RECENT STUDIES ON THE PRODUCTION OF SODIUM ALPHA OLEFIN SULFONATES AS CONCENTRATES AND DRY PRODUCTS

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Abstract

Production of sodium alpha olefin sulfonates from a variety of normal alpha olefin blends has been studied at the pilot plant scale. Results for the sulfonation, neutralization, and hydrolysis of commercial grade C14, C1416, C1418, and C1224 normal alpha olefins are presented, and the application of a new surfactant drying technology for producing ultra-concentrated AOS is discussed. Physical properties of AOS are reviewed in relation to their impact on process design.

Résumé

La production de sulfonates à base d'oléfine sodium alpha à partir d'une variété de mélanges normaux d'oléfine alpha a fait l'objet d'études à l'usine pilote. Les résultats de la sulfonation, la neutralisation et l'hydrolyse d'oléfines alpha normaux de catégories commerciales C14, C1416, C1418 et C1224 sont présentés, et l'application d'une nouvelle technologie traitant du séchage de l'agent tensioactif concernant la production d'AOS ultra-concentré est discutée. Les propriétés physiques de l'AOS sont examinées compte tenu de leur impact sur la conception du traitement.

Zusammenfassung

Die Erzeugung von Natrium-Alpha-Olefinsulfonaten aus verschiedenen normalen Alpha-Olefinmischungen wurde im Rahmen eines Pilotwerkes untersucht. Die Resultate der Sulfurierung, Neutralisation und Hydrolyse der handelsüblichen C14, C1416, C1418 und C1224 normalen Alpha-Olefine werden dargestellt, und die Anwendung einer neuen Tensid-Trocknungsmethode zur Erzeugung von ultrakonzentrierten AOS wird diskutiert. Die physischen Eigenschaften der AOS werden im Hinblick auf ihre Auswirkungen auf die Prozessplanung besprochen.

Introduction

Over the past several years, a renewed interest has been expressed in commercial alpha olefin sulfonation, mainly due to the competitive price of alpha olefin (AO) feedstocks versus detergent industry mainstays such as linear alkylbenzenes. Alpha olefin sulfonates (AOS), in the chain length of C14 to C18, offer very good detergency, excellent foaming properties and mildness, and they rapidly biodegrade in the environment.[1,2]

Alpha olefin sulfonates, primarily C1416, C1418, and C1618 blends, have been produced as low active solutions (<40%) for several decades. Recent attention, however, has focused on producing AOS as concentrated pastes (70% - 75%) or as ultra-concentrated dry products (>90%). The ultra-concentrated product is formed into needles, noodles, or flakes that may be packaged and sold as almost pure surfactant. These forms can also be ground into a powder and admixed with other compounds using an agglomeration step to make a granular detergent formula. This paper will present information of general interest for producing AOS as concentrated pastes, and will discuss the application of a new drying technology for producing ultra-concentrated AOS. Results from pilot plant tests involving the high active production and drying of C14, C1416, C1418 and C1224 alpha olefin sulfonates will be presented. Viscosity data for high active C1418 AOS and hydrolysis data for C1416 AOS is presented.

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Feedstocks

The surfactant characteristics of sulfonated alpha olefins are influenced primarily by the carbon chain distributions of the starting feedstock. The foaming properties, tolerance to water hardness, and detergency of the finished product can be controlled by adjusting the blending ratio of different alpha olefin cuts in the feed. Information is available in the literature on the application and performance of various sulfonated olefin blends used in the detergent industry.[3,4,5]

There are three main manufacturing processes available for producing detergent grade alpha olefins; namely: the SHOP method, the Ziegler method, and the peaked Ziegler method. Both the SHOP method and the Ziegler method produce feedstocks that are high in linear alpha olefins and low in branched olefins; the peaked Ziegler method produces a feedstock that has a higher branched olefin content. Table 1 shows typical carbon distributions and olefin distributions for a variety of straight cuts and blends produced from the Ziegler process. The C1224 blend is a new broad-cut olefin that is not yet widely used for sulfonation.

