

Recent developments and trends in ASA Sizing

Author: Stan Jenkins – Papertex Limited, Skipton, UK

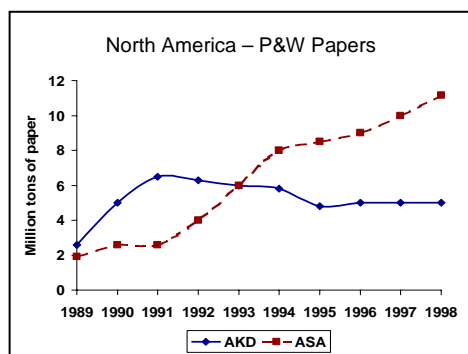
Abstract

In recent years, the use of Alkenyl Succinic Anhydride (ASA) for the sizing of paper and board has become common throughout the globe. This paper looks at the reasons for this growth, the current state of this technology referring back to past experiences, and examines opportunities for ASA sizes in the paper industry.

Examples are given of applications covering a wide range of fibre types as well as a broad variety of paper and board grades. The financial benefits of alkaline sizing are discussed, and the impact of raw material costs on the competitiveness of ASA is studied.

Introduction

Alkenyl Succinic Anhydride (ASA) was developed in the early 1960's by O.Wurzburg and E. Mazzerella of National Starch and Chemical Company in order to make a hydrophobic starchⁱ. Later this product was further developed to produce the type of ASA material that is in common use as a neutral or alkaline size today. The 70's and early 80's saw a small number of mills start to use this technology both in Europe and in North America, while AKD made strong inroads into the European market.



In the late 80's and early 90's the North American Printing and Writings market began the switch from acid to alkaline sizing, generally following the European lead and using AKD as the size. Then suddenly in the early 90's, ASA began to grow its market share, as a marketing chartⁱⁱ from that period shows.

The European market began to follow the North American trend in the mid 90's, and by the end of the century we saw South America, South Africa and Asia starting to favour ASA over AKD in acid to alkaline conversions or start-ups in most printing and writing grades. In recent years however, a small number of major Asian mills have gone back to AKD.

This history raises some obvious questions:

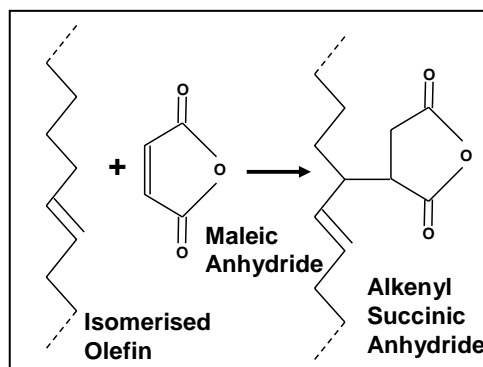
1. Why did it take so long for ASA to become accepted?
2. What drove the switch from AKD to ASA in the 90's?
3. Why are some mills switching back to AKD?

4. What does the future look like?

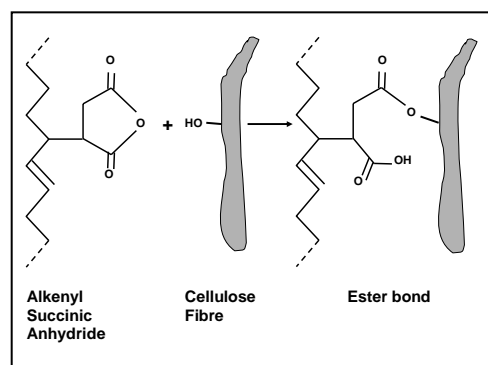
To answer these questions, we must look at some chemistry, discuss papermaking processes, study the subsequent conversion and use of these papers and finally examine the economics of supply and demand.

