

The Use of Adducts of N-Alkylalkanolamines (AAA's) with Alkenyl Succinic Anhydrides (ASA's), AAA carboxamides and structurally unique AAA's as Emulsifiers in Metalworking Fluids.

Michael D. Gernon
Taminco, N.V.
Pantserschipstraat 207
B-9000 Gent, Belgium
Michael.Gernon@Taminco.com

Kurt Buyse
Taminco, N.V.
Pantserschipstraat 207
B-9000 Gent, Belgium

Robert Ash
Taminco Higher Amines
Allentown, PA
USA

Summary:

The reaction of alkenyl succinic anhydrides (ASA's) with N-alkylalkanolamines (AAA's) provides mixed amide ammonium carboxylates with good emulsifying properties. Analogous completely ammonium compounds can be prepared by pre-hydrolysis of the ASA followed by neutralization with AAA. AAA alkanolamides can be prepared by the reaction of secondary AAA's with carboxylic acids and/or esters. Structurally unique AAA's can be prepared by adaptations of standard methods. This talk will describe the preparation of a number of amide/ammonium ASA/AAA adducts, the analogous all-ammonium compounds, AAA amides and structurally unique AAA's. A comparison of the emulsifying, corrosion inhibiting, metal staining and biostabilizing properties of these different alkanolamine derivatives will be presented. Formulation guidelines and economic considerations will be summarized, and the overall applicability of these materials to metalworking fluids will be discussed.

1) Introduction:

Many commercially important metalworking fluids are formulated and used as oil in water (O/W) emulsions. Emulsions are liquid/liquid colloidal systems wherein a dispersed phase of one liquid is contained within a continuous phase of a separate immiscible liquid. Oftentimes, one of the immiscible phases is aqueous in nature and the other immiscible phase is organic in nature. These two phases are oftentimes referred to as "oil" and "water" phases. The formation of an emulsion results in a large increase in the total area of surface contact between the two phases. This increased surface contact between immiscible phases leads to an increase in the internal energy of the system. Note that there must be interfacial tension (positive energy per unit length) between immiscible liquids. If there were a negative interfacial tension at

the interface of two liquids, then the liquids would spontaneously keep increasing their mutual surface contact until it became infinite (i.e., the two liquids would form a single phase). An emulsion is an inherently unstable situation that attempts to rectify itself by coalescence of the two immiscible phases. Various forms of kinetic stabilization can be used to create emulsions that last long enough to be useful, but these methods do not alter the underlying instability of the emulsion. Decreasing the interfacial tension between the two phases decreases the thermodynamic instability of the emulsion. If the interfacial tension can be lowered to the point where the mixing entropy exceeds the enthalpic surface contact energy, then the emulsion will become thermodynamically stable.

Various methods for the measurement of liquid/liquid surface tension are known. Most of these methods

involve drop shape and/or drop weight analysis. Harkens and Humphrey reviewed an early use of the drop weight method in 1915 [1,2]. The pendant drop method was employed by Butler to measure the interfacial tension between water, mercury and benzene [3]. The pendant drop method was also applied by Donahue and Bartell to measure the interfacial tension between water and a number of organic liquids [4]. In more recent work, Hool & Schuchardt have developed automated instrumentation for liquid/liquid interfacial tension measurement based on the drop weight method [5]. A number of current approaches to the evaluation of drop shape and/or related contact angles employ digital photography coupled with image expansion techniques [6]. Digital image manipulation effectively alleviates many of the problems associated with obtaining accurate contact angles from hanging drops, drops on tables and/or menisci within a capillary tube. Drop shape/weight analysis has the advantage of providing for a direct measurement of liquid/liquid interfacial tension while the indirect use of contact angles has the advantage of experimental simplicity and ease of use. The paper of Good *et al.* provides an example of how a theoretical relationship between surface tension (air/liquid interfacial tension) and liquid/liquid interfacial tension can be developed [7]. A number of detailed theoretical descriptions of the capillary rise phenomenon have been published [8]. Note that a number of textbooks offer a broad coverage of interfacial tension and the stability of colloidal systems [9,10]. The authors of this paper have previously developed a technique for liquid/liquid interfacial tension measurement based on the analysis of capillary contact angles [11].

Not surprisingly, the interfacial tension between two liquid phases is generally found to increase as the phases become less miscible in each other. For example, the interfacial tension between water and partially miscible amyl alcohol is lower (approximately 4 dynes/cm) than the interfacial tension between water and almost totally immiscible hexane (approximately 50 dynes/cm).⁴ The origin of interfacial tension is the attraction of the molecules within a given phase for themselves as compared to their attraction/repulsion of the molecules of another phase, and the magnitude of the interfacial tension will manifest itself in many ways including liquid/liquid cosolubility (higher interfacial tension implies lower cosolubility) and emulsion stability (higher interfacial tension between phases implies lesser emulsion stability).

2) N-Alkylalkanolamines:

In this work, we have examined the impact of various additives on the emulsion stability of metalworking fluids. Taminco is a company that specializes in amine synthesis and technology development, and the work contained herein is focused almost exclusively on amines and amine derivatives.

The variation of liquid/liquid interfacial tension for some aqueous alkanolamine solutions versus soybean oil, methyl oleate and dodecane as measured by the technique described in reference [11] (bibliography) are presented in Figures 1, 2 and 3 below.