Table 1: Typical Carbon Distribution and Olefin Distribution for Alpha Olefin Straight Cuts and Blends Produced by the Ziegler Process

Carbon Distribution Wt%	**C14**	**C16**	**C18**	**C1416**	**C1418**	**C1224**
C12	0.3	0.0	0.0	0.2	<0.1	27.0
C14	99.4	0.0	0.0	65.4	15.2	21.0
C16	0.3	99.0	1.4	34.2	49.7	17.0
C18	0.0	1.0	98.3	0.2	34.9	13.0
C20	0.0	0.0	0.3	0.0	0.2	10.0
C22	0.0	0.0	0.0	0.0	0.0	7.0
C24	0.0	0.0	0.0	0.0	0.0	5.0
Olefin Type Wt%						
Linear Alpha Olefins	93.9	92.9	91.7	93.4	92.3	92.3
Branched Olefins	5.1	5.9	6.6	5.6	6.6	6.2
Cis & Trans Internal	0.2	0.1	0.2	0.1	0.1	0.3
Other Olefins	0.6	0.9	1.2	0.7	0.8	<1.0
Paraffin	0.2	0.2	0.3	0.2	0.2	0.3
Di-olefin	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Average Molecular Weight						
	197	225	253	205	230	224

The sulfonation chemistry of alpha olefins is complex and will not be discussed in detail in this paper. There is an abundance of information available in the literature for interested readers.[6,7,8]

Commercial Production of AOS

The commercial production of alpha olefin sulfonates from alpha olefins is a multi-step process involving reacting the olefin with dilute SO_3, digesting the crude sulfonic acid mixture, neutralizing with NaOH, and hydrolyzing the remaining sultones to product. This process yields a mixture of 1, 2, 3, and 4-alkene sulfonates, 3-hydroxysulfonate, and 4-hydroxysulfonate. The hydrolyzed product has traditionally been produced in the form of a 30% to 40% active matter solution, suitable for formulation into liquid products, or for use in conventional spray drying processes for low density detergent powders. More recently, interest has been demonstrated in producing high active matter pastes, which can be stored and transported for significantly less cost. High active matter pastes can be readily diluted for use in traditional liquid applications, and they can also be dried to produce an almost-pure surfactant in solid form. A novel drying process recently introduced to the market will be briefly discussed in the next section.

Figure 1 shows a schematic of a typical industrial air/SO_3 sulfonation reactor.[9,10] The alpha olefin is first contacted with a dilute stream of gaseous SO_3 in a continuous thin film reactor. Precise control of the mole ratio of SO_3 to organic is required both at the macro and micro scales in order to produce a high quality sulfonic acid that is low in residual oil, low in sulfuric acid, and low in colour. Leaving the reactor the sulfonic acid typically contains 40% - 60% gamma and delta sultones. The organic acid mix is pumped through a continuous plug flow digester, typically for 15 - 20 minutes at 35°C - 40°C. The aging step serves to reduce slightly the residual oil through reaction with pyro-acids and dissolved SO_3 and has some influence in determining the final product isomer composition.[11] Care must be taken to avoid excessively high temperatures or long acid digestion times as these will result in a darker product.