Chemistry of Alkenyl Succinic Anhydride

The early ASA's were manufactured from a cracked mix of olefins, which meant that the chain length could have from 15 to 21 carbon atoms in it. The olefins were then reacted with maleic anhydride to form Alkenyl Succinic Anhydride, and any excess olefin was stripped off. Today, the olefins are all manufactured from ethylene, which means that the chain always has an even number of carbon atoms. C₁₆ and C₁₈ olefins are the most common, although C₂₀ and even C₂₂ products have been tried.



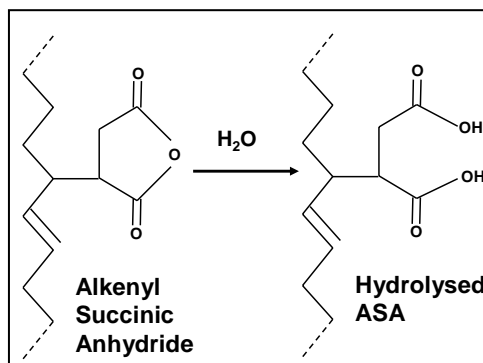
Alpha-olefins are first produced, and then these are isomerised to move the double bond to as close to the centre of the chain as possible. This is a critical step, and mistakes here can affect the quality of the final ASA. Many manufacturers of ASA purchase the olefins already isomerised from one of the big oil companies such as Shell or Innovene.



ASA is a very reactive chemical, far more so than AKD, and will readily react with hydroxyl groups on available materials, such as cellulose. This reactivity is very attractive to the papermaker, as it ensures on-machine cure of the size – something that is not always achievable with AKD sizes.

Papermakers running machines with flooded nip size presses immediately recognised the benefits of ASA over AKD. The extra sizing that was achieved gave better control of starch pick-up and fewer machine breaks. They also found that they did not have to dry so hard before the size press, and so were able to use this to speed the machine up – often gaining about 7-10% in productivity.

This reactivity did not come without its problems however. Although ASA will react with hydroxyl groups on cellulose, it will also react with the same group on water – thus hydrolysing the ASA to form a di-acid. This material has both hydrophobic and hydrophilic ends, which is



a standard definition of a surfactant. This indeed is the case with this material, and so hydrolysed ASA will encourage water penetration into the sheet of paper. As a result of this, ASA cannot be supplied as an emulsion, like AKD or rosin, but must be prepared in the mill just before addition to the paper machine. This means that suitable emulsification equipment must be installed, operated and maintained in the mill.

Another consequence of the formation of hydrolysed ASA is that it can react with the calcium or magnesium ions commonly found in water systems, leading to a sticky precipitate. This material often acts as a seed to other sticky materials, leading to deposits that can appear on wires, felts and machine rolls.

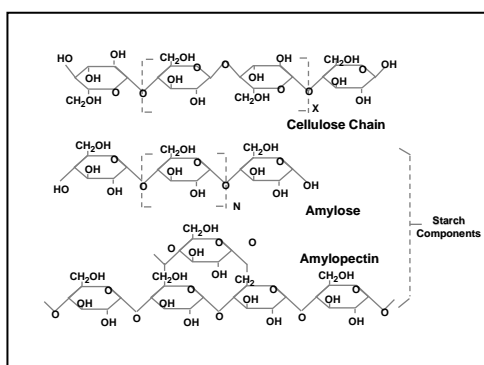
In the years following the introduction of ASA as a sizing agent, these two issues – equipment and machine deposits – slowed down the adoption of ASA, despite the fact that its cost of application was less than AKD. There were however a number of mills where ASA seemed to work very well, and so by the mid 80's, considerable study was being undertaken to understand the properties of ASA, and the optimum application techniques.

Optimising the Application of ASA Size

Understanding the chemistry leads to some obvious conclusions and directions in order to optimise ASA sizing:

- ASA hydrolysis must be kept to a minimum, in order to ensure it cannot react with the calcium or magnesium ions in water
- ASA usage must be minimised
- ASA retention must be enhanced to prevent ASA from staying in the water system where it could hydrolyse

ASA, as it is delivered to the mill, is an oil that is not soluble in water and has no natural affinity for the papermaking fibre. This means it must be put in a form that can spread easily across the papermaking stock, and be readily retained. To do this, the ASA is emulsified in a cationic medium to form small droplets.