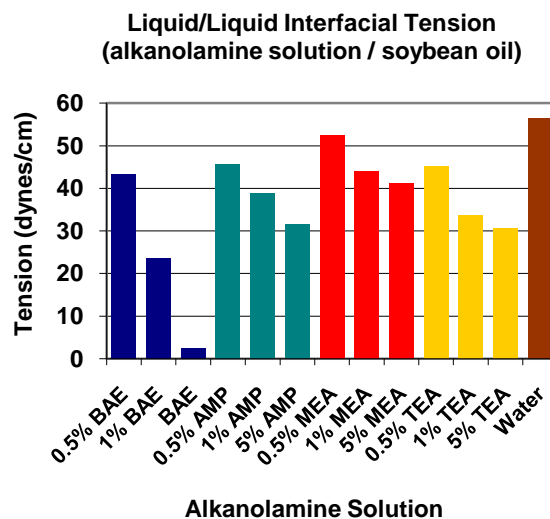


Figure 1: The liquid/liquid interfacial tension @ 20 °C of some aqueous alkanolamine solutions at 0.5%, 1% and 5% concentrations versus soybean oil. BAE = butylaminoethanol, AMP = 2-amino-2-methyl-1-propanol, MEA = monoethanolamine, TEA = triethanolamine.

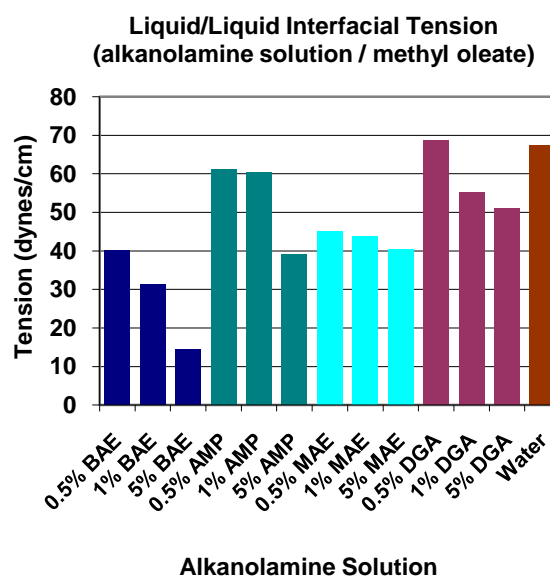


Figure 2: The liquid/liquid interfacial tension @ 20 °C of some aqueous alkanolamine solutions at 0.5%, 1% and 5% concentrations versus methyl oleate. BAE = butylaminoethanol, AMP = 2-amino-2-methyl-1-propanol, MEA = monoethanolamine, TEA = triethanolamine.

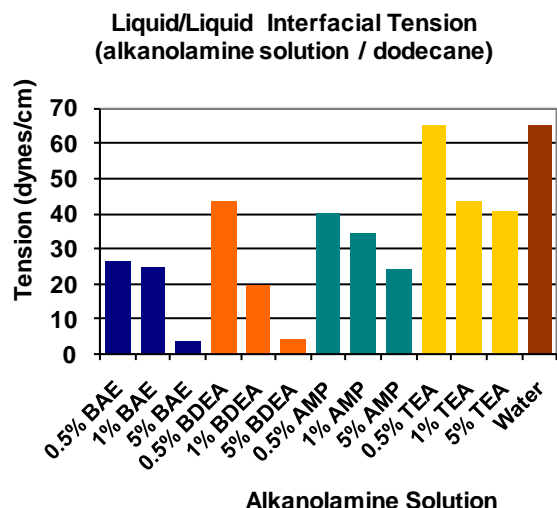


Figure 3: The liquid/liquid interfacial tension @ 20 °C of some aqueous alkanolamine solutions at 0.5%, 1% and 5% concentrations versus dodecane. BAE = butylaminoethanol, BDEA = butyldiethanolamine, AMP = 2-amino-2-methyl-1-propanol, TEA = triethanolamine.

It can be seen that alkanolamines like BAE and BDEA show a marked decrease in liquid/liquid interfacial tension at higher concentrations. The alkanolamine MEA shows very little variation in liquid/liquid interfacial tension with concentration. The greater the decrease in interfacial tension between an oil phase and an aqueous solution phase with increasing solute concentration, the more pronounced the “supplementary” surfactant type properties of the solute. N-alkylalkanolamines (AAA’s) like BAE tend to have substantially greater surface-active effects than do simpler and more purely hydrophilic AAA’s like AMP, MAE, DGA, MEA and TEA. This same trend has been seen in all the data collected; BAE, BDEA and similar types of “mid-fatty” (mid-fatty is defined as an alkyl chain length greater than 2 but less than 6) alkanolamines allow for the greatest decrease in liquid/liquid interfacial tension between aqueous solutions and nonpolar liquids (*i.e.*, oils). Reduced liquid/liquid interfacial tension is oftentimes the key to stabilizing emulsions.