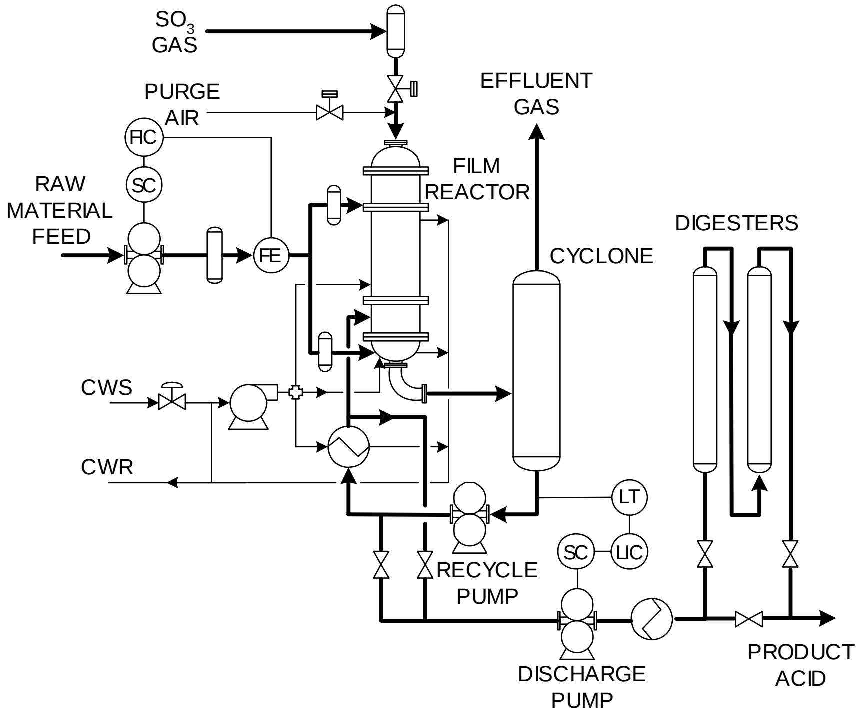

Figure 1: Schematic of Commercial Air/SO_3 Sulfonation Process

From the digester, the sulfonic acid is forwarded to a continuous dominant bath neutralizer, where it is neutralized with a large amount of excess caustic, typically 1.0 wt% to 1.5 wt%. If an excessive amount of base is used, the viscosity of the resulting paste may increase, yet if inadequate base is used the material will turn acidic during the subsequent hydrolysis step, leading to corrosion and colour problems. The base, sulfonic acid, and dilution water are combined in a high shear in-line mixer to ensure intimate micro-mixing and to eliminate the potential for gel-spots. A continuous recycle stream of neutral paste is pumped through a heat exchanger to remove the heat of neutralization, and is re-introduced at the suction of the in-line mixer. This equipment configuration enables tight control of the paste temperature in the neutralization loop and allows operation of the process at temperatures that produce optimal viscosity characteristics. Rheology studies have shown complex dependencies on paste composition, and therefore accurate metering of all ingredients is necessary to avoid entering a difficult phase regime. Figure 2 shows a schematic of the neutralization system.

After neutralization, a hydrolysis step is required to convert the remaining sultones into hydroxyalkane sulfonates and alkene sulfonates. The hydrolysis process occurs in a plug flow vessel with a typical residence time of 60-90 minutes. The hydrolysis temperature is typically controlled to between 140°C and 150°C. If the hydrolysis temperatures are too low, there is insufficient conversion of the sultones, and if the temperature is too high, there can be a significant increase in the final product colour. Figure 3 shows a schematic of the hydrolysis system.