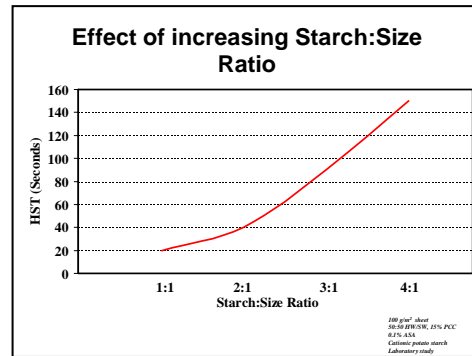


There are a number of cationic materials that can be used for this, including starch or synthetic polymers but some seem to work a lot better than others. Going back to the reaction with cellulose we looked at above, we can see the ASA forming an ester bond with the hydroxyl groups on the fibre. If we now study the molecular structure of cellulose, we can see that it is a complex sugar. Likewise, other natural materials – including starch – are also complex sugars. This means that if we

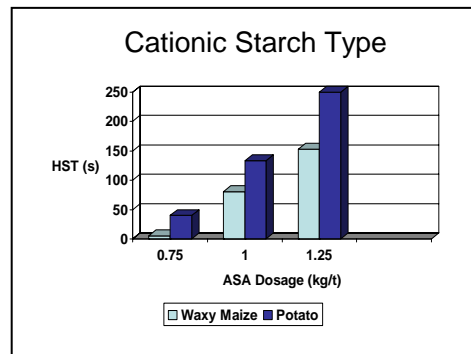
add starch to the papermaking system, we are also adding possible bonding

sites for the ASA. Lab studies have indeed shown that this is the case, and as the ratio of starch to ASA in the size emulsion is increased, so sizing in its turn improves.

We also know from food technology that starch is a very good emulsifying medium and emulsion stabiliser. Finally – cationic starch is often used as a dry strength additive in papermaking systems. All this points us in the direction of starch over a synthetic polymer for emulsification. Saying this, a number of successful applications using cationic polymers have been established, but these are a very small minority of the total number of systems worldwide.



So which starch should be used? Well, a lot of starches were studiedⁱⁱⁱ, and they all showed different sizing performance. The best type found was potato starch. Why this should be is not certain, but there are a number of theories. Certainly we know that different plant sources produce starches with different amylose to amylopectin ratios, and also that the molecular weight of these starch components are different. As an example, the amylopectin in potato starch has a typical molecular weight of 600 thousand, compared to less than 500 thousand in corn starch. Amylopectin is a better emulsifying agent than amylose. In Asia,



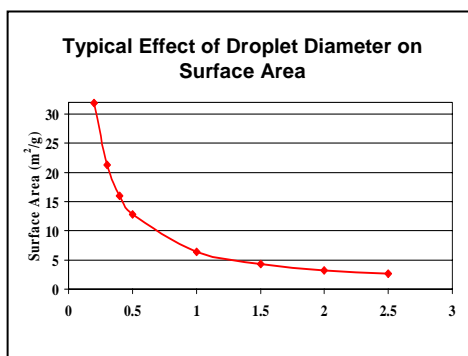
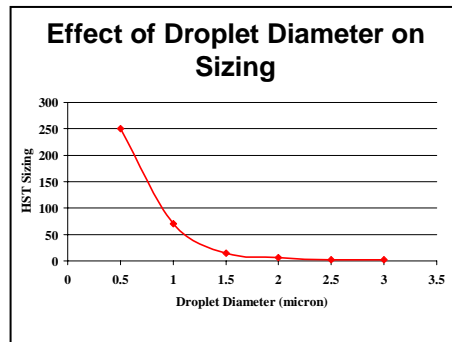
tapioca starch is the most common emulsifying agent for ASA because of its availability and performance.

