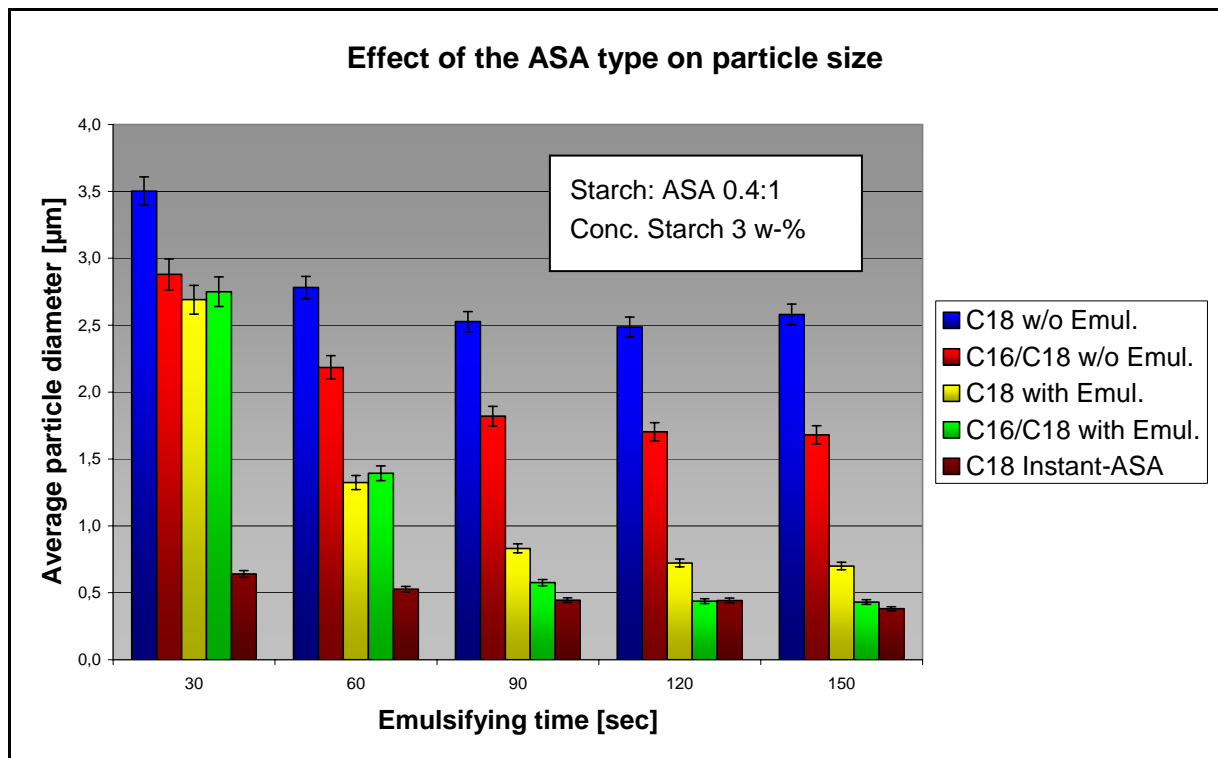


Figure 9: Effect of the ASA type on particle size

Surely, also the investigation of these ASA types as regards their sizing effect would be very interesting. This is due to the fact that especially surface-active substances (which are present in emulsifying agents) can have a detrimental effect on sizing. The challenge is to find an emulsifier, which gives good particle sizes but does not affect sizing.

The following table summarises the most important factors on particle size and shows that there are many possibilities to change and optimize the particle size during emulsification.

Table 4: Summary of the most important factors on particle size

Parameter	Impact (if increased)
Emulsification time [1 - 3 min]	++
Shear forces [8000 - 20000 U/min]	++
Concentration ASA emulsion [5 - 25 %]	---
Viscosity [50 - 1000 mPas]	+
Molecular weight PAM [2 – 10 x10 ⁶]	-
Temperature [20 - 60 °C]	+
Starch : ASA ratio [0.1:1 - 1:1]	- / + / -
C16/C18 share [60 - 95 % C18]	-
Emulsifier [0 - 1 %]	+++

+++ strongly positive effect 0 no effect - negative effect

4.2 Emulsion stability

Apart from the initial particle size after emulsifying, it is also important during which time this particle size is stable. It doesn't help if one achieves very small particle sizes by good emulsifying, but they, however, are only stable for a short time. For the determination of the emulsion stability, therefore, the change of the particle size during a certain period can be measured. The investigations usually were done in a model water with 350 ppm Ca²⁺ (corresponds approx. to 50 °dH), 1500 µS/cm conductivity and at pH 8. Thus, a clear difference in the particle size could already be determined after 30 minutes.

The stability of an emulsion depends greatly on the kind of the used protection colloid. Usually for emulsifying and stabilization of ASA emulsions, cationic starches are used, since they are often already available and relatively low-priced. However, there can be done variations within the same product group (starch) or even investigations with chemically different systems (synthetic polymers).

In Figure 10, the influence of two starch types (standard cooking starch and liquid starch) as well as of four polymers on the stability of the emulsion is represented. As a parameter for the evaluation of stability, the percentile portion of particles smaller than 2 μm was selected. The best stabilization of the emulsion can be achieved by polyacrylamides. These polymers have a comparatively high molecular weight and seem to stabilize the ASA particles mainly sterically and thus preventing agglomeration. Also, the two starch types stabilize the emulsion relatively well. However, after 20-25 minutes, a stronger agglomeration compared to PAM takes place. It is surprising that with the highly cationic polymers such as polyamine, with a charge density of 9.4 meq/g, almost no stability is given and the particle size already decreases strongly after a few minutes. Thus, the molecular weight of polymers seems to be more decisive for the stabilisation of ASA emulsions than the cationic charge.

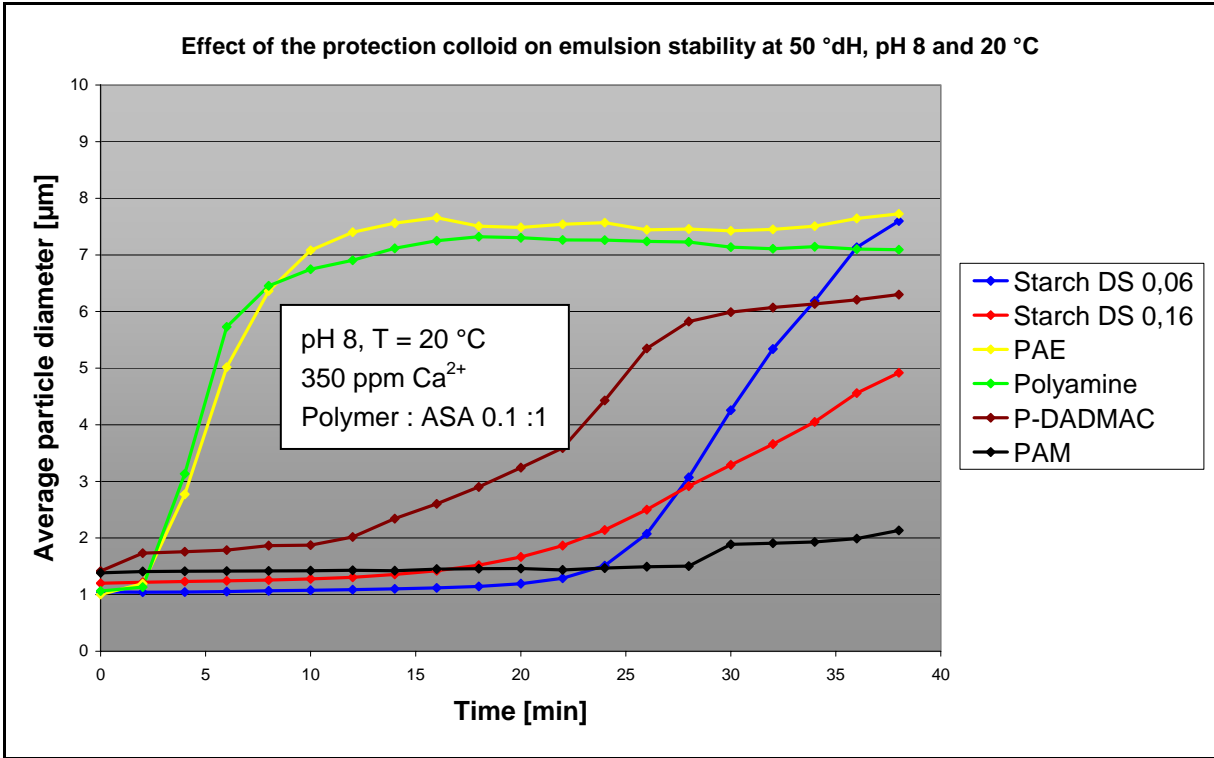


Figure 10: Effect of the protection colloid on emulsion stability

Thus, high cationic liquid starches are a very good alternative compared to standard used cooking starches for the emulsification of ASA. The following figure illustrates some more advantages of liquid starches compared to cooking starches.