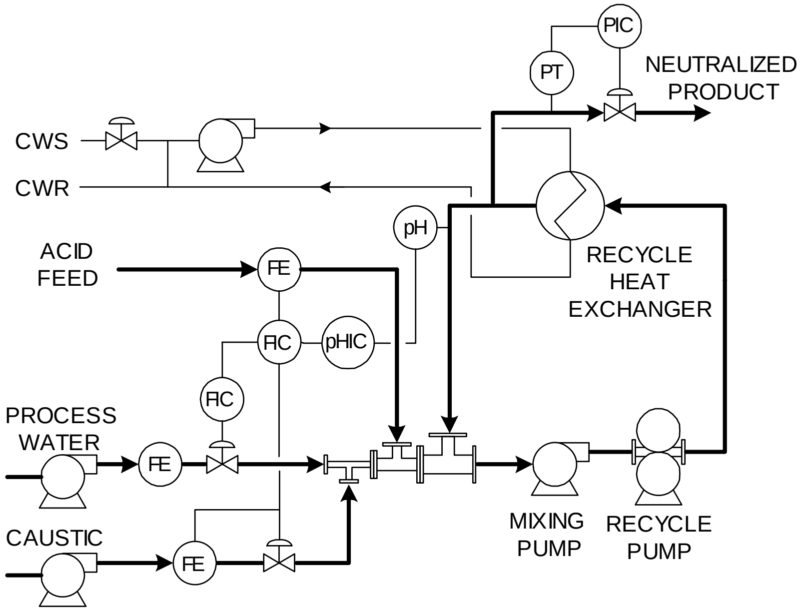

Figure 2: Schematic of AOS Neutralization System

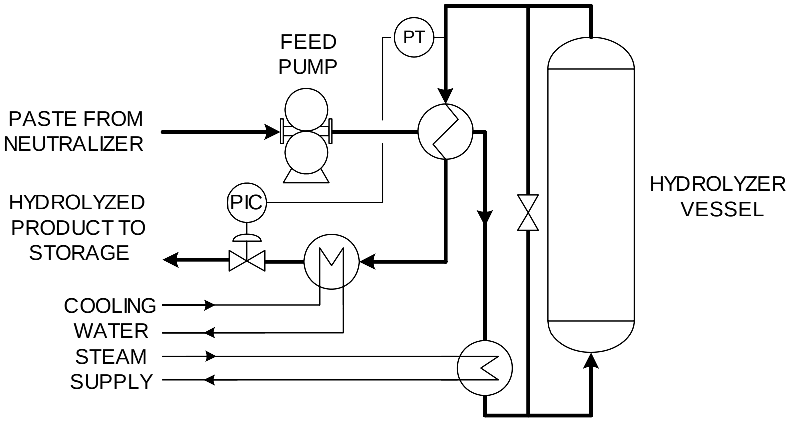

Figure 3: Schematic of AOS Hydrolysis System

The effect of critical sulfonation process variables on AOS quality has been thoroughly modeled in previous pilot plant work. Table 2 summarizes the key process controls for C1416 alpha olefin sulfonation.[12]

Table 2: Summary of the Effect of Process Variables on C1416 Alpha Olefin Sulfonation

Factor	Control Range	Effect
Mole Ratio	1.02 to 1.06 (1.04 typical)	Increasing MR increases conversion, di-sulfonation, and color
SO_3 (Vol %) concentration	2.5% to 4% (3.5% typical)	Increasing %SO_3 increases color
Reactor Jacket Temperature	18ºC to 32ºC (20ºC typical)	Cooler temperatures lower color, but below 20ºC, sultone freezing may occur
Recycle Temperature	20ºC to 40ºC	Cooler temperatures produce lower colors down to the point sultones freeze.
Digestion Temperature	25ºC to 60ºC (40ºC typical)	Higher temperatures lower 1-alkene, increase hydroxy-alkanes, and increase color. Slight improvement in conversion.
Digestion Time	10 to 60 minutes (15 minutes typical)	Similar to temperature, but less effect on 1-alkene
Neutralization Temperature	50ºC to 100ºC (90ºC typical)	High active must run at the high temperature. No undesirable effect
Hydrolysis Temperature	140ºC to 150ºC (High Active)	Cooler temperatures yield better color, but longer times
Hydrolysis Time	60 to 90 minutes (High Active)	This is usually fixed for a plant, and inversely proportional with rate. Adjust temperature as needed.

The processing requirements for high active AOS pastes differ from those of low active liquids primarily in the design of the neutralizer and hydrolyzer. High active AOS pastes are considerably more viscous, and exhibit a distinct non-Newtonian rheology. The range of active concentrations in which the paste is manageable is relatively narrow, typically between 68% and 76% - this being the region in which a viscosity minimum exists. Pump design, heat exchanger design, and line size must all be considered carefully in the design of high active neutralizers and hydrolyzers.[13]

The rheology of high active alpha olefin sulfonates, like other high active sulfonates and sulfates, is complex and dependent on many factors. High active paste viscosity from a given olefin sulfonate is largely dependent on active concentration, temperature, and shear rate, but is also impacted to varying degrees by the total sodium ion concentration (NaOH, Na_2SO_4), pH, free oil content, and paste aeration. Furthermore, the degree of branched olefins in the starting feed also influences the rheological properties. The viscosity characteristics of high active AOS have been qualitatively observed to change if the paste passes through freeze / thaw cycles in storage.