Until this development work, many ASA systems involved using holding tanks to store the ASA emulsion, but it was realised that the size would be hydrolysing while in the tank. Many suppliers therefore made the decision to feed direct to the paper machine, and indeed this has been the standard approach in most mills for the last twenty years. Even making this change, it was important to understand what would cause hydrolysis. Most chemists will immediately say that the rate of reaction will increase with temperature, and since an acid is being formed, with pH. This was indeed found to be the case.^{iv} By keeping the starch temperature low, and the pH on the acid side, we can minimise hydrolysis. But there are other factors at play here.

Emulsion Droplet Diameter

When I first started working with ASA – in the mid 1980's – the target droplet diameter was 3.0 micron. Work was soon carried out that indicated that this was too large for optimum sizing.

Indeed the target nowadays is normally in the 0.5 – 1.5 micron range. In some cases, for example where the stock is extremely hot (eg 60°C), the droplet size may need to be greater – perhaps 2 micron, but this is the exception rather than the rule.

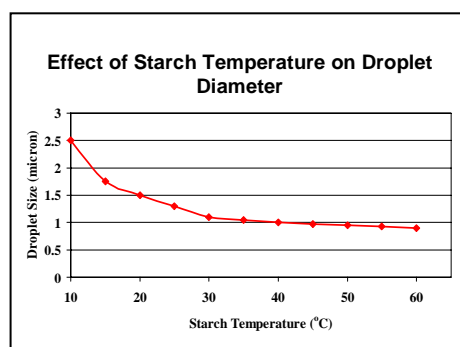


When we look at the chart included here, and we compare it to a similar chart looking at the impact of droplet diameter on surface area – we can see an almost identical layout. In this case, the surface area rockets upwards once the average diameter drops below 0.5 micron. This is an important fact, as this increase in surface area, not only increases the ability for the size to cover the papermaking fibres, but it also increases the tendency

for the ASA to react with water. This in turn can lead to deposits on the paper or board machine. Machine trials where the droplet size was taken well below 0.5 micron have indeed resulted in considerable runnability issues. For this reason, most ASA suppliers nowadays prefer to keep the average droplet diameter above 0.5 micron.

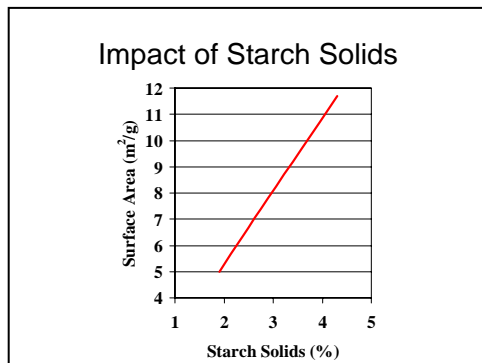
We know that different starch types will affect the emulsion droplet size, but there are two other factors that also have an impact – starch temperature and starch solids.

The chart shows the impact of temperature. As the starch gets hotter, the ASA will also see its temperature increase, and consequently the viscosity will drop. This allows a smaller droplet diameter to be obtained, as is shown on the chart. The effect starts to reduce around 35-45°C, although the droplet size will continue to slowly decrease. The higher temperature will however affect the rate of hydrolysis at the same



time, so most mills run their starch at around 40°C. This is often achieved by using a heat exchanger to cool the cooked starch to the desired temperature. With accurate control of this process, tests can be run at different starch temperatures to see when the best sizing is obtained. Different mills will run

their systems at different temperatures – dependent upon the results of these tests. Generally the target is established in the range 35 – 45°C.



Starch solids also affects the droplet diameter and surface area, especially with high shear emulsifiers. This is probably due to the impact of starch viscosity on the amount of work that can be imparted into the emulsion. As the solids increase, the surface area of the emulsion also increases, and so sizing gets better. This chart is critically important, as in many mills, starch solids does vary from batch to batch. This in

turn results in variability in the sizing results. Indeed, in many mills, the greatest cause of issues relating to ASA sizing is the cationic starch. Good management of this part of the process is essential to obtaining good sizing.