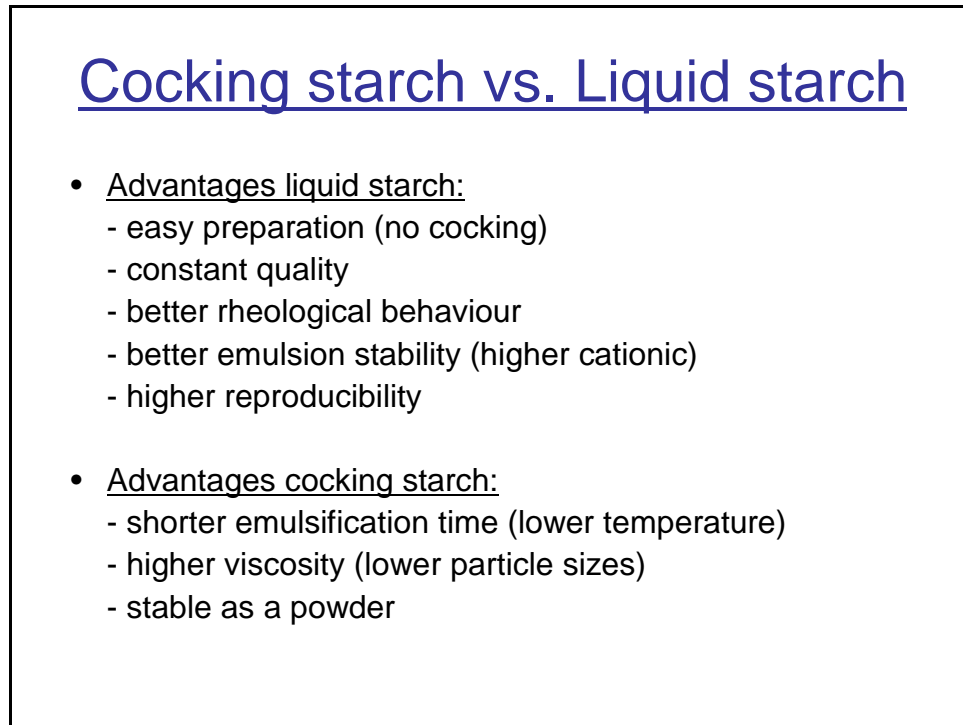


Figure 11: Comparison of cooking and liquid starches for the ASA emulsification

In Figure 12 the influence of the investigated polyacrylamides as regards their stability can be seen. Due to the extremely good stabilisation of the high molecular polyacrylamides the pH had to be raised to 9 for this trial. Otherwise no differences between the different products can be seen. As expected higher molecular weights are beneficial for the emulsion stability. Especially the PAM with low molecular weight ($\sim 2 \cdot 10^6$ g/mol) shows a very strong tendency to build up agglomerates. Between the medium level ($\sim 7 \cdot 10^6$ g/mol) and the high level ($\sim 13 \cdot 10^6$ g/mol) of molecular weight there is only a quite small difference as regards stabilisation. However, it is surprising that the cationicity (at the same molecular weight of roughly $7 \cdot 10^6$ g/mol) seems to have a negative effect on the ASA stability. This can clearly be seen looking at the PAM with 90 % cationicity that shows almost the same stability as the PAM with low molecular weight.

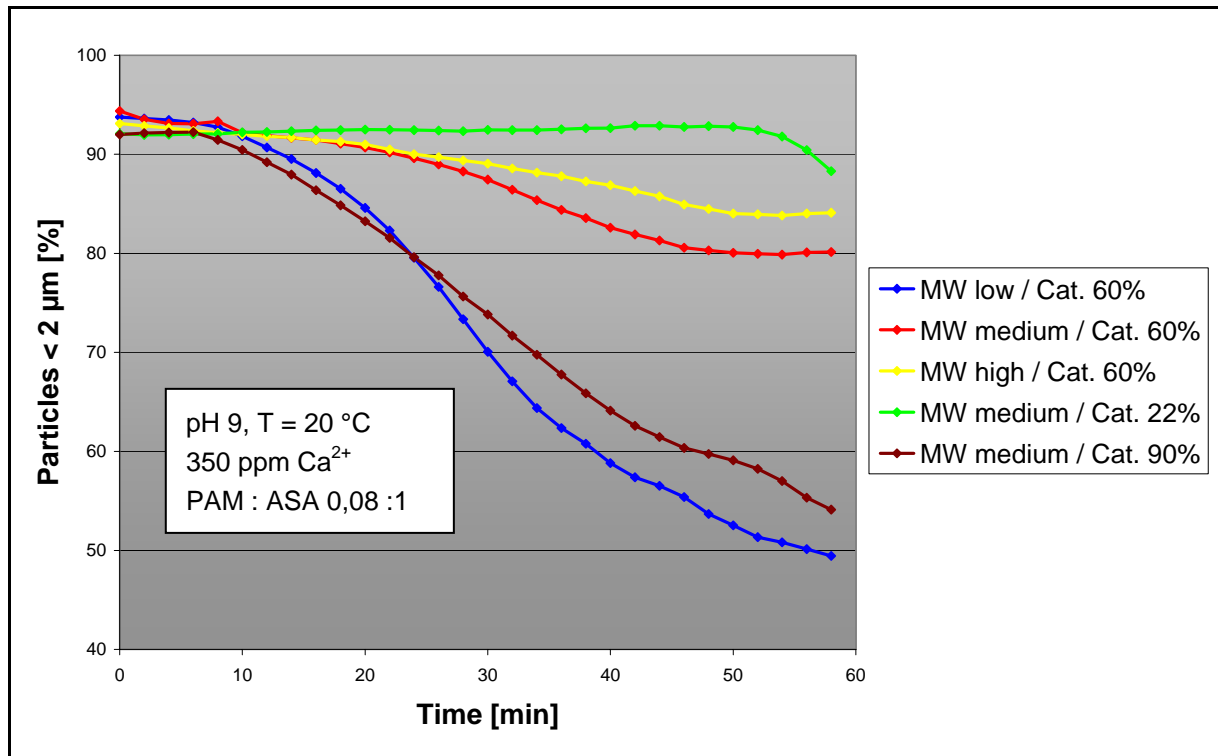


Figure 12: Effect of molecular weight and cationicity on emulsion stability

One possibility to reduce the agglomeration tendency of ASA particles is to increase the addition of the protection colloid, i.e. starch. Figure 13 shows the influence of the starch to ASA ratio as regards the emulsion stability. It can be recognized that with rising starch addition, the emulsion can be better stabilized. Already with 20 % starch related to ASA, there can be achieved a relatively stable emulsion. Only with a starch addition of 10 % there is a strong agglomeration of the particles above average. The optimum choice would be in the range of 20 to maximally 50 % starch related to ASA, since a further increase of starch brings only a small improvement in stability.

