Patrick Brutto

By Karl M. Phipps / Managing Editor

This senior technical service and development specialist for Dow Consumer & Industrial Solutions discusses the regulatory requirements of using amines in metalworking fluids.

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The Quick File:

Patrick Brutto, CMFS, is a senior technical service and development specialist for Dow Consumer & Industrial Solutions in Buffalo Grove, Ill. His primary responsibilities include leadership in the application of specialty additives for metalworking fluids, paints and coatings and other industrial applications.

Pat joined ANGUS Chemical Co. in 1987 as an application research chemist and served in that role for 11 years. He was promoted to his current role in 1998 prior to Dow Chemical's acquisition of ANGUS in 1999. Before joining Dow, Pat was technical director of the Magie Bros. division of Pennzoil Products Co., with responsibilities for lubricating grease development for the steel and automotive industries, as well as technical service and development support for Magie's specialty distillates in the printing ink and aluminum cold-rolling industries.

Pat holds a bachelor's degree in chemistry from the University of Illinois at Chicago and a master's degree in chemistry from DePaul University in Chicago. He is an active STLE member, serving most recently as chairman of the Chicago Section, and holds STLE's Certified Metalworking Fluids Specialist designation.

TLT: How did you get started working in the industry?

Brutto: My first job in the lubricants industry was in 1980 working with the Penreco division of Pennzoil Products Co. I formulated industrial and automotive greases and managed the environmental and safety compliance activities for our production facility. It was a challenging, multifaceted job that was also very rewarding.

I also attended my first STLE Chicago Section meeting that same year, as well as my first STLE annual meeting in 1985. In 1987, I decided to look for an opportunity in an R&D-focused role and was fortunate to land a job at ANGUS Chemical Co., which was acquired by The Dow Chemical Co. in 1999. In my years at ANGUS and Dow, I've learned about metalworking fluids and the problems our specialty additives can help solve. I knew very little about MWFs and really expanded my knowledge and skill set by working at the lab bench, meeting with customers and attending courses at STLE and SME meetings.

TLT: What do you enjoy most about your job?

Brutto: I enjoy working closely with customers and helping them understand how our chemistry can solve problems. It's also gratifying to see a new product advance from inception to commercialization and then have it succeed in the field. And, of course, I enjoy the impact my work plays in helping our business grow.

In addition, serving on various STLE committees with dedicated colleagues and serving as an officer with the Chicago Section has been a rewarding experience. I also enjoy giving presentations to customers, industry technical forums and education course participants because they are all great opportunities to stay in tune with issues affecting the MWFs industry.

Who is it? Despite earning huge sums of money in his lifetime, this Serbian-borne genius inventor

TLT: What role do amines play in helping MWF formulators meet their requirements, as well as those of their end-user customers?

Brutto: Amines, or more commonly amino alcohols, provide neutralization, alkaline pH adjustment and reserve alkalinity, a requirement for all water-dilutable MWFs. However, these components are often selected as much for their secondary benefits as the primary ones. Secondary benefits, usually achieved in combination with acid-functional components, include corrosion inhibition, emulsification and lubrication. Perhaps an even bigger consideration is the impact amines can have on microbial resistance, either positive or negative. Ethanolamines like monoethanolamine (MEA) and triethanolamine (TEA) are readily degraded by microorganisms, while branched amines like monoisopropanolamine (MIPA) and 2-amino-2-methyl-1-propanol (AMP) resist microbial degradation. Finally, there are products which improve fluid longevity (at recommended dosages) through enhancement of registered biocides while being readily biodegraded in the environment. An example is 3-amino-4-octanol (3A4O).