High active AOS pastes have been successfully produced from the C14, C1416, C1418 and C1224 alpha olefin blends listed in Table 1. The work was performed in The Chemithon Corporation's pilot plant facilities in Seattle, WA, U.S.A. The purpose of the work was to evaluate the production of high active pastes from a broad variety of alpha olefin blends, and to produce material for evaluating the performance of the new drying process. No attempt was made to optimize the sulfonation of each feed in these pilot plant tests; with judicious selection of the mole ratio, sulfonator cooling water temperatures, acid digestion conditions, and hydrolysis conditions, it is possible to produce material with lower free oil and lower colour. Average sulfonation conditions are reported in Table 3, and the average analyses for composite samples are shown in Table 4. The %PEX represents petroleum ether extractable oils. The 5% AM Klett was measured using a blue #42 filter, a 20X40 mm sample cell (40 mm path length), and a Klett-Summerson colourimeter. AOS has been observed to slowly autobleach with time, the result being a substantial decrease in colour over the course of weeks. The reported colours in Table 4 are for freshly made high active paste.

Table 3: Average Process Settings Used in Pilot Plant Sulfonation

Process Variable	C14	C1416	C1418	C1224
Mole Ratio SO_3 / Org	1.05	1.05	1.07	1.10
SO_3 Concentration (Vol%)	3.5	3.5	4.0	2.8
Reactor SO_3 Load (kg / hr / cm)	0.95	0.95	0.93	0.95
Organic into Reactor (°C)	18	30	30	25
Reactor Jacket (°C)	20	20	21	20
Acid Recycle Temp (°C)	29	32	29	29
Acid Digest Time (min)	18	24	28	24
Acid Digest Temp (°C)	38	37	35	39
Neutralizer Temp (°C)	85	82	100	96
Hydrolysis Time (min)	95	95	95	90
Hydrolysis Temp (°C)	140	140	135	140

Table 4: Average Analyticals Obtained in Pilot Plant Sulfonation

Analytical	C14	C1416	C1418	C1224
Wt% Hyamine Active	74.3	72.9	71.8	75.7
Wt% PEX As is	1.5	1.4	1.5	2.1
5% AM Klett	46	63	55	100
Wt% NaOH As is	0.0	0.1	0.3	0.1
10% pH	5.4	10.6	11.6	10.9
Wt% Na_2SO_4 As is	0.9	0.7	1.0	0.8

In general, high active material containing low residual oil could be made readily from each of the feedstocks studied. For the C14 alpha olefin sulfonation, citric acid was added as the material exited the hydrolyzer to lower the pH, and this had a noticeable effect on decreasing the viscosity. A high residual oil was noted for the C1224 product, and this is likely due to the presence of high molecular weight components that do not sulfonate as readily as the lower molecular weight components.

The C1418 high active blend, due to the large amount of C16 and C18 olefins, produced the most viscous product and necessitated operating the neutralization loop at higher temperatures to thin the paste and improve its pumpability. Figure 4 shows a plot of the viscosity for 71 wt% C1418 hydrolyzed AOS (1.5% PEX, 1.0% Na2SO4, 0.3%NaOH, all as-is) as a function of shear rate, for three different temperatures. The data was collected on fresh paste samples exiting the hydrolyzer using an in-line dynamic tube viscometer. The data points were fitted by regression analysis. The dashed lines represent extrapolation to shear rates beyond those for which data was actually gathered; past experience with high active sodium neutralized sulfonates has generally shown such extrapolation to be reasonable within limits. At all temperatures, the apparent viscosity of the paste was observed to follow a power-law relationship with the shear rate. At the two highest temperatures, the curves have very similar, but not identical, slopes. Some high active alpha olefin sulfonates pass through a minimum in viscosity as temperature increases. Although a minimum was not observed for the three temperatures examined for C1418 AOS, a minimum was observed for the high active C14 AOS with citric acid.