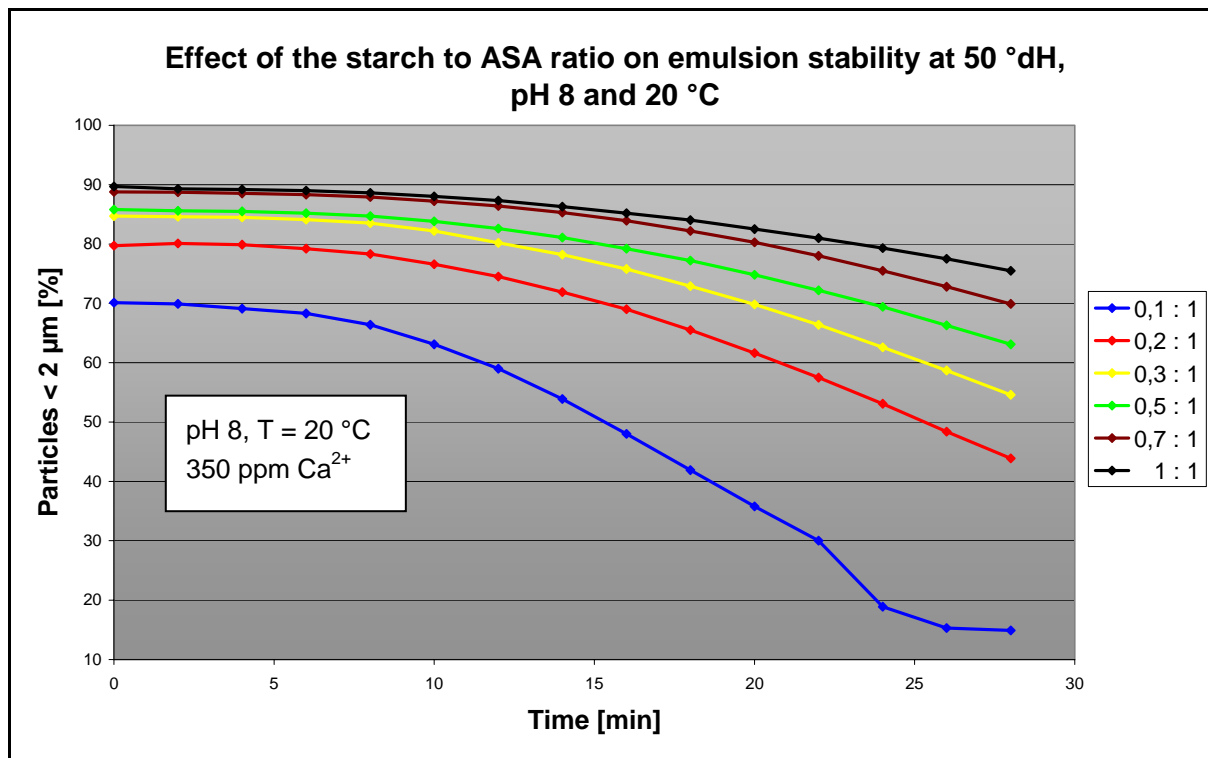


Figure 13: Effect of the starch to ASA ratio on emulsion stability

In the next figure, the influence of the pH-value on the emulsion stability is represented. It can be seen that at a pH value of higher than 7, the emulsion begins to agglomerate very strongly. Especially high pH-values promote the formation of ASAacid calcium salts and lead to a faster hydrolysis, which results in an increase of particle size.

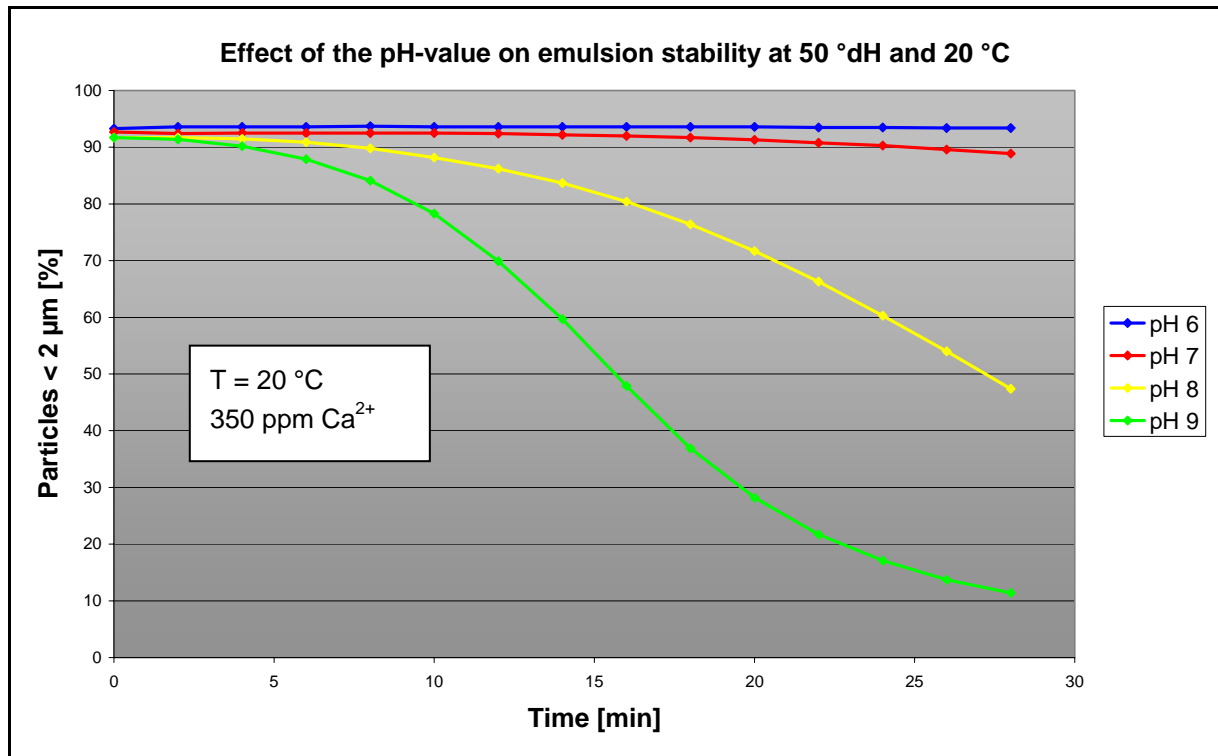


Figure 14: Effect of the pH-value on emulsion stability

In further investigations it has been examined, which influence individual ions have on the agglomeration of ASA. In Figure 15, the influence of 6 different salts (with same molecular quantity of the cation) on the emulsion stability is represented. The first four salts with univalent cations (sodium and potassium) cause only a relatively weak agglomeration of the ASA particles. The percentage of particles smaller than 2 μm falls from 90 % to approx. 70 - 75 %. Besides the different anions, such as chloride, sulphate and hydrogen carbonate do not show significant influence on the agglomeration. The bivalent cations show a very strong agglomeration for calcium chloride, while with the magnesium chloride there is almost no degradation of the particle size. This must suggest that only the calcium salt of the alkenyl succinic acid shows an increased tendency towards the formation of agglomerates due to the much lower solubility compared to the magnesium salt. Also, the build up of deposits can, therefore, mainly be attributed towards the presence of calcium ions. A 0.1 M CaCl₂ solution corresponds to a water hardness of approx. 60 °dH or 420 ppm Ca²⁺.