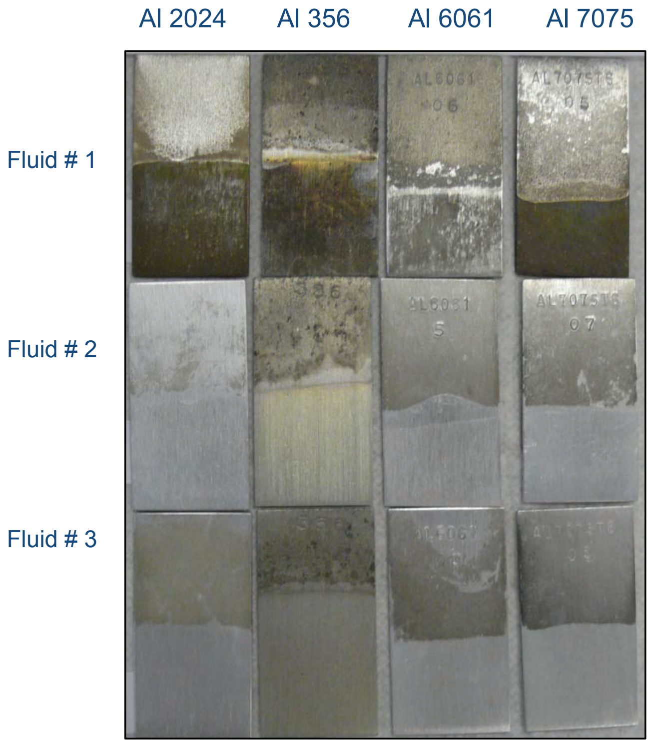
Sometimes products are selected for what they don't do. This can include (1.) not generating ammonia, (2.) not leaching cobalt, copper or lead, (3.) not contributing to foam generation and (4.) not staining aluminum, copper, galvanized steel and even magnesium alloys. It goes without saying that the environmental, health and safety profile of an amine is a more important selection factor than ever. Registration of the amine across multiple geographies is also critical, especially for multinational fluid formulators and end-users.

TLT: Aren't all amines basically the same functionally?

Brutto: Yes, the basic functionality of all amine and amino alcohol products is similar. They all contain nitrogen, which acts as a Brønsted base to deprotonate acid functional ingre-

Neutralizer	Molecular Wt.	pKa	Performance Characteristics
Monoethanolamine (MEA)	61	9.5	Most efficient amine, microbially degradable (forms ammonia), leaches cobalt, more aggressive on Al alloys
Monoisopropanolamine (MIPA)	75	9.6	Better microbial resistance (doesn't release ammonia), leaches cobalt
2-amino-2-methyl-1-propanol (AMP)	89	9.7	Good microbial resistance (doesn't release ammonia), leaches less cobalt and lead
Diglycolamine (DGA)	105	10.0	Leaches less cobalt and copper, microbially degraded (fungi)
Butylethanolamine (BEA)	117	10.0	Enhances biocide performance, secondary amine
Diisopropanolamine (DIPA)	133	9.0	Some microbial resistance, secondary amine
3-amino-4-octanol (3A4O)	145	9.8	Significantly enhances biocide performance, maintains ferrous corrosion control, leaches some cobalt
Triethanolamine (TEA)	149	7.8	Best pH buffer, inhibits ferrous corrosion, microbially degradable (forms ammonia), leaches cobalt
Dicyclohexylamine (DCHA)	181	10.4	Significantly enhances biocide performance, maintains ferrous corrosion control, secondary amine, extracted into tramp oil

Figure 1 | **Amine Properties**



Ingredient	Fluid	Fluid	Fluid
Dicarboxylic Acid	3%	3%	2.5%
Inversely Soluble Ester	8	8	8
Phosphate Ester	1	1	1
3-amino-4-octanol	**--**	**4**	**4**
Triethanolamine	**15**	**4**	**4**
Monoethanolamine	**5**	**5**	**5**
Triazine Biocide	2	2	2
Deionized Water	66	73	73.5
pH at 5% Dilution	9.1	9.3	9.3