3) Low $\gamma_{\text{Oil/Solution}}$ and Emulsion Stability:

One of the most significant consequences of the liquid/liquid interfacial tension between oil and water is its influence on the stability of O/W emulsions. The energy of a biphasic oil/water system can be calculated as shown below (E = energy, G = free energy, γ = interfacial tension, A = interfacial area):

$$E = G_{\text{water}} + G_{\text{oil}} + \gamma_{\text{water/glass}}A_{\text{water/glass}} + \gamma_{\text{water/air}}A_{\text{water/air}} + \gamma_{\text{water/oil}}A_{\text{water/oil}}$$

Upon examination of the five terms in this expression, it is apparent that only the last term and the entropy of mixing (contained in G_{water} & G_{oil}) change significantly upon formation of an emulsion. The energy of emulsion formation (*i.e.*, change in energy between the emulsion and the two coalesced phases with minimal interfacial surface contact) can thus be calculated as shown below (T = temperature, S = entropy, A = interfacial area, γ = interfacial tension)

$$\Delta E = (\gamma_{\text{water/oil}})\Delta A_{\text{water/oil}} - T\Delta S_{\text{mixing}}$$

The $\Delta A_{\text{water/oil}}$ term represents the change in interfacial area between the oil and water phases upon mixing. This change in area is an unavoidable consequence of emulsion formation. An idea of the magnitude of this interfacial area change can be obtained with a quick calculation. The surface area of a sphere is $4\pi r^2$ and the volume of a sphere is $(4/3)\pi r^3$. If we imagine a drop of oil with radius 1 cm (μ = micron, radius = $1 \times 10^4 \mu$, surface area of drop = $1.26 \times 10^9 \mu^2$, volume of drop = $4.19 \times 10^{12} \mu^3$) being mixed into an aqueous phase until it is dispersed into drops of radius 1 micron (surface area of drop = $1.26 \times 10^1 \mu^2$, volume of drop = $4.19 \mu^3$), then 1×10^{12} drops ($4.19 \times 10^{12} \mu^3 \div 4.19 \mu^3$; conservation of total volume) form with a total surface area of $1.26 \times 10^{13} \mu^2$ (1×10^{12} drops \times $1.26 \times 10^1 \mu^2$ per drop). Thus, the increase in interfacial area is 10,000 fold. If the drops were 1 nm in radius, then the increase in interfacial area would be ten million fold. It is interesting to note that if a 1 cm radius oil drop is emulsified as 1 micron radius drops in 10 ml of water wherein an interfacial tension between the oil and water of 30 dynes/cm exists, then the total enthalpy of interfacial area change will be 0.09 calories (*i.e.*, not much heat).

The entropy of emulsification is usually positive (*i.e.*, the emulsion is more “disordered” than are the coalesced phases), and the $T\Delta S_{\text{mixing}}$ term will typically contribute to emulsion stability. The enthalpy change ($\gamma_{\text{water/oil}}\Delta A_{\text{water/oil}}$) caused by the increase in interfacial area of the two immiscible phases will, on the other hand, always lead to emulsion instability. Only if the liquid/liquid interfacial tension is very low will it be possible for the emulsion to become thermodynamically stable. Most emulsions are thermodynamically unstable but kinetically stable owing to a small energy barrier required for coalescence. The kinetic stability of an emulsion can be increased by manipulating the surface charge on the dispersed phase drops (liquid zeta potential) and/or through steric mechanisms. Most work on emulsion stability focuses on kinetic stabilization, but one should not forget that lowering the interfacial tension between the immiscible liquid phases is also an effective way to increase emulsion stability. A low liquid/liquid interfacial tension decreases the underlying inherent

thermodynamic instability of the system and thus decreases the driving force for phase coalescence.

The magnitude of the liquid/liquid interfacial tension between an immiscible organic liquid and aqueous liquid will be inversely proportional to the “stability” of an emulsion of the organic liquid (dispersed phase) in the aqueous liquid (continuous phase). An example of a correlation of emulsion stability with measured interfacial tensions is given below in Figure 4. The correlation is not perfect, but the higher interfacial tension pairs tend to form less stable emulsions.

Organic	Aqueous Phase	Time (sec)	Interfacial Tension (dynes/cm)
Dodecane	Water	8	65.1
Dodecane	5% BAE	480	3.6
Dodecane	5% BDEA	900	4.4
Dodecane	5% AMP	20	24.4
Dodecane	5% MAE	60	22.5
Dodecane	5% DGA	20	34.2
Dodecane	5% MEA	60	37.2
Dodecane	5% TEA	120	40.5

Figure 4: Emulsion stability as assessed by the time it takes for an emulsion to “break”. Emulsions were based dodecane in aqueous alkanolamine solutions. Emulsions were created by shaking 18 ml of dodecane with 18 ml of aqueous alkanolamine for 30 seconds.

4) Alkanolamines HLB and Emulsion Stability:

A good way to rationalize the performance differences of N-alkylalkanolamines is through the concept of HLB (HLB \equiv hydrophile-lipophile balance). As an example of the clear relationship between HLB and physical properties for an N-alkylalkanolamine, the air/liquid interfacial tension of some aqueous alkanolamine solutions as a function of concentration arrayed according to their calculated HLB values are given in Figure 5 below.