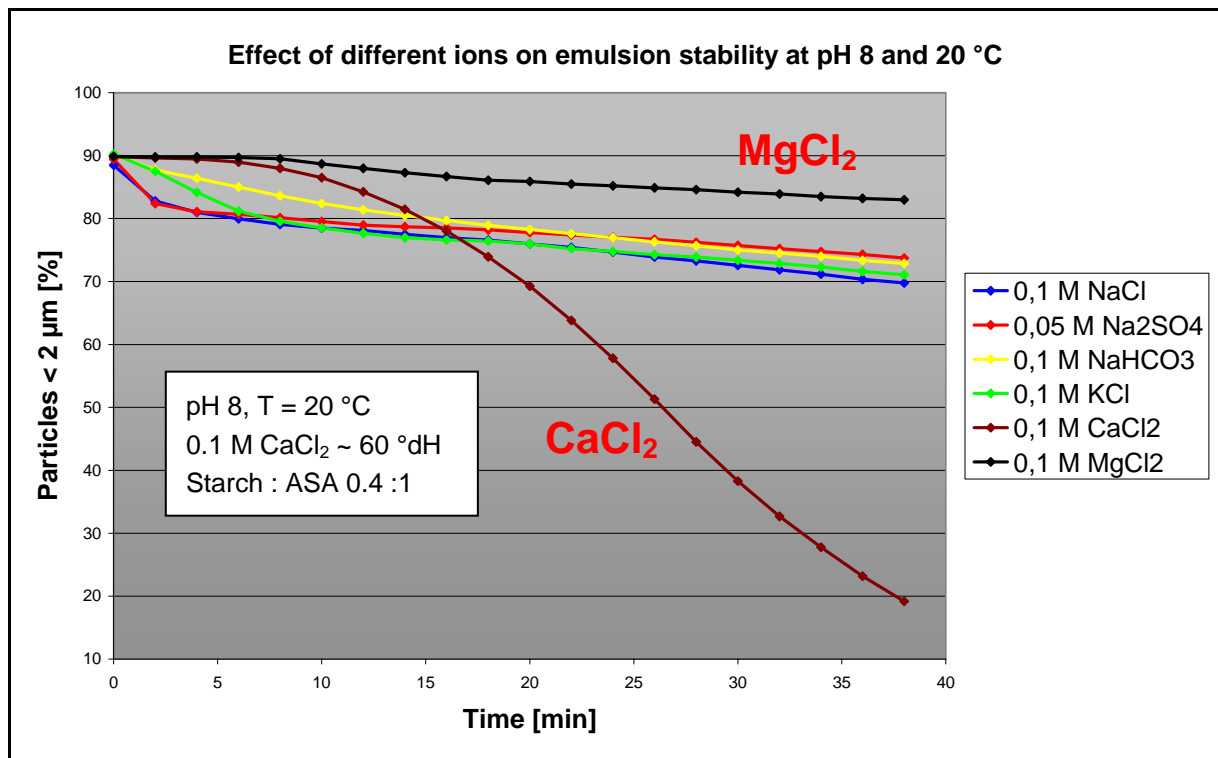


Figure 15: Effect of different ions on emulsion stability

Figure 16 shows the effect of increasing temperatures of the emulsion stability. It is obvious that already changes of 10 °C have a significant effect on the agglomeration tendency of the ASA particles.

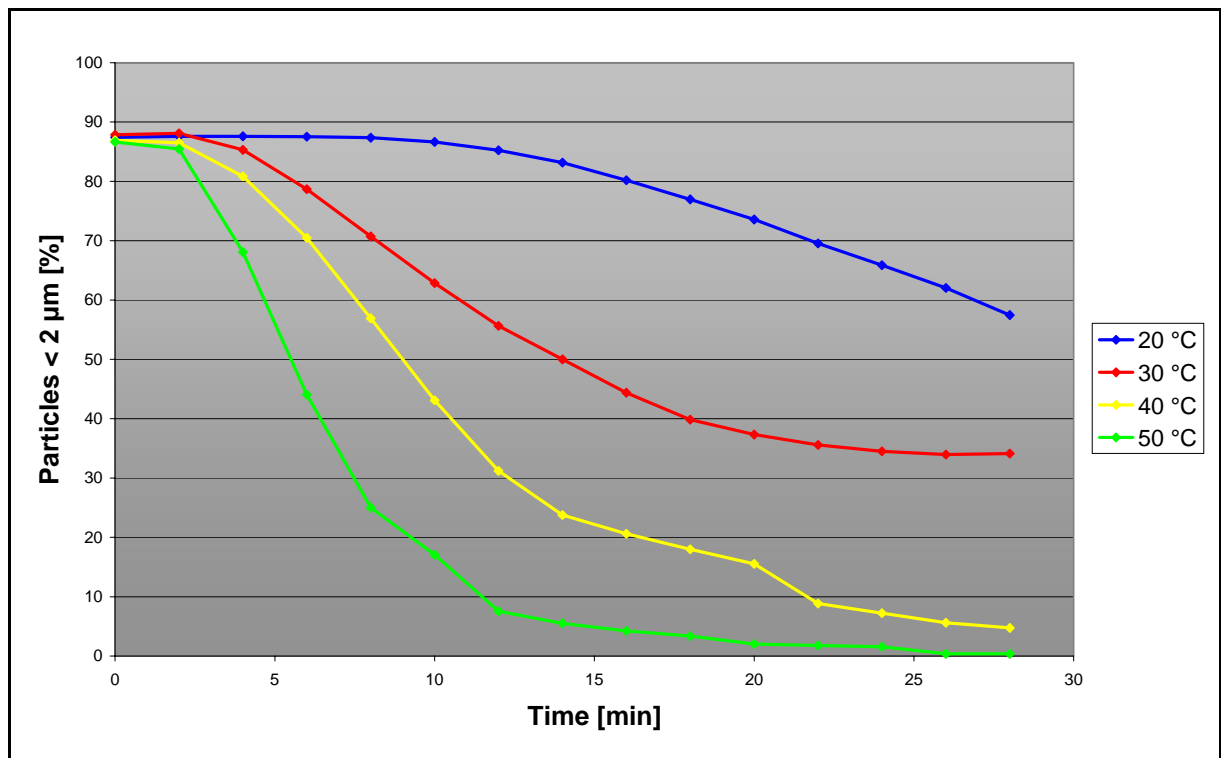


Figure 16: Effect of the temperature on emulsion stability

In Table 5, the most important factors on emulsion stability are summarised. Furthermore, the parameter of emulsion stability can be compared very closely with the tendency of deposition, which today is still one of the biggest challenges in ASA sizing.

Table 5: Summary of the most important factors on emulsion stability

Parameter	Impact (if increased)
Temperature [20 - 50 °C]	- - -
pH-value [4 - 9]	- -
Ca ²⁺ concentration [15 - 100 °dH]	- -
Cationic charge starch / polymer	O / -
Molecular weight polymer	+ +
Starch : ASA ratio [0.1:1 - 1:1]	+
Dilution ASA emulsion [0,05 - 5 %]	O / -

+ + + strongly positive effect O no effect - negative effect

4.3 Hydrolysis

The third important quality criterion of an ASA emulsion is the hydrolysis stability. While during the measurement of the emulsion stability, the agglomeration is evaluated by the determination of the hydrolysis speed the actual chemical reaction from ASA to the succinic acid (ASAcid) is evaluated. For the determination of the hydrolysis speed, the consumption of a 0.1 M sodium hydroxide solution was measured (see 3.4).

In the following, the most important factors that influence hydrolysis stability should be discussed, and possible differences compared to the measurements of the emulsion stability should be pointed out.

Figure 17 shows the influence of temperature on the hydrolysis speed of the ASA. As expected, the hydrolysis runs faster with increased temperature. However, the increase of the hydrolysis rate does not run linearly. At 20 - 40 °C the increase of hydrolysis speed is relatively low, whereas at temperatures from 50 to 70 °C, the

hydrolysis runs superproportionally fast. Thus, especially high temperatures (over 50 °C) are very problematic for the handling of ASA, because here already after 10 - 15 minutes a large part of the ASA is hydrolysed.