Another important piece of work from this period was reported by Scalfarotto^V, who identified that the calcium and magnesium salts of hydrolysed ASA are key components of deposits on machines and a cause of press picking. He also reported that by using an aluminium salt in the system, the tackiness of the organic salt formed from the hydrolysis product is much less. For this reason, either alum or polyaluminium chloride has been used very effectively in ASA systems since.

Emulsification Equipment

Emulsification equipment is one area where there has been continuing development since the 1980's, and now the systems available from suppliers are generally of very high quality and reliability.

Emulsification can be carried out chemically – using surfactant chemistry – or mechanically, using shear. Over the years, four main approaches to emulsification have been developed:



1. Venturi system
2. Regenerative turbine pump
3. Cavitron type homogeniser
4. Multi-stage centrifugal pump

The venturi system is simple and has no moving parts, but it does require high levels of surfactant to be added. One disadvantage of using surfactants to make the emulsion is that most of these surface active agents will interfere with the sizing of the paper sheet. For this reason, the industry has generally moved away from these systems to high shear techniques. Regenerative turbine pumps are

the most commonly used approach for this.

The cavitron type system gained popularity during the 90's in Europe, mainly due to the high maintenance demands of regenerative turbine pumps. In recent years these maintenance issues have been overcome, and there has been a trend back to turbine pumps due to the high cost of the cavitron type homogenisers. Multi-stage centrifugal pumps have been used by one major supplier, but they are not in common use.

ASA Chain Length

There has been considerable discussion regarding the optimum chain length of the olefin used to manufacture ASA. Most commercially available products are manufactured from C₁₆, C₁₈ or a mixture of the two. There has been work with longer chain lengths – even up to C₂₄ – but these materials do not have FDA approval for certain grades of paper, and so most work has focussed on the lower molecular weights.

It has been suggested^{vi} that C₁₈ ASA's may be less susceptible to steam distillation in the drying section, and consequently can result in a cleaner machine. In a separate study^{vii}, there was a suggestion that the higher chain length products are less likely to result in machine deposits in water systems with high levels (>500ppm) of dissolved calcium. In practice, the need to move to a higher chain length seems very machine and mill dependant, but a number of size suppliers have used this as a competitive tool to grow sales. The cost of purchasing the higher chain length olefins is however greater than the lower molecular weight products (see below).

Paper converting and use

We can see that by the mid to late 80's, the application of ASA had been developed enough to ensure that it could allow trouble free running in a variety of paper grades and on machines ranging from just a few tonnes to over a thousand tonnes per day. What caused the sudden growth of ASA in the 90's? To understand the trigger that started this, we need to look at one of the main uses for white P&W papers in North America at that time.

The largest woodfree mills in the United States were manufacturing paper for two main uses - computers and for photocopiers. When these mills decided to convert to alkaline papermaking, the obvious choice was to follow the European papermakers where this trend was 10-15 years in advance of North America. This meant using AKD as the size.

AKD is a wax, which means that if there is too much in the sheet, the coefficient of friction may be reduced. This was not perceived to be an issue, as dosages were low, and no obvious difference was seen in tests on the paper. Paper that was destined for computer listing or forms bond applications were being printed on high speed presses, that printed lines or forms on the paper, perforated the sheets and cut holes at each side for the

tractor feed systems. These Hamilton printing presses were very specialised and obviously needed extreme accuracy in their operation.

The first AKD sized paper that arrived at these presses caused problems, and the presses needed to run as slow as half speed to maintain accuracy. The reasons were probably due to the build up of free wax on gripper rolls within the press itself, which then could not grip in the same way. Whatever the reasons for the problem, one mill received so many complaints that it decided to either try ASA or go back to rosin. The ASA trial was run within days, and the first reel off was rushed to the printers – it ran at full speed.