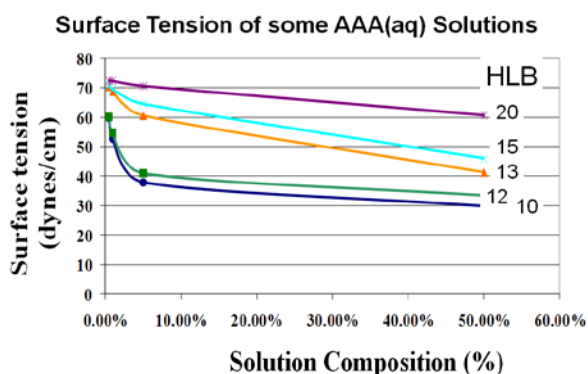


Figure 5: Measured surface tensions (details in Experimental Section) for some aqueous alkanolamine solutions arrayed according to their calculated HLB.

The following formula was used to calculate the HLB value for an alkanolamine.

$$\text{HLB} = \frac{20(\text{hydrophilic molecular weight})}{(\text{total molecular weight})}$$

In the case of simple ethoxylated amines (alkanolamine produced by the reaction of an alkyl amine with ethylene oxide), the hydrophilic molecular weight is 59 for a monoethoxylate (reaction of a monoalkylamine or dialkylamines with one equivalent of ethylene oxide) and 104 for a diethoxylate (reaction of a monoalkylamine two equivalents of ethylene oxide). The following list of calculated HLB values (rounded to the nearest whole number) is illustrative:

Hexane*:	HLB = 0
BAE:	HLB = 10
BDEA:	HLB = 12
AMP	HLB = 13
Methylaminoethanol:	HLB = 15
Monoethanolamine:	HLB = 20

* The HLB of hexane is not defined on this scale, but hexane can be regarded as 100% hydrophobic. Note that a limited range of alkanolamines (*e.g.*, GMW = 50 to 200) can be reasonably compared based on calculated HLB values.

The mid-range HLB alkanolamines (HLB = 8 – 12) tend to better enhance the stability of O/W emulsions. The value of mid-range HLB alkanolamines derives from their supplementary surfactant activity. Mid-range HLB AAA's tend to partition between oil and water phases whilst lower HLB AAA's tend to reside solely in the oil phase and higher HLB AAA's tend to reside solely in the aqueous phase. Of course, the AAA's must also function well as pH adjusting agents, and low HLB AAA's and amines tend to have high equivalent weights. The midrange HLB values are low enough to impart surfactant activity to the molecules while not being so low as to limit aqueous solubility and drive excessive partitioning into the oil phase.

5) Alkanolamines & Biostability:

A number of previous authors have published papers describing the beneficial effects of certain AAA's on the long-term stability of metalworking fluids [*e.g.*, 12, 13, 14]. Certain AAA's can significantly enhance the “biostability” (ability of a fluid to resist degradation by microorganisms) of aqueous formulations. This effect can be demonstrated by challenge testing of actual fluids [12], or by the use of simple microbiological techniques. For instance, one can use high-throughput microtiter assay techniques to compare the impact of different amines on the biostability of nutrient media. As an example, the results of an assay experiment

wherein TSB media was challenged with heavy doses of *Proteus mirabilis* (ATCC 7002) culture are given below in Figure 6. The bacterial titer, as indicated by dark blue lines inside the cells, was determined by light scattering at 660 nm. The concentration of 80% aqueous MEA triazine added is given on the left. The cells in columns 1 -12 contained no added amine (12 replicates of identical media), cells 13 -24 contained 4000 ppm of the amine indicated (each in sets with 4 replicates of identical media). The white blank rows were not operational. The pH of all the biological growth media was buffered at 8.5 by the use of TRIS. Synergex® is a tradename for N-butylethanolamine (BAE). The high efficacy of certain AAA's in the suppression of biological growth may be the result of both physical and metabolic factors. On the physical side, the enhanced emulsification that certain AAA's provide results in less microbiological viability (microbes tend to be emulsified and destroyed). On the metabolic side, certain AAA's may interfere with microbe phospholipid synthesis by being "accidentally" incorporated into otherwise natural lipid molecules. The diacylphosphatidyl choline type lipids require monoethanolamine, methylaminoethanol, dimethylaminoethanol and/or choline as a raw material. AAA's which are present in the vicinity of microorganism lipid synthesis "factories" may be "accidentally" be used in place of natural AAA raw materials.

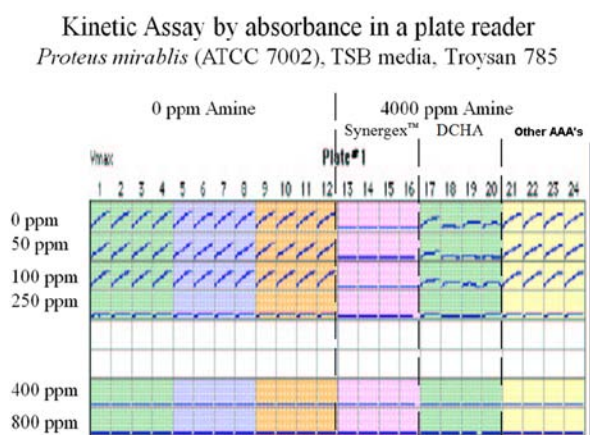


Figure 6: Microtiter assay experiment showing that TSB nutrient containing 4000 ppm of certain amines is much more biostable than comparable media with identical concentrations of more hydrophilic amines.

The impact of metalworking fluid additives on the emulsification of microorganisms can be assessed by basic microbiological techniques such as the RBC (red blood cell) lysis test.