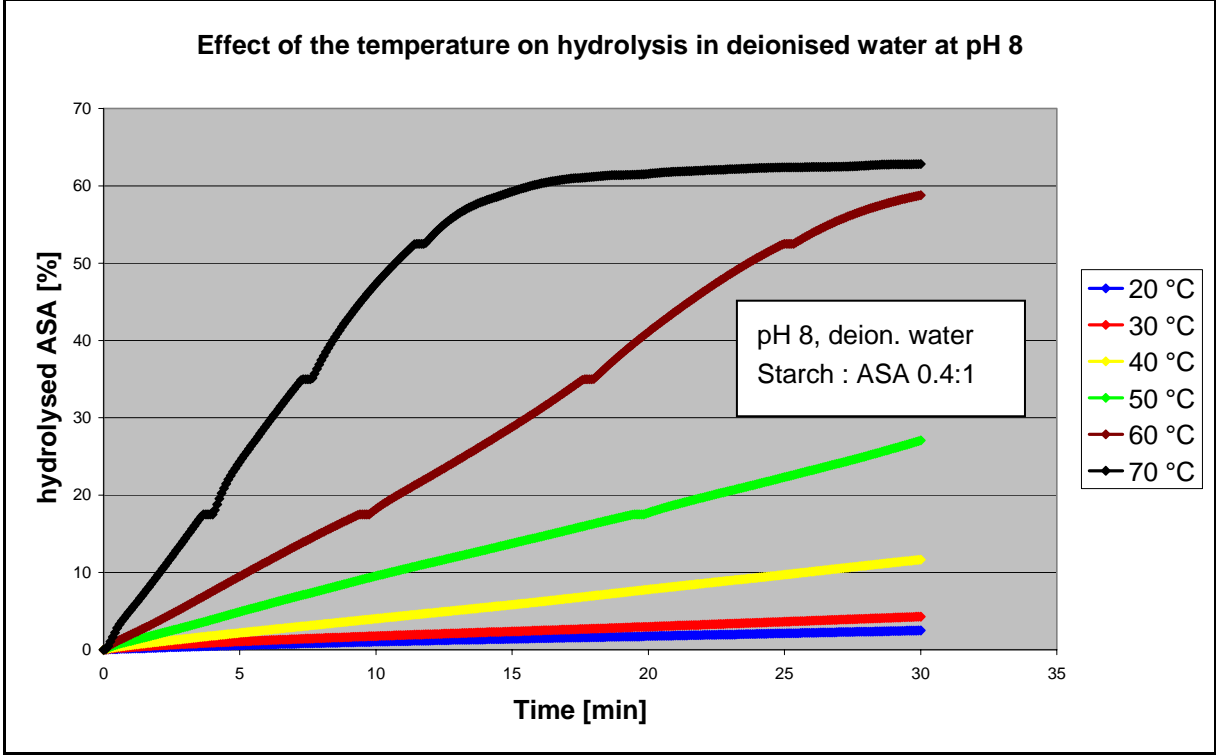


Figure 17: Effect of the temperature on hydrolysis

In the next figure the exponential relationship between the temperature and the hydrolysis is made clear. This interrelation had to be displayed after 10 minutes due to the emulsion at 70 °C coming already in the region of complete hydrolysis after 12 minutes.

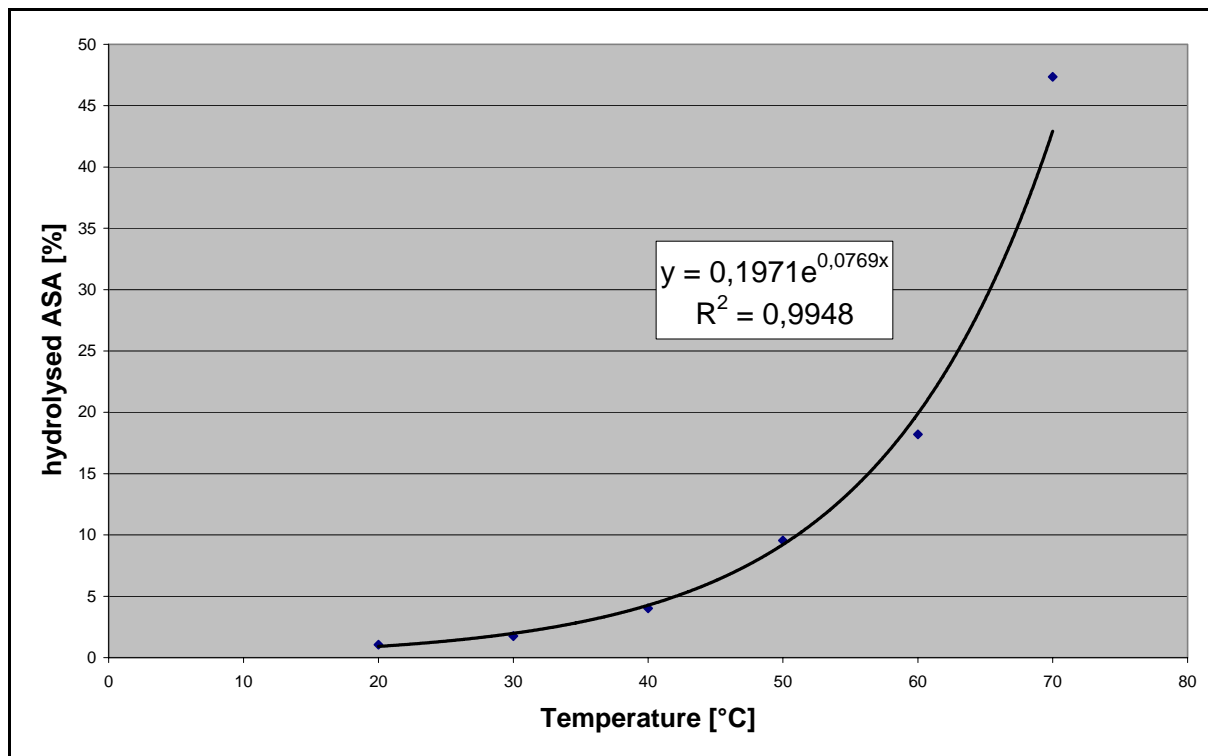


Figure 18: Interrelation between temperature and hydrolysis after 10 minutes

In Figure 19, the influence of the pH-value on the hydrolysis is presented. With increasing pH-values, the hydrolysis speed of the ASA also increases. At low pH values of 5 – 6, almost no reaction takes place. At pH-values from 7 – 8, the ASA begins to hydrolyse noticeably. At pH values of over 8, it is similar as with the influence of higher temperatures, where the hydrolysis accelerates exponentially. Therefore, the pH-value should be kept as low as possible during ASA sizing. Surely at neutral papermaking there is a border at 6.5 due to the use of calcium carbonate as a filler but it should be paid attention that the pH-value lies not too much over 7, which in combination with high water hardness, strongly increases the formation of deposits.