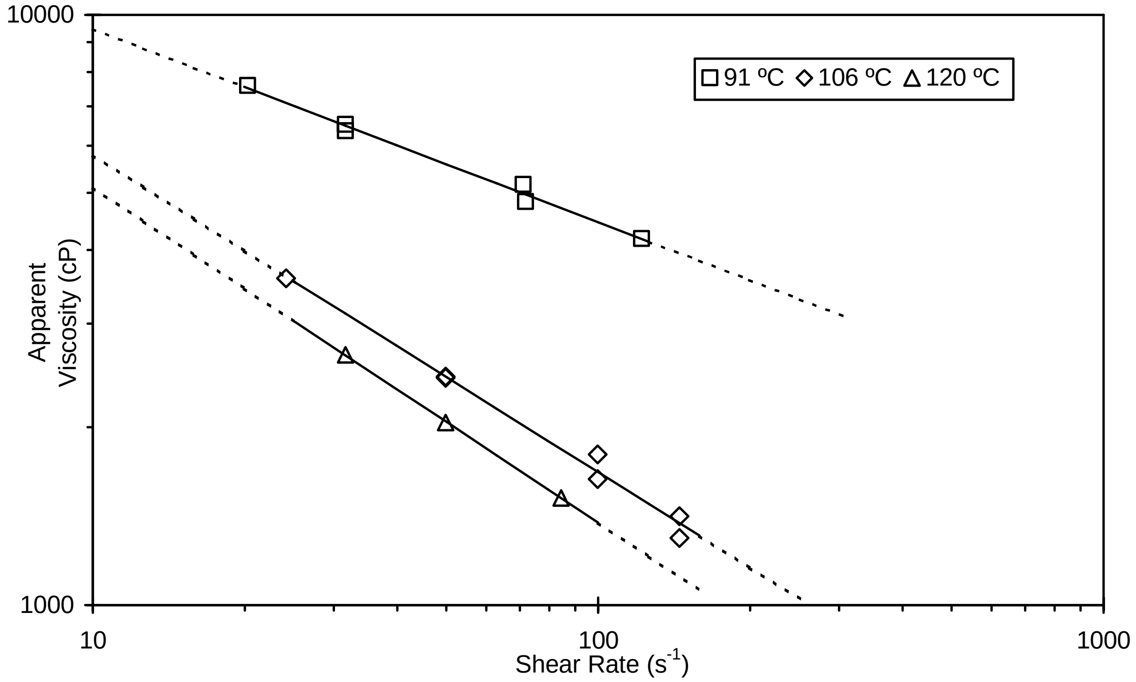

Figure 4: Viscosity Versus Shear Rate for 71 Wt% C1418 AOS

There is little information available in the literature examining how hydrolysis conditions impact sultone levels in high active paste. Consequently, in a simple experiment, samples of 72 wt% C1416 AOS were batch hydrolyzed at three different temperatures and the alkane 1,4-sultones (delta) and alkane 1,3-sultones (gamma) were monitored by gas chromatography as a function of time. The delta sultone was always observed to be present in the larger quantity, as can be seen from Table 4 (the detection limit was 1 ppm). Delta sultones are reported to have a low skin sensitization potential,[14] and this would be especially true at the small concentrations found in thoroughly hydrolyzed pastes. Recent attention has focused on gamma sultone residues as the more potent skin sensitizers. As can be seen from Table 5, essentially all the delta and gamma sultones can be hydrolyzed if a high enough temperature and adequate hydrolysis time are used.

Since the delta sultone hydrolysis rate is much slower than the gamma sultone rate,[15] the reaction can be characterized by looking at just the delta sultone content. Figure 5 shows a plot of the total delta sultones in the high active C1416 AOS as a function of hydrolysis time, for the three different hydrolysis temperatures. As can be seen, at a temperature of 120°C, there was still a substantial delta sultone concentration even after 4 hours of hydrolysis. At 140°C the delta sultone level was approximately 35 ppm after about 60 minutes, and at 160 °C the reduction rate was even more rapid. As the sultones are hydrolyzed to hydroxyalkane sulfonates and alkene sulfonates, sodium hydroxide is consumed, resulting in a decrease in the pH. The rate of hydrolysis is often treated as first order in sultone concentration,[16] but at low pH there may be influences from caustic concentration. In hydrolyzing AOS, both high and low active forms, care must be taken to avoid allowing the paste to become acidic as a result of insufficient addition of caustic to the neutralizer. If the paste becomes acidic, the result will be increased product colour mainly due to corrosion products.