Figure 2 | **Half-immersed aluminum alloy coupons exposed to synthetic MWF dilutions *(see chart for concentrate formulations)*. Fluids #2 & 3 are less aggressive due to reduced alkalinity, even though dilution pH is slightly higher than Fluid #1.**

dients (and degradation products), forming the corresponding amine-acid salts. In many cases, neutralization is needed to dissolve or emulsify the corresponding acid in water; an example is oleic acid. Once all acid groups are deprotonated, the amine group deprotonates water (usually the weakest acid present), forming hydroxide anions which increase the fluid pH. Each amine differs in its ability to deprotonate water based on its acid constant (Ka). The negative log of Ka or pKa is a measure of base strength; the higher the pKa the stronger the base. Stronger bases like 2-amino-2-methyl-1-propanol (pKa 9.8) are much more efficient in developing alkaline pH than weaker bases like triethanolamine (pKa 7.8). However, greater amounts of weaker bases can be added without developing excessive pH. This is why triethanolamine has been widely used in MWFs for building reserve alkalinity.

Combinations of amines are almost always used to balance cost and performance. Smaller, stronger amines like MEA have traditionally been used in combination with TEA, providing a cost-effective balance of pH development and reserve alkalinity. This is still a popular combination in economy fluids. Three disadvantages of this system are (1.) lack of resistance to microorganisms, (2.) generation of ammonia as a biodegradation product and (3.) leaching of cobalt during manufacturing of carbide tools. These disadvantages can be reduced by completely or partially replacing these materials with others. For improving bioresistance in combination with registered biocides, products like AMP, 3A4O and butylethanolamine (BEA) are useful. To reduce the inherent cobalt leaching of a formulation, we recommend AMP and diglycolamine (DGA) as two of the lowest leaching amines. To enhance the corrosion control of iron and mild carbon steel, 3A4O is quite useful.

Another important factor in amine selection is the polarity of the resulting salt reaction products formed *in situ*. For example, salts of smaller amines like MEA, MIPA and AMP with fatty acids like oleic are relatively polar and effective as oil-in-water emulsifiers. Similar salts of larger amines like 3A4O are less polar, and therefore less effective in forming oil-in-water emulsions. Therefore, combinations of the smaller and larger amines will usually be required.

TLT: How are regulatory factors affecting the availability and selection of amines and biocides?

Brutto: Regulatory and registration requirements in various countries may limit the selection of registered biocides for MWFs in the future. For example, the French Legislation on Workers Safety (Code du travail, sub-section 6, Article R231-56) specifies risk reduction measures for all activities exposing workers to formaldehyde (including formaldehyde releasers). Employers have the obligation to evaluate the risk to workers and to provide information and monitoring, among other requirements. Furthermore, employers are required to replace formaldehyde or formaldehyde-releasing agents whenever it is technically possible. This means usage of some of the most effective registered biocides will become more difficult for

At age 17 Nikola Tesla could perform integral calculus in his head, leading his teachers to accuse him of

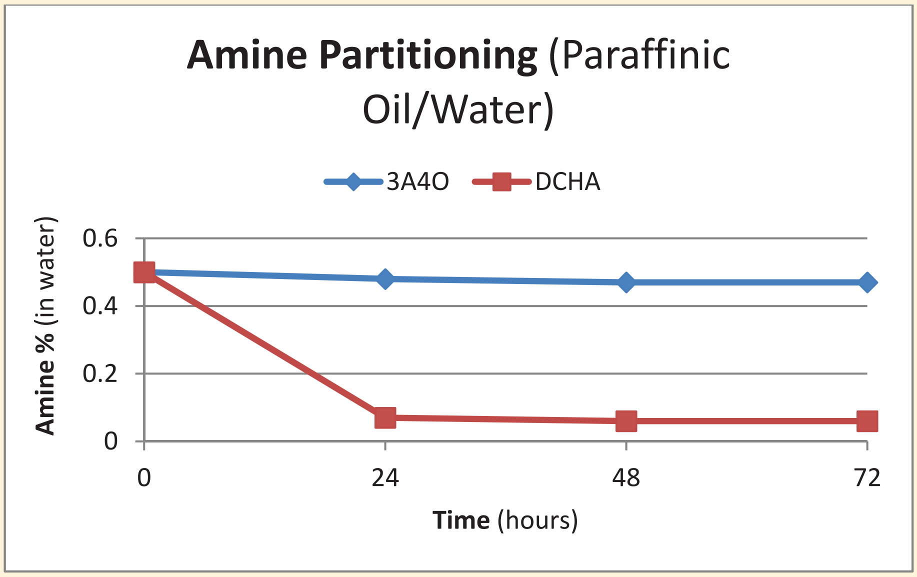


Figure 3 | **Partitioning of amines from water (95 percent) into paraffinic oil (5 percent).**