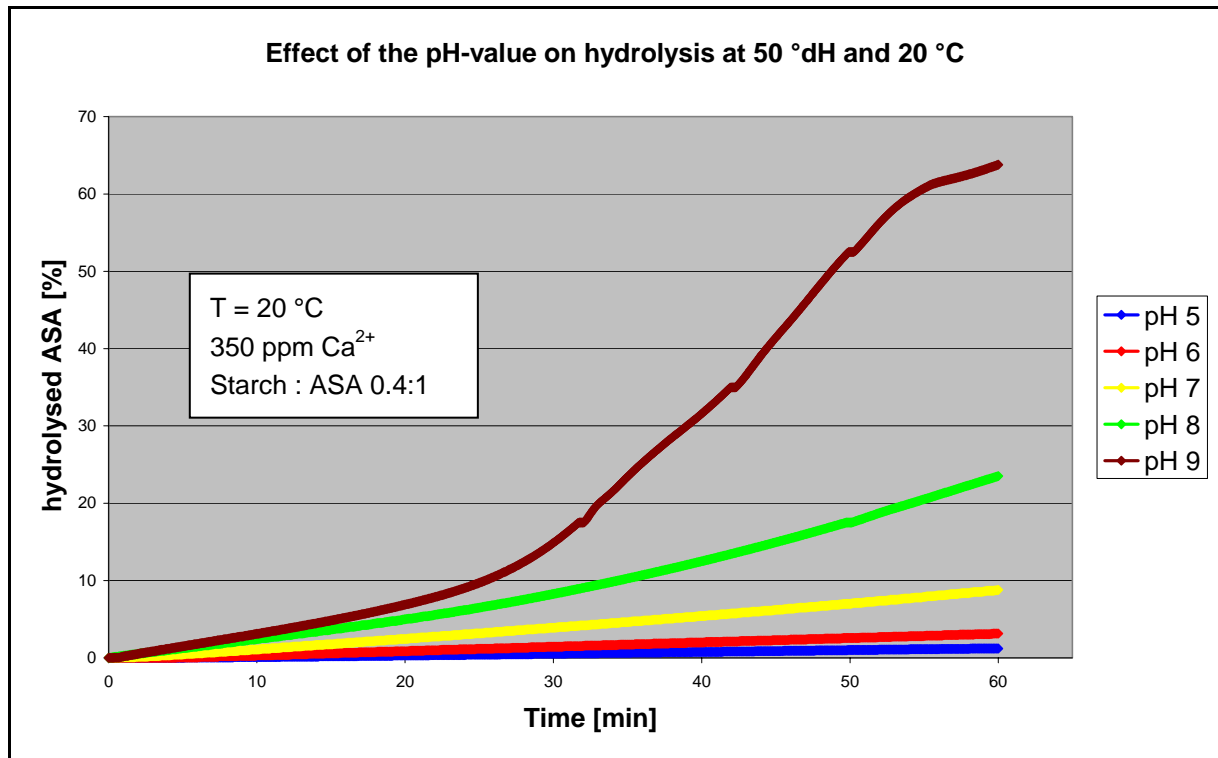


Figure 19: Effect of the pH-value on hydrolysis

As well as for the temperature also here the relationship between the pH-value and the hydrolysis is shown as a function. The dependency of the hydrolysis on the pH is almost exactly e^x . Since the pH is being defined as $-\log [H^+]$, this means that the hydrolysis is linear dependant on the concentration of H^+ ions.

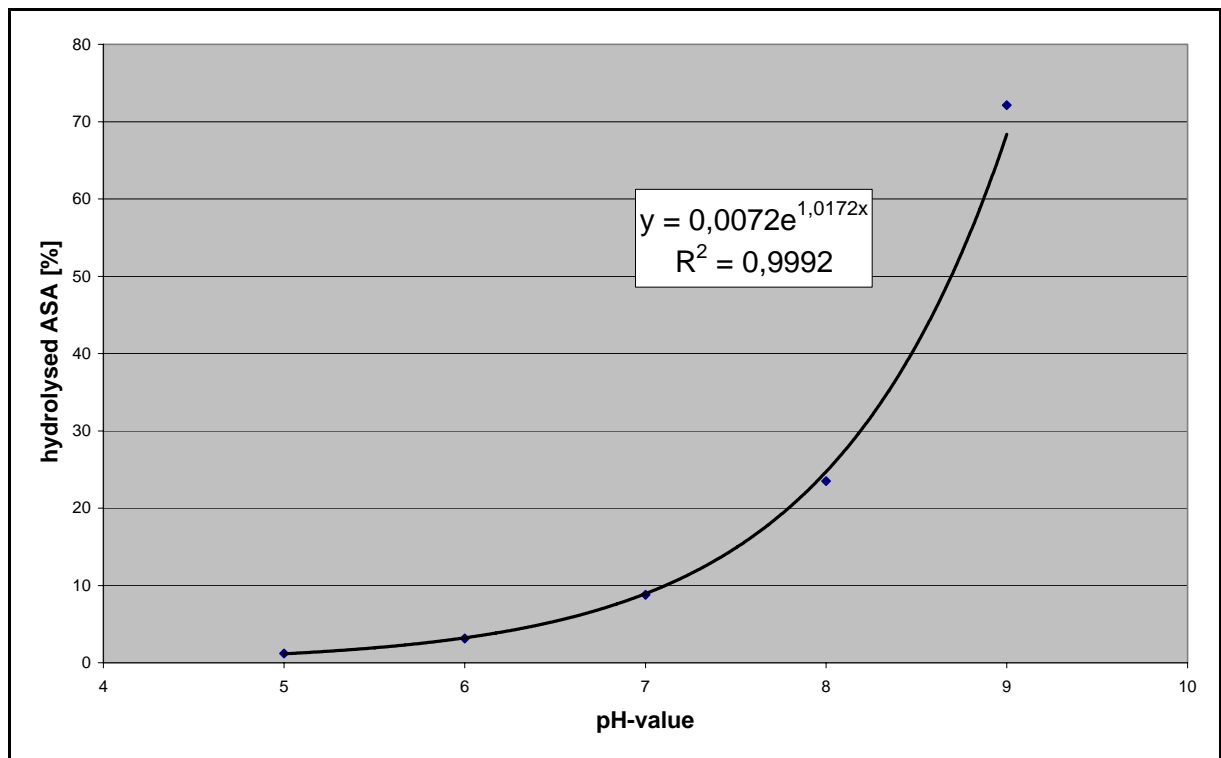


Figure 20: Interrelation between pH-value and hydrolysis after 60 minutes

For the formation of deposits, mainly the ASAcid calcium salt is responsible. Therefore, it should be investigated which influence the water hardness has on the hydrolysis of ASA. In Figure 21, it can be seen that the hydrolysis speed increases significantly with water hardness.

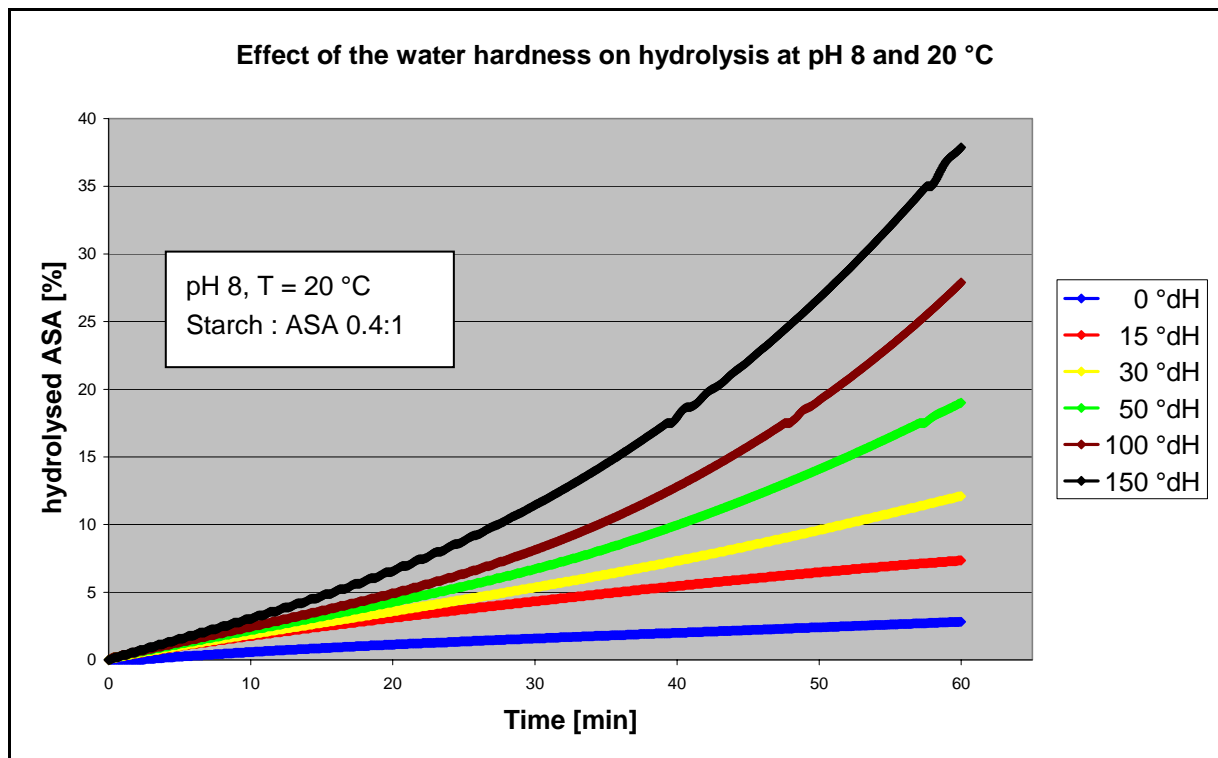


Figure 21: Effect of the water hardness on hydrolysis

In order to investigate whether there are further ions, which accelerate the hydrolysis of ASA, the hydrolysis speed was also determined as a function of different salts. Figure 22 shows that beside the calcium ions, magnesium ions also clearly accelerate the hydrolysis. Here, the speed is even higher than with calcium. All other univalent and trivalent cations ($AlCl_3$) show almost no tendency to promote the hydrolysis of ASA. Also, the examined anions (chloride, sulphate and hydrogen carbonate) do not have significant influence on the hydrolysis rate of ASA.