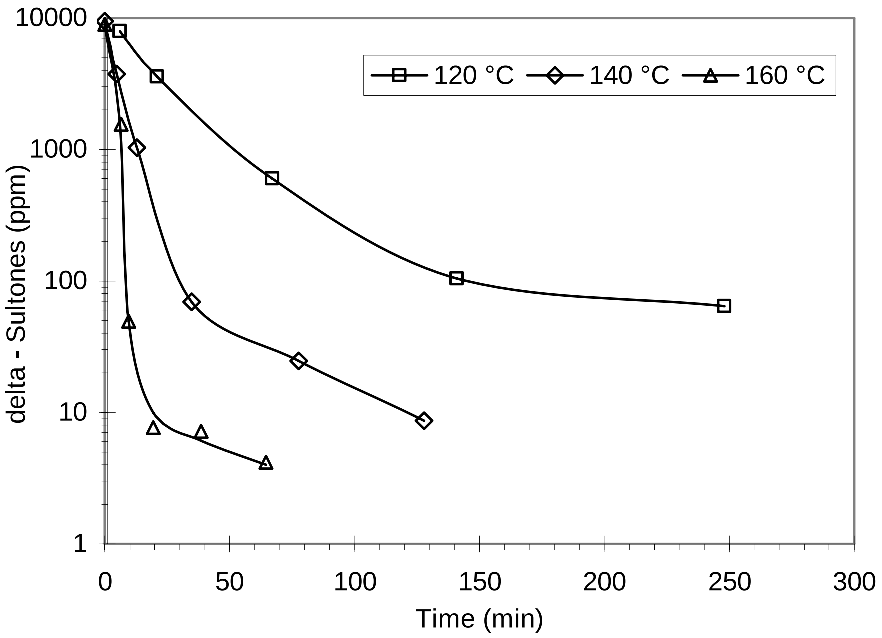

Figure 5: delta-Sultones Versus Hydrolysis Time for 72 Wt% C1416 AOS

Table 5: Tabulated Results of Hydrolysis Study for 72 Wt% C1416 AOS

Temp (°C)	Time (min)	NaOH (Wt%)	C14 delta Sultone	C14 gamma Sultone	C16 delta Sultone	C16 gamma Sultone
120	0	0.87	4432	337	2321	153
	6	0.56	5147	34	2829	34
	21	0.35	2350	21	1259	15
	67	0.18	409	1	196	1
	141	0.15	72	ND	33	ND
	248	0.14	43	2	22	1
140	0	1.04	6081	633	3393	289
	5	0.44	2383	7	1382	5
	13	0.35	705	2	326	2
	35	0.25	45	ND	25	2
	78	0.18	16	ND	9	ND
	128	0.04	7	ND	2	ND
160	0	0.87	5862	270	3107	125
	7	0.27	990	2	559	2
	10	0.16	33	ND	17	ND
	20	0.12	5	ND	2	ND
	39	0.09	5	ND	2	ND
	65	0.09	3	ND	1	ND

In general, if the hydrolysis temperature is increased, there is an increased colour penalty in the finished product. Consequently, there exists a trade-off between increasing temperature to accelerate the rate of destruction of sultones and to reduce the hydrolyzer residence time requirements, and in decreasing temperature to minimize the impact on colour. Based on tests with both high active and low active C1416 AOS, it appears that hydrolyzing at lower temperatures for longer periods of time leads to lower colors than hydrolyzing at higher temperatures for shorter periods of time. Assuming that adequate caustic has been added in the neutralization stage, temperatures of 140 °C - 150°C and times of 60 - 90 minutes should be adequate to achieve low sultone levels with high active paste. The exact temperature and time that would be required is, of course, dependent on the feed material. Hypochlorite bleaching of AOS is not recommended as it is believed that under certain process conditions there is a potential to form gamma chlorosultones and unsaturated gamma sultones, known to be potent skin sensitizers.[17,18,19]

Table 6 shows the ^{13}C NMR isomer distribution for grab samples of paste hydrolyzed at 140 °C. As can be seen, the isomer distribution changes during hydrolysis. Of particular interest is to note that 2-hydroxyalkane sulfonate, a low solubility isomer that is often associated with precipitates in AOS solutions, was not observed.