6) Atypical Tertiary AAA Structures:

We define atypical tertiary AAA's as those wherein the two 2-hydroxyalkyl groups bound to the nitrogen are different. Our definition of the typical alkanolamine is

one produced via the reaction of a mono-substituted amine (usually a monoalkylamine) or a di-substituted amine (usually a dialkylamine) with ethylene oxide (EO) or propylene oxide (PO). When the alkoxylation reaction is carried out with a monoalkylamine base, the product will be a mixture of "monoethoxylated" secondary AAA and "diethoxylated" tertiary AAA ("monopropoxylated" secondary AAA and "dipropoxylated" AAA if PO is used in place of EO). When the alkoxylation reaction is carried out with a dialkylamine base, the product will be a "monoethoxylated" tertiary AAA ("monopropoxylated" AAA if PO is used in place of EO). Typically, pure EO or pure PO is used. Some polyoxyalkylene surfactants are prepared as random EO/PO copolymers via the use of EO/PO blends, but these materials, even when an amine is used as the starting hydrophobic base, are not considered AAA's owing to the presence of long polyoxyalkylene chains.

An atypical AAA can be prepared by the reaction of a pre-made and purified secondary AAA with an alkylene oxide (epoxyalkane) which is different from that used to make the secondary AAA. An example of an atypical AAA preparation is given in Figure 7 below.

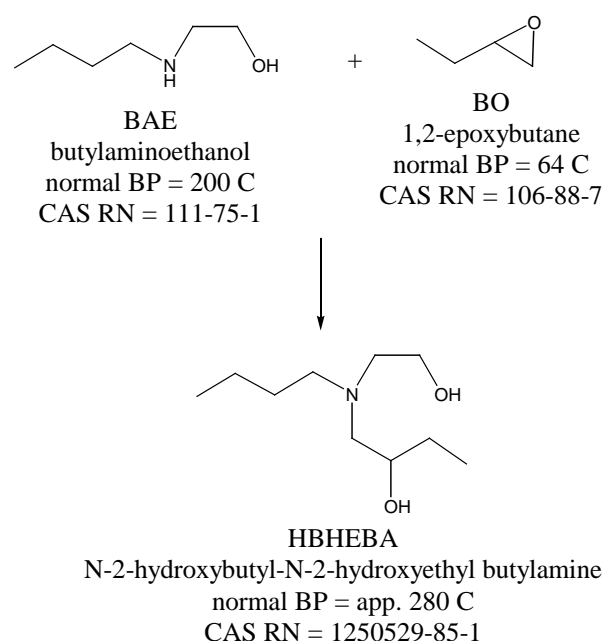


Figure 7: The preparation of an atypical AAA by the reaction of a secondary AAA (butylaminoethanol) with an alkylene oxide (BO; epoxybutane) other than the one used to make the secondary AAA.

7) Alkenyl Succinic Anhydrides + AAA:

Alkenyl succinic anhydrides (ASA's) are mostly produced by the reaction of maleic anhydride with olefins via the thermally driven Ene reaction (see Figure 9); though some other preparative variations are practiced. The olefins employed can be terminal α -

olefins or internal olefins. ASA's derived from polyisobutylene (PIB) are known as PIBSA's. ASA's produced from propylene tetramer (PT) are oftentimes referred to simply as dodecene succinic anhydride (DDSA), though the properties of DDSA produced from PT are different from those of DDSA produced from an α -olefin or an isomerized α -olefin.

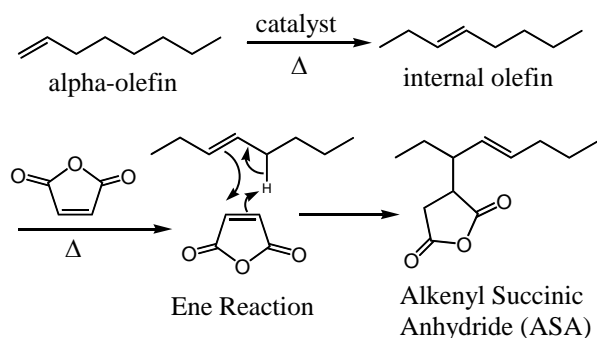


Figure 9: The formation of an alkenyl succinic anhydride.

The reaction of an alkenyl succinic anhydride with a AAA can lead to several different products (see Figure 10). The reaction of a primary amine with an ASA followed by exhaustive removal of water leads to an imide. ASA based imides are sometimes referred to as a neutral ASA derivatives. ASA based imides are commonly used as dispersants in fuels and permanent motor lubricants. The reaction of an ASA with a tertiary N,N-dialkylalkanolamine results in the formation of the hemi-ester internal salt type ASA derivative. Hemi-ester internal salt ASA derivatives are commonly used as emulsifiers in explosive formulations. The reaction of an ASA with a secondary AAA results in a mixture of amide and ester with some “crosslinked” (joining of two ASA molecules) product. The reaction of a tertiary N-alkyldiethanolamine with an ASA results in a blend of esters that may include “crosslinked” products.

Alternatively, ASA can be pre-hydrolyzed by reaction with water to yield a succinic acid derivative which can be subsequently neutralized with an amine to yield an ammonium compound (see Figure 11). Prehydrolyzed ASA ammonium compounds are commonly used as emulsifiers in emulsion metalworking fluids. The secondary AAA derivatives of ASA's are known to be useful as emulsifiers in metalworking fluids and as components of adhesive formulations, but the commercial preparation of these molecules requires a greater degree of process control. ASA imides, ASA derivatives of tertiary N,N-dialkylethanolamines and pre-hydrolyzed ASA ammonium salts can be produced as the sole product of the reaction of ASA and amine.