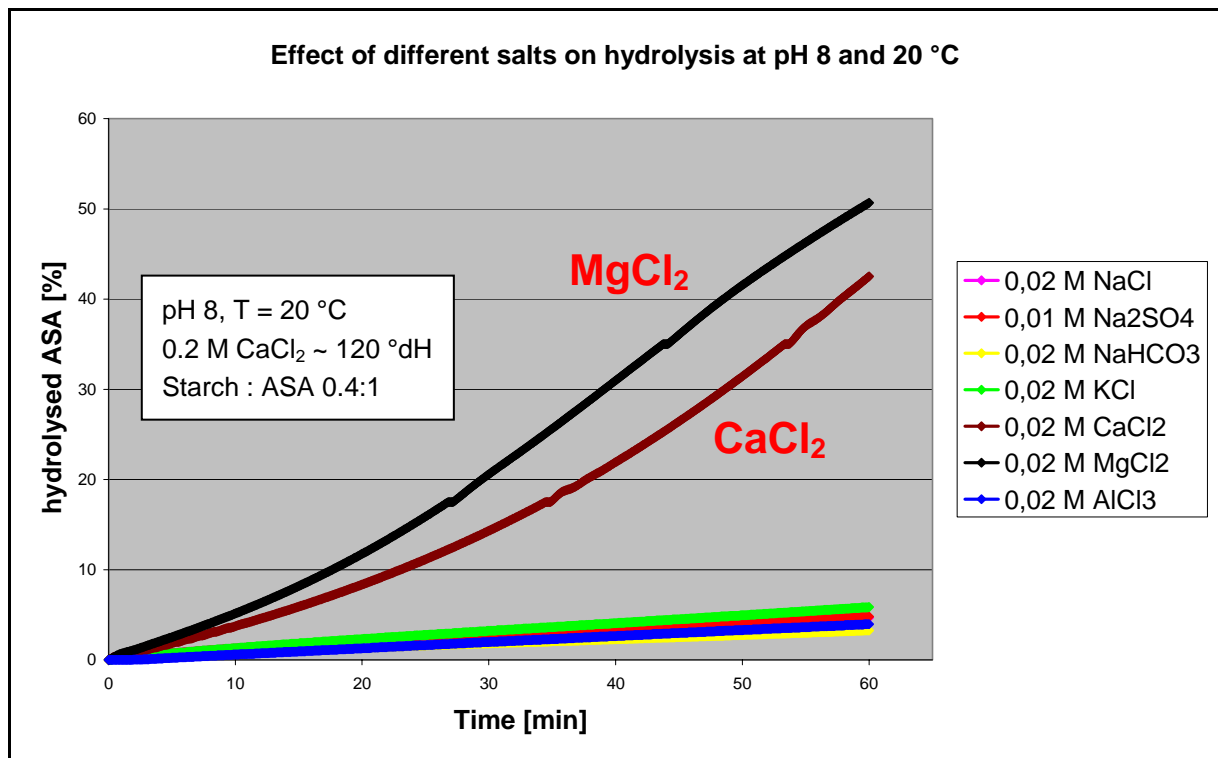


Figure 22: Effect of different salts on hydrolysis

In many investigations regarding the hydrolysis stability or deposition tendency of different protection colloids, the parameter particle size is often not mentioned or even neglected. However, Figure 23 shows that the particle size has a very big influence on the hydrolysis rate of ASA. The hydrolysis speed increases almost linearly with smaller ASA particles. Therefore, it is very important to always compare different emulsions at the same particle size. Otherwise, the danger exists to define hydrolysis stable protection colloids only due to the fact that they supply larger ASA particles (see Figure 2). Therefore, attention should be paid to the fact that the particle size is included and evaluated in future works.

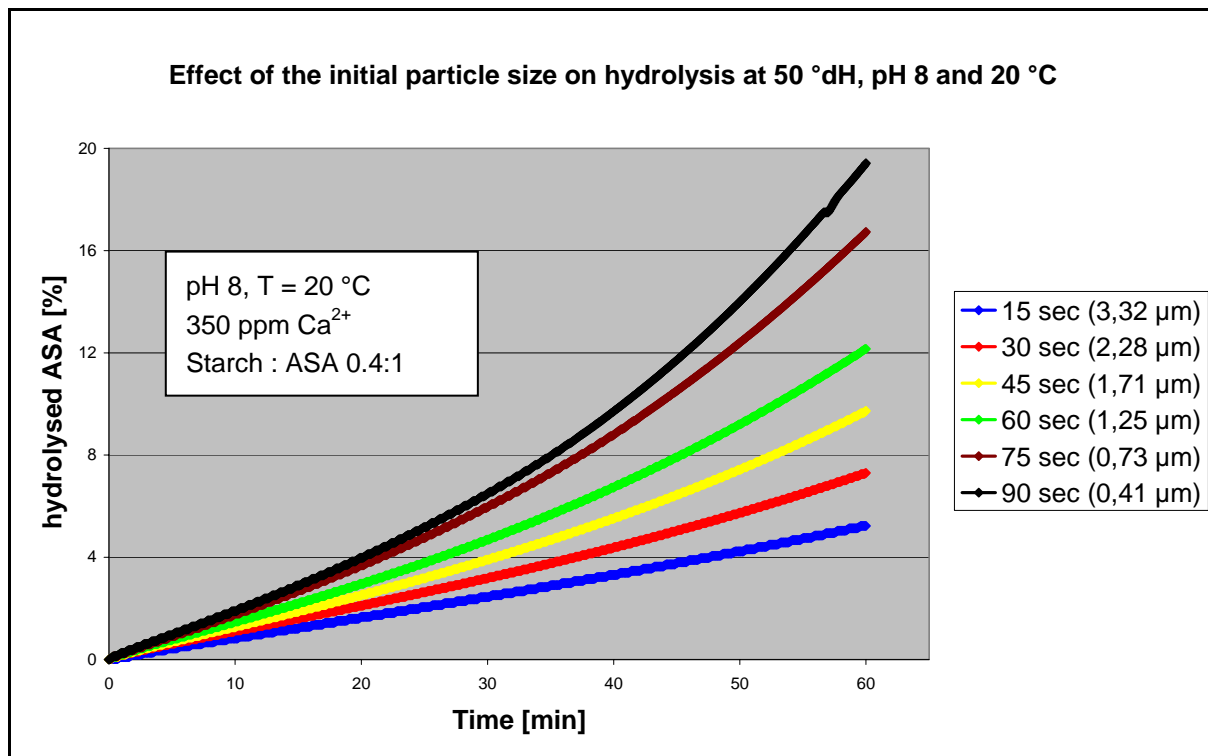


Figure 23: Effect of the initial particle size on hydrolysis

In Figure 24, the comparison of different protection colloids as regards their hydrolysis stability is shown. The average particle diameter for all samples was around $1 \mu\text{m} \pm 0.1 \mu\text{m}$. The particle size has been adjusted by different emulsifying times. Apart from the starches, above all the polyacrylamide and the polyamide epichlorhydrin resin show a good hydrolysis stability. Here, the hydrolysis speed is more and more delayed with time. It is supposed that with higher molecular weights, a better sterical stabilization of the ASA particles takes place (in particular with PAM). The high cationic but low molecular polymers (polyamine, P-DADMAC) show a comparatively bad hydrolysis stability. With the polyamine, for example, already after 5 minutes approx. 20 % of the ASA is hydrolysed under the indicated conditions.