The news of this went around the industry, and there was a sudden move to ASA. Today Hamilton presses are no longer very common, but the trend that was started in the early 90's continued. Large mills in Europe did not have the same problems, so they tried ASA somewhat later, but still found benefits for their customers and for their financial statements. One example from a major European producer of office papers allowed them to stop using surface size on all but their highest quality ink-jet papers, and also permitted them to lift their sizing specification from a one minute Cobb of 22 to a figure closer to 30 g/m²/min. This resulted in considerable cost savings, yet their customers saw no difference in the performance of the paper in their offices.

The benefits are not restricted to white papers. Producers of linerboard from waste paper have found that the calcium carbonate present in their fibre source has forced them to lift the pH on their machines. ASA has become very well established in this grade of paper – especially in those mills that use cationic starch as a strength additive. A white-top linerboard producer in Africa also saw financial and quality benefits following a conversion to ASA^{viii}. In this example the mill was able to add calcium carbonate filler to the top ply, improve the ply's opacity, reduce the ply's grammage and increase sheet quality. The cost savings reached many millions of dollars when all the benefits were added up.

Economics

Having seen ASA become accepted globally as an alkaline sizing agent, and seen the growth in its use by a variety of paper manufacturers – we hear that some large mills in Asia have decided to switch to AKD. Why is this happening?

Well the answer lies in global economics – and to understand this we need to go back to the raw materials used to manufacture ASA. Two main products are used – Maleic Anhydride and an Isomerised Olefin.

Maleic Anhydride

Maleic anhydride (MA) is derived from butane in the US, and from both butane and benzene in Europe and Asia. MA is used primarily as a feedstock for the production of unsaturated polyester resins (UPR) which accounts for more

than 50 percent of consumption. UPR is used to reinforce fibreglass going into boat hulls, vehicle bodies, building panels, storage tanks or cast to form putty resins for automobile repairs.

The market for MA experienced significant surpluses in the early years of this century^{ix}, when recession curtailed demand for manufacture of boats and buildings, especially in the United States. With an excess of supply, prices dropped causing manufacturers to close plants or switch to more profitable products.

Slowly demand from the boat and building industries began recovering, bringing demand back to close to 95 percent of capacity utilization. Then suddenly, in 2004, demand shot up, and there was a shortage of product.

To compound matters, all five major North American suppliers experienced supply disruptions. Caught between rising demand and reduced supply, some customers struggled to obtain product. Prices in the United States rose more than 50 percent in a year, and in Europe some purchasers saw prices double.

Since then, there has been greater stability, but there have been no reductions in price. All this had an immediate impact on the cost of manufacturing ASA. The situation is unlikely to be relieved until new capacity comes on stream, and that looks improbable until the end of 2008 at the earliest.

Isomerised Olefins

The situation with isomerised olefins is no better. Olefins are normally manufactured from ethylene – which in turn is mainly produced from natural gas, although some producers do take a cut from oil or coal distillation. There is a strong impact by oil prices on the price of gas, and recent years have seen considerable volatility in this market – generally pushing prices up.

Olefins are used for a variety of applications. Polyethylene is the largest market, but other applications include detergents and lubricants, and plasticisers. For many years, the C₁₆-C₁₈ olefins that are used for ASA sizes were produced virtually as a by-product – and consequently the opportunity to use these to manufacture ASA for paper at a low cost was ideal. In recent years, with a higher demand for the lower olefin products, manufacturers have chosen not to produce olefins with the molecular weights required for these ASA's. Those that do, are also selling these products into new markets for lube additives and oilfield chemicals.

It is this latter market – oilfield chemicals – that has mainly lifted the price for these olefins^x. Isomerised C₁₆-C₁₈ olefins are now also used to manufacture products that are used for drilling and enhanced oil recovery. As a result of the current price of oil, the demand for these products has leapt up, and the price of the olefins has gone up too. This has had a huge impact on both the availability and the cost of the higher chain length olefins. The situation is much worse for C₁₈ materials than for C₁₆ products.