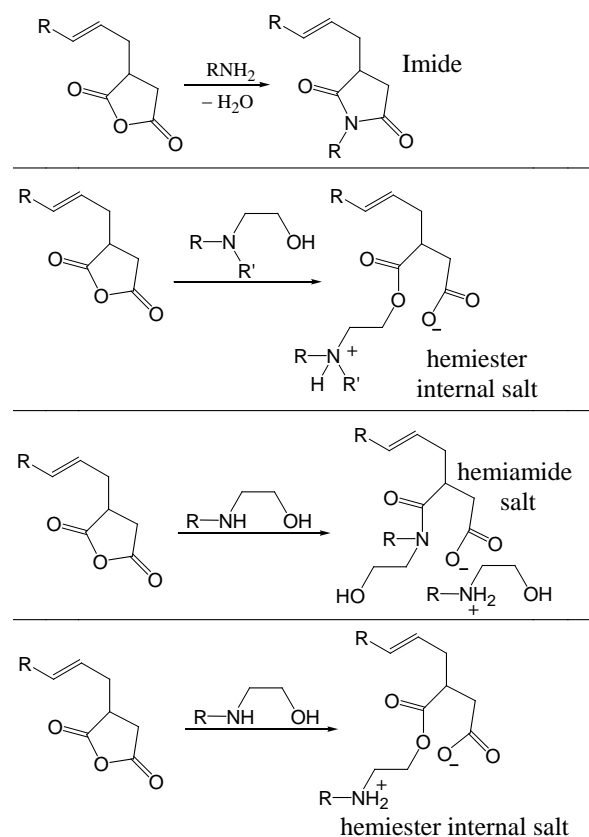


Figure 10: The reaction of a ASA (alkenyl succinic anhydride) with a AAA (N-alkylalkanolamine) can result in several different types of product.

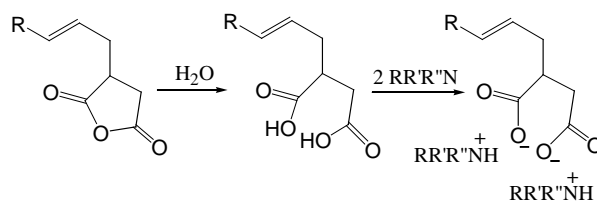


Figure 11: The pre-hydrolysis of an ASA followed by neutralization with an amine yields a useful emulsifier.

The reaction of a secondary AAA and/or tertiary N-alkyldiethanolamine with an ASA results in a mixed product composed of several different molecules. The order of addition can be used to push the reaction in a given direction. For instance, the addition of an ASA to an excess of secondary AAA produces a product that is mostly hemiamide ammonium carboxylate, but some hemi-ester internal ammonium carboxylate and “crosslinked” product will also be formed. We have found that the ASA/AAA products produced by the addition of ASA to N-butylaminoethanol (BAE) are useful as emulsifiers in emulsion metalworking fluids.

9) Alkanolamides from AAA's:

The reaction of a secondary AAA with a carboxylic acid or ester results in a useful alkanolamide compound (see example below in Figure 12).

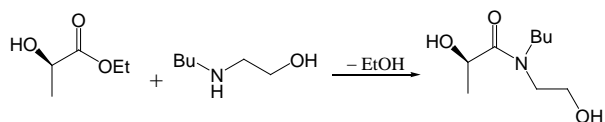


Figure 12: The reaction of ethyl lactate with butylaminoethanol to yield N-butyl N-(2-hydroxyethyl) lactamide (BAE lactamide).

Obviously, only monoalkylamine monoethoxylates or monoalkylamine monopropoxylates can take part in this reaction. The reaction is typically driven forward by the removal of byproduct water or alcohol. Alkanolamides produced from AAA's like BAE show enhanced emulsion stabilizing benefits as compared to simple diethanolamides of similar HLB. The enhanced performance properties of secondary AAA alkanolamides compared to diethanolamides may result from the distribution of hydrophobic groupings throughout the AAA alkanolamide molecule, as opposed to the localization of hydrophobic properties on a single alkyl chain in the diethanolamides.

10) Off-Diagonal Effects:

Ultimately, the commercial value of novel molecules is demonstrated through enhanced price/performance and/or through the provision of enabling benefits. In the metalworking industry, enabling benefits include indefinite emulsion stability, long-term biostability and very low volatility (zero-VOC). The off-diagonal benefit grid is a useful paradigm for visualization of the enhanced benefits available from more structurally sophisticated alkanolamines (see Figure 13).

	Heat transfer	Solvency,	Lubricity	Emulsion Stability	Surface Tension	Coupler	pH	Corrosion Rate	Biostability
Solvent	√	+/-	+/-	+/-	+/-	+/-	+/-	+/-	+/-
Lubricant	+/-	√	+/-	+/-	+/-	+/-	+/-	+/-	+/-
Emulsifier	+/-	+/-	√	+/-	+/-	+/-	+/-	+/-	+/-
Surfactant	+/-	+/-	+/-	√	+/-	+/-	+/-	+/-	+/-
Coupler	+/-	+/-	+/-	+/-	√	+/-	+/-	+/-	+/-
Alkanolamine	+/-	+/-	+	+	+/-	√	+/-	+	+
Corrosion Inhibitor	+/-	+/-	+/-	+/-	+/-	+/-	√	+/-	+/-
Biocide	+/-	+/-	+/-	+/-	+/-	+/-	+/-	√	√

Figure 13: Off-Diagonal grid for metalworking fluids.