companies producing or selling MWF products in France. A dedicated Website for sharing experiences of successful substitution of carcinogenic, mutagenic or reprotoxic agents has now been made available at **www.substitution-cmr.fr.**

Although most amines and amino alcohols are not restricted by regulation, the Technical Rules for Dangerous Substances (TRGS 611) in Germany limits the content of secondary amines in water-miscible cooling lubricants, which results from impurities or byproducts, to a maximum 0.2 mass percent (based on the fluid concentrate). This regulation also states that secondary amine components cannot be intentionally added to these fluids. Certain secondary amines may be exempted, however diethanolamine (DEA) is not. DEA is considered to be "possibly carcinogenic to humans (Group 2B)," according to the International Agency for Research on Cancer (IARC) monograph volume 101. DEA was also added to the Proposition 65 list in California in June 2012 as "Known to the State of California to cause cancer."

In addition to the above, certain end-users of MWFs may not allow fluids used in their facilities to contain some registered biocides or secondary amines. All of these factors are limiting the selection of acceptable biocides and amines for MWF formulators, while also trying to meet the demands for more stringent fluid life and microbial control requirements.

TLT: What new formulating approaches do you suggest for accommodating multimetal machining?

Brutto: Production of parts from aluminum alloys is increasingly important due to their favorable strength-to-weight ratio and corrosion resistance. However, some of these alloys are susceptible to staining from contact with alkaline MWFs. Balancing these considerations is forcing formulators to reduce fluid pH and/or add staining inhibitors; these inhibitors can cause unwanted side effects. For example, phosphorus-based products can stimulate microbiological growth and reduce fluid life. Silicate-based inhibitors can block ultrafiltration membranes during wastewater treatment. Reduction of fluid pH can result in shorter fluid life, due to a more favorable environment for microbiological growth.

We suggest modifying formulations, where possible, to make the base fluids less aggressive on aluminum alloys. This involves reducing total fluid alkalinity while maintaining sufficient pH to help keep the microbes in check. As mentioned previously, TEA is a good buffer for MWFs. However, high levels of TEA can cause staining of aluminum, and TEA rapidly biodegrades, resulting in microbial problems. So even though TEA effectively buffers pH, it can actually contribute to pH drop due to the formation of acidic biodegradation products.

An alternative approach is to partially or completely replace TEA with biocide enhancing amines such as 3A4O and AMP. In this case, other formula modifications may be needed to achieve the required corrosion control of iron and steel for multimetal fluids. Improved bioresistance of the modified formulations enables better pH stability without high levels of reserve alkalinity. Assuming phosphorus-based staining inhibitors are used, it is often possible to reduce their dosage and further improve bioresistance. This may not be acceptable, however, if the phosphorus compound is needed for extreme pressure and antiwear lubrication.

TLT: Are there other factors that should be considered when selecting an amine?

Brutto: Another important factor is the solubility of the amine in lubricants leaking into the MWF systems (hydraulic oils, slideway lubricants, etc.). More specifically, the partitioning behavior of the amine and its salt reaction products between the MWF and tramp oil is key. Lipophilic amines and their salts partition more readily into tramp oil and can be rapidly depleted from the MWF. This is particularly true with amines having high oil solubility and low water solubility, an example being dicyclohexylamine (DCHA). Selective depletion of such components can necessitate tankside replenishment, which is undesirable from both cost and maintenance standpoints. This can also be an issue with highly oil-soluble biocides. TLT

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