So the result of these factors has been to force ASA manufacturers and suppliers to raise their prices in the market place. Unfortunately the market is a complex entity, and is not always willing to accept these higher prices – hence the suppliers are being squeezed. At the same time, the raw materials for the manufacture of AKD are in plentiful supply. Indeed there has been a general downward trend over the past few years – so AKD suppliers have the ability to adjust pricing to achieve a competitive edge. It is this that has driven a few of the larger Asian paper companies to switch to AKD. They have retained the ASA emulsification equipment however, so that they can switch back as soon as market conditions allow.

The future

And what of future market conditions? Well, there will be new olefin capacity coming on stream in the next year or so. Not all of this will be making the higher olefins, but there should be some easing of pressure. More maleic anhydride will also become available in 2008. Both of these will hopefully ease pressure – but possibly not until 2009.

In the meantime, the raw materials for AKD may also come under pressure. Typically these are derived from plants, which are dependent upon climate and harvests. There is also increasing demand for these materials for the manufacture of bio-diesel. There has been a surplus of these products, but indications are that this situation is ending – just when ASA prices start to ease, we may see AKD prices rise as a result. A recent paper^{xi} published by the Food and Agriculture Office of the United Nations showed the price of palm oil falling over the last seven to eight years. The author predicted a gentle climb in prices over the coming years, although not to the level seen in the mid 1990's. The forecast may be optimistic, as palm oil suppliers have already started introducing price increases.

While all this is happening, size suppliers continue to compete, and to seek better ways of applying ASA sizes. New emulsification equipment and emulsifying agents are being developed. The use of natural anionic products such as starch or CMC has been used as an additional additive to the paper stock. These provide more bonding sites for the ASA, as well as increasing size and overall retention. Work on alternative polymeric emulsifiers continues, trying to balance sizing performance, emulsion quality and stability, and machine runnability. Additional additives to reduce the hydrolysis rate of the ASA are also being studied.

Concluding Comments

Following a path from the 1960's, we have explored the growth of ASA sizing globally, and looked at the development of application techniques that now allow papermakers to obtain considerable benefits from using this technology. We have also studied the impact of global economics on the cost of manufacturing these products. With this in mind, many may be wondering whether it is worthwhile to look closely at ASA in the future or not.

My own view is that ASA does offer considerable benefits over competitive materials in many applications – but not all. Even with the recent increases in cost for this technology, the benefits both on-machine and subsequently with your customers, are so substantial in many cases, that this is a small price to pay.

ⁱ Wurzburg, O.B. and Mazzarella, E.D., U.S. Patent 3,102,064, 1963

ⁱⁱ Goldsberry, H.A., Internal Correspondence, Cytec Industries, 1999

ⁱⁱⁱ Hubbe, M.A., “Paper’s resistance to wetting – A review of internal sizing chemicals and their effects”, *BioResources* 2(1), 2006

^{iv} Wasser, R. B., “The Reactivity of Alkenyl Succinic Anhydride”. TAPPI Seminar Notes, Alkaline Papermaking, 1985

^v Scalfarotto, R.E., “Remedies for press picking boost efficiency of ASA synthetic sizing”, *Pulp & Paper*, April 1985

^{vi} Gess, J.M. & Rende, D.S., “Alkenyl Succinic Anhydride”, *TAPPI Journal*, 4 (9), 2005

^{vii} Fernandes, S. and Duarte, A.P., “Influence of wet-end variables on the sizing efficiency of ASA on fine papers produced with Eucalyptus globulus kraft pulps”, *TAPPI Journal*, 5 (12), 2006

^{viii} Krüger, K., “The conversion of a kraft linerboard machine from acid to alkaline sizing”, *TAPPSA African Pulp & Paper Week, Seminar Notes*, 2002

^{ix} Sullivan, T., “Ground Shifting Under Lube Additives”, *Lube Report*, 5 (5), 2005

^x van den Heuvel, E., “The global alpha olefin market – A five year outlook”, *Conference notes- Pira Sizing conference*, December, 2005

^{xi} Thoenes, P., “Biofuels and Commodity Markets – Palm Oil Focus”, *conference proceedings, Agralinforma “The Impact of biofuels on commodity Markets”*, 2006