In the off-diagonal grid, the main benefit for which a component is added to a formulation appears along the diagonal. The off-diagonal benefits are those which are gained in addition to the main benefit. Note that there can also be off-diagonal disadvantages

(detriments). For instance, the use of an aqueous solvent or an aqueous emulsion continuous phase in an O/W emulsion markedly improves a metalworking fluid's heat transfer capabilities as compared to straight oil, but the use of water can significantly increase the bio-susceptibility of the fluid. In other words, fluid biostability is a significant off-diagonal detriment of using water. With respect to the use of more structurally elaborate alkanolamines, such as BAE (butylaminoethanol), OAE (octylaminoethanolamine) and ODEA (octyldiethanolamine), in place of simpler alkanolamines like monoethanolamine, the significant benefits include emulsion stability, corrosion inhibition and biostability.

11) Conclusions:

The use of N-alkylalkanolamines (AAA's) of optimal calculated HLB (HLB = 8 – 12) allows for enabling improvements in the emulsion stability and biostability of metalworking fluids. The fluid improvements typically observed are especially important in emulsion systems, and these benefits can be rationalized by reference to various physical measurements including surface tension and liquid/liquid interfacial tension. Certain chemical derivatives of advantaged AAA's also show enhanced emulsion stabilizing and biostabilizing benefits in metalworking fluids, and the use of optimized AAA/ASA (alkylalkanolamine + alkenyl succinic anhydride) compounds and/or AAA alkanolamides along with advantaged free AAA's provides for additional synergy. It has been found that AAA's and AAA derivatives with hydrophobic regions distributed throughout the molecule provide for emulsion stabilizing benefits in excess of that predicted by their overall calculated HLB.

12) Experimental Section:

Surface Tension Measurements: The air/liquid surface tensions were measured by the maximum bubble pressure method on a Sita online t60 bubble tensiometer. The bubble life was one second. The sample size was less than 4 ml, and a slow bubble rate was used to keep the liquid level constant. Ten bubbles were averaged per reading with five readings were taken per sample for a total of 50 readings per sample. All surface tension measurements were taken at 20 °C.

Liquid/liquid Interfacial Tension Measurements: The liquid/liquid interfacial tension measurements were calculated via measurement of capillary contact angles. The contact angle photos were taken using a 5 megapixel Kodak digital camera. The camera was positioned on a tripod 4 inches away from capillary tube containing the sample. The camera was set in macro mode with flash and spot focus. No zoom was used. The capillary tubes were the Drummond Microdispenser (100-200µl) type. The capillary tubes

were dipped into the aqueous phase and withdrawn from the liquid with the top of capillary sealed by a stopper. The bottom of capillary was then capped with a rubber septum and the top opened to the atmosphere. For triphasic contact angles, the oil phase was layered on top of the aqueous phase using an eighteen gauge stainless steel flat tip syringe needle. All contact angle determinations were taken at 20 °C. The rest of the measurement technique is described in reference 11.

Solution Density Measurement: Solution densities were obtained using an Anton Parr Density Meter (model number DMA 4500). The density meter sample loop was rinsed with IPA and DI Water and air dried between samples. All density measurements were taken at 20 °C.

Emulsion Stability Measurements: The emulsion stability measurements were started by adding 18 grams of the aqueous phase to a 9 dram glass vial. The liquid level was then marked to give a point of reference. Next, 20ml of the oil phase was layered on top of the aqueous phase, and the vial was shaken vigorously for 30 seconds. The dispersions were set on a bench, and the time it took for the two mixed phases to separate was measured with a stopwatch. The time necessary for the phase separation to reach within ½ inch of the original reference line was taken as the separation time.

Preparation of AAA's:

A 1 mole quantity of 1,2-epoxyalkane (99% purity by GC/TCD, water < 0.2%) was added slowly over 30 minutes to 1 mole of N-alkylethanolamine (99% purity by GC/TCD, water < 0.2%) at RT. The solution temperature was monitored, but in no case was an exotherm observed. Note that the reaction of epoxides and amines can display an induction period followed by an exotherm. Water is known to catalyze this reaction, and increased levels of water may markedly increase the reaction rate. The solution was stirred at RT for several days with the course of the reaction monitored by GC/TCD. In some cases, cooling was occasionally applied for the first 8 hours in order to keep the reaction solution close to RT (mild heating to about 35 °C was occasionally observed). The reaction could be run in a cool room (T < 15 °C) in order to reduce the amount of monitoring necessary. Alternatively, the reaction can be run in a sealed pressure vessel at elevated temperature and pressure (e.g., @ T = 80 °C, the reaction is complete within several hours) or in an open apparatus with accommodation for reflux of the AAA and/or epoxide. The RT reaction was left unmonitored after the first day. When the RT reaction reached 95% plus conversion, the product was transferred and directly vacuum distilled to yield the product as a clear liquid. When the reaction was run in a pressure reactor, a slight excess of epoxide was employed and the reaction

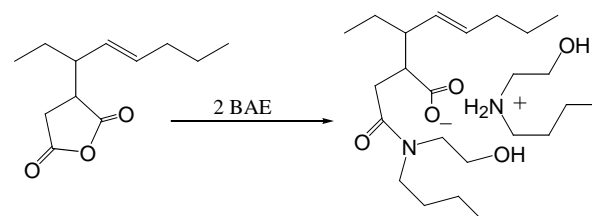
was run to near completion. The small amount of epoxide and/or AAA remaining at the end was removed by distillation *in-vacuo* and the product was taken as is or distilled.