In Figure 25, further protection colloids for the ASA emulsification are represented. Here, the particle diameter is also $1 \mu\text{m}$ with exception of the Guar ($2.5 \mu\text{m}$). It can be seen that bentonite and colloidal silica show a good hydrolysis stability, too. With the guar, the hydrolysis would run much faster with a particle size of $1 \mu\text{m}$. Thus, no good hydrolysis stability would be given.

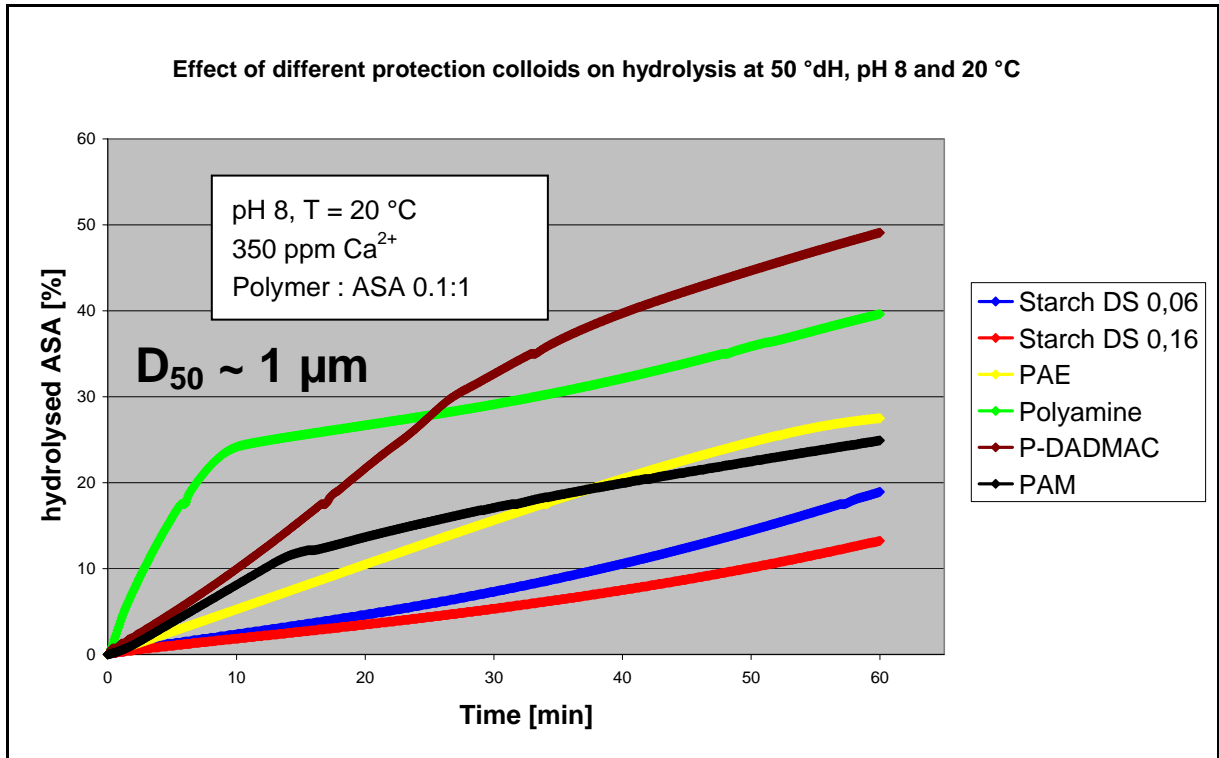


Figure 24: Effect of different protection colloids on hydrolysis

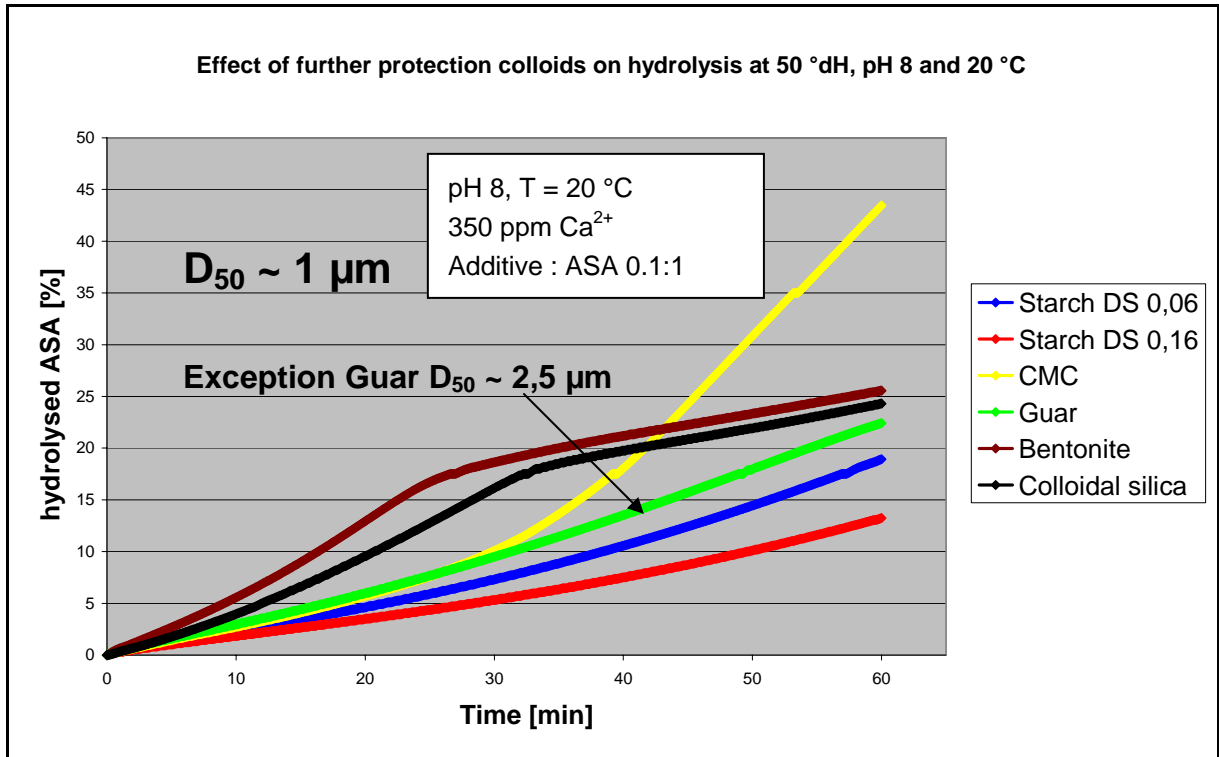


Figure 25: Effect of further protection colloids on hydrolysis

In Table 6, the influencing factors on hydrolysis of ASA are summarised.

Table 6: Summary of the most important factors on hydrolysis

Parameter	Impact (if increased)
Temperature [20 - 70 °C]	- - -
pH-value [4 - 9]	- -
Ca ²⁺ / Mg ²⁺ concentration [0 - 1000 ppm]	- -
Cationic charge starch / polymer	O / -
Molecular weight starch / polymer	+
Starch : ASA ratio [0.1:1 - 1:1]	O / +
Initial particle size [0,5 - 3 µm]	- -

+ + + strongly positive effect O no effect - negative effect

4.4 Conclusions

It can be concluded that even small changes in pH (0.5 - 1 unit) or temperature (5 - 10 °C) can have a significant effect on the handling of ASA. Especially pH values higher than 7.5 and temperatures higher than 40-50 °C have an extremely negative effect on hydrolysis and formation of deposits. To avoid deposits above all, the calcium concentration should be as low as possible and aluminium products such as PAC and PAN should be used. If hydrolysis and deposition of ASA can be controlled, this sizing agent has several advantages compared to the still predominantly used AKD.

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