Table 6: Isomer Mole % Distribution Vs. Time for 72 Wt% C1416 AOS Hydrolysis at 140 °C

Isomer	0 min	5 min	123 min
1-alkene	24	20	14
2-alkene	35	33	36
3-alkene	6	7	12
4-alkene	0	1	2
>4-alkene	0	0	0
2-hydroxy	0	0	0
3-hydroxy	34	34	32
4-hydroxy	0	4	4
delta sultone	2	0	0

Production of Ultra-Concentrated AOS

A new process was used in the pilot plant to produce AOS as a dense, almost pure solid suitable for incorporation into non-tower agglomeration systems.[20,21] Figure 6 shows a schematic of this continuous drying process, which was successful in producing AOS with 3.5% moisture or less from each of the high active pastes. The concentrated paste is first pumped through a pre-heater and is maintained under back-pressure while being heated to above the normal boiling point of water. A system of orifices at the inlet to the dryer uniformly distributes the detergent to a series of parallel tubes, or drying channels, as discretely atomized particles. Exiting the drying channel the particles disengage from flash vapour in a collection vessel maintained under a partial vacuum. The molten, substantially dry AOS is continuously plodded from the vessel. The material can be extruded as 1mm or 3mm needles directly into storage bins and will not stick together as it cools to ambient temperatures. More rapid cooling can be achieved through means of a chill belt or forced convection air. In the freshly dried form, AOS is a non-hygroscopic pliable semi-solid that crystallizes as it ages to form a friable product. Once the AOS has aged, it can be readily ground into powder form.

Table 7 shows the wt% active, wt% PEX, and wt% H2O for the dried AOS. The colour and sodium sulfate levels were not observed to change significantly in the drying process, however a reduction in residual oil was noticed when compared with the high active paste charged to the drier. All products were produced as either 1mm or 3mm needles that were observed to be free-flowing and non-dusting.

Table 7: Composite Average Analytical Results for Drying of High Active AOS

Analytical	C14	C1416	C1418	C1224
Wt% Hyamine Active	94.1	95.6	93.9	94.3
Wt% PEX As is	1.2	1.0	1.6	1.9
Wt% H2O	3.0	2.4	3.5	2.8

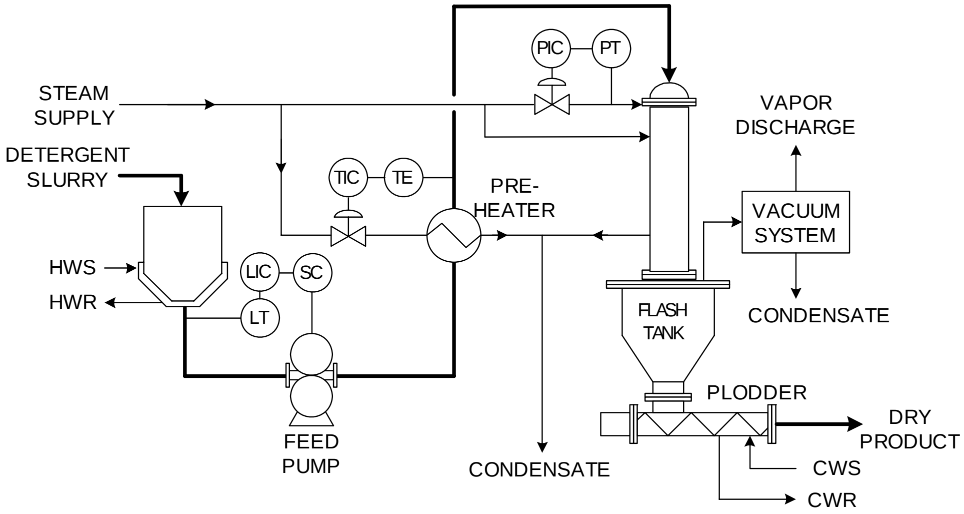

Figure 6: Schematic of AOS Drying System

Conclusions

High active pastes and dry products have been successfully produced from a wide variety of alpha olefin feedstocks. The design and operation of modern AOS plants has been discussed with regards to the physical properties of concentrated AOS. Operating conditions and analytical data for pilot plant trials involving the sulfonation and high active neutralization of alpha olefins has been presented. Viscosity behaviour of high active alpha olefin sulfonates has been reviewed and the results of a hydrolysis study for high active C1416 AOS has been reported.

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