N-(2-hydroxybutyl)-N-(2-hydroxyethyl)-N-butylamine (CAS RN = 1250529-85-1): The crude reaction product was double vacuum distilled (110 °C @ 2 Torr) to yield material that was 99.8% pure by GC/TCD (88% yield). The distilled material was definitively identified by GC/MS, ¹H NMR & quantitative ¹³C NMR (10 carbon atoms, referenced to CDCl₃; 69.3, 60.8, 59.8, 56.5, 54.9, 29.1, 27.6, 20.5, 14.0, 9.9).

N-(2-hydroxyoctyl)-N-(2-hydroxyethyl)-N-butylamine: The crude reaction product was vacuum distilled (150 °C @ 2 Torr) to yield material that was 99.5% pure by GC/TCD (96% yield). The distilled material was definitively identified by GC/MS, ¹H NMR & quantitative ¹³C NMR (14 carbon atoms; referenced to CDCl₃; 67.9, 61.1, 59.7, 56.4, 54.8, 34.8, 31.7, 29.4, 29.0, 25.6, 22.5, 20.4, 14.0, 13.9)

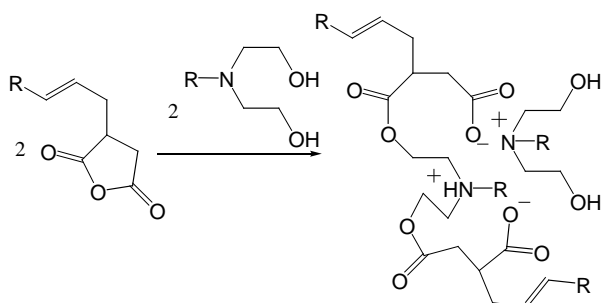
N-(2-hydroxybutyl)-N-(2-hydroxyethyl)-ethylamine (CAS RN = 16681-36-0): After the reaction reached ≈ 95% conversion (several days), the crude reaction product was analyzed as is. The crude reaction solution was determined by GC/TCD to be 95% of the target compound (HBHEEA) with 0.6% butylene oxide and 1.6% ethylaminoethanol remaining. The butylene oxide was stripped *in-vacuo*, and the HBHEEA was definitively identified by MS (GC/MS; CI; parent M+1 peak = 162, 130, base peak = 102, 72, 58, 42, 30).

Preparation of ASA/AAA Compounds: Typically, 0.5 mole of the alkenyl succinic anhydride (ASA, weight determined based on neutralization equivalent provided on TDS) was added to 1 mole of a neat liquid secondary AAA in a 1 liter beaker. The addition rate was adjusted to keep the temperature of the exothermic reaction below 60 °C. After the addition was complete, the thick liquid product was poured hot into a storage bottle. This order of addition was used to obtain the highest possible yield of the hemiamide ammonium carboxylate type product (see below).



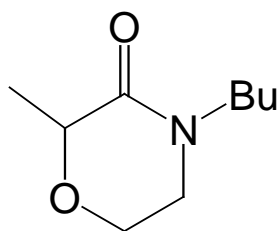
The order of addition and the temperature setpoint of the reaction were changed to achieve different product compositions. For instance, when the maximum amount of “crosslinked” ASA/AAA (see below) was sought in the reaction of a tertiary AAA

diethanolamine with an ASA, then a 1 mole quantity of neat liquid AAA was very slowly added to a 1 molar quantity of the ASA in a 1 liter beaker. Note that this type of product oftentimes solidified in the reaction beaker to become an intractable amber solid.



Preparation of AAA Alkanolamide Compounds:

These compounds could be prepared several ways. Typically, a one mole quantity of neat carboxylic acid or neat ester was reacted with a 1 mole quantity of neat secondary AAA (e.g., BAE). The reaction mixture was heated to about 80 °C and placed under sufficient vacuum to quickly remove the water (or the ester alcohol) as it is produced. The T/P conditions could be adjusted so that the lowest boiling reactant refluxed gently. In a typical procedure, a nearly equimolar quantity of neat BAE and neat ethyl lactate (slight excess) was heated at 80 °C at an absolute pressure of 50 mbar for 18 hours. The apparatus was set up to return gently refluxing ethyl lactate back to the reaction. The volatile material removed was found to be mostly ethanol along with a little ethyl lactate and water. The material remaining after 18 hours of heating was taken and used as is. The product was a thick brown liquid that was found by GC/FID and GC/MS analysis to be 90% N-butyl N-(2-hydroxyethyl) lactamide (BAE lactamide) along with 5% BAE and smaller amounts of other impurities including 2% of a six membered heterocyclic molecule resulting from etherification of the two different hydroxyl groups in BAE lactamide (see below).



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