Metalworking fluids are used in machining operations to improve the efficiency of heat removal, provide lubrication to aid in chip removal and to improve surface finish. Further metalworking fluids are often expected to provide corrosion protection to parts after they are made. Water-based fluids — soluble oils, semi-synthetic fluids and synthetic fluids — are materials that depend on the water in the formulation for heat removal. The introduction of water into a metalworking formulation leads to corrosion, staining, foaming, and enhanced bacterial activity. The formulation components are expected to counteract the negative effects of adding water. Huntsman Corporation offers a wide range of formulation components to the metalworking industry. The SURFONIC® surfactants provide emulsification and lubricity as well as hard water tolerance to a formulation. The JEFFOX® line of functional fluids and block polymers provide lubricity. Huntsman manufactures several different amines to the metalworking market — the JEF-FA MINE® amine polyetheramines, DIGLYCOLAMINE® Agent (DGA®), BHEMA (Bishydroxyethyl methylamine) and traditional ethanolamine. Amines such as these are used to provide reserve alkalinity, and corrosion protection. In conjunction with fatty acids the amines have emulsification and lubricity attributes.

In recent years several metalworking fluid components have been replaced with more worker or ecofriendly actives. Several years ago certain secondary amines implicated, in conjunction with sodium nitrite were found to form nitrosamines. The replacement of nitrites and secondary amines drastically lowered the nitrosamine levels observed in the workplace. For instance, currently in some situations it is perceived that monoethanolamine (MEA) may have a higher vapor pressure, and thus more odor than desired. In Europe some formulators are trying to remove triethanolamine (TEA) from formulations. Formulators are also evaluating new materials to gain technical advancements in areas such as cobalt or copper leaching, aluminum staining, simplification of formulations, enhanced hard water tolerance, etc.

BHEMA is an amine that has drawn some interest from the metalworking community. This product has a desirable profile from both a worker exposure and a performance standpoint. BHEMA is produced by the ethoxylated formulation of methylene and subsequent purification. The CAS # of BHEMA is 105-59-5, and the amine itself has TSCA, DSL and EINCS registration. Huntsman Performance Products is in the process of registering several salts of BHEMA. The structure of BHEMA is shown in Figure 1. Some of the important physical properties of BHEMA are compared in Figure 2 with other commercially significant amines. BHEMA Health And Safety

Paramount when evaluating a new candidate for a metalworking formulation is to understand the environmental and health effects of the material. In Figure 3, several criteria used to evaluate the environmental impact of BHEMA are presented. The octanol/water partition coefficient is very low, indicating that BHEMA is not likely to accumulate in the fatty tissues of aquatic organisms, and thus not enter the food chain. A 28-day biodegrada-
tion test indicated that BHEMA is biodegradable. In some studies BHEMA biodegradation is initially delayed, but presumably due to acclimation, proceeds rapidly after a few days. The toxicity of BHEMA to fish and aquatic invertebrates is quite low – practically nontoxic. But to algae, BHEMA had a LC 50 of about 35 parts per million and qualifies under EPA guidelines as slightly toxic. Given that BHEMA presents low impact to the environment, a review of the effects of BHEMA on mammals was undertaken. BHEMA was shown to not be genotoxic. In rabbits the LD 50 was 2000 mg/kg – a practically nontoxic value. In acute skin contact tests BHEMA was found to be nonirritating, meaning that incidental contact with BHEMA does not represent an issue. BHEMA is, however, irritating in an ocular context, and eye contact is to be avoided. The irritation to the eyes is likely due to the alkalinity of BHEMA, which is characteristic of most amines. In long-term skin contact studies BHEMA was shown to cause some skin effects, the no observable effect dose is 250 mg/kg/d for 90 days. The skin effects – lesions – were reversible. BHEMA is an amino alcohol which means that considerable hydrogen bonding can occur in water. This compatibility with water results in very low volatility of BHEMA in water solutions. In Figure 4 VLE determinations of 10% amine solutions is shown as a function of temperature. It is apparent from this data that as the number of ether linkages and terminal hydroxyls increases the volatility in water of an amine is reduced. This indicates that BHEMA is not likely to contribute to the vapor load in a metalworking workplace.

**BHEMA Performance Attributes**

While a desirable Health and Safety profile is a benefit, several important performance measurements indicate that BHEMA is highly functional in metalworking formulations. In Figure 5, the titration curves for several amines used to neutralize INVISTA CORFREE® M1 are displayed. The primary amines MEA, DGA® Agent, and aminomethyl propanol alternative (AMP) are clustered together showing a higher pH vs. amount of amine added to 50g of a 5% CORFREE M1® solution. The tertiary amine triethanolamine is a much weaker amine and even after 120 ml of the 5% amine solution is added the pH only approaches 8.0. Typically for ferrous alloys a pH of 9-9.5 is desired to prevent corrosion. Formulators utilize the high pH offered by the primary amine, like MEA, and the low pH response of triethanolamine to fine tune the pH and reserve alkalinity of a formulation. Interestingly BHEMA, which is also a tertiary amine, shows a much higher pH than the equivalent triethanolamine-based mixture. This is likely due to the electronic effects associated with the methyl group on BHEMA. The pH response of BHEMA approximates the response of a 25:75 mixture of MEA: TEA blend. This suggests that BHEMA could be used to produce a formulation with desirable pH and reserve alkalinity with only one amine. Several metalworkers have formulated commercial products successfully, and avoided the need of a primary amine like MEA or AMP. This technique does limit the flexibility often needed by formulators to vary pH and reserve alkalinity independently, but with the addition of DGA®.
Agent this flexibility can be restored.

The intentionally made salts formed by BHEMA and important fatty acids may need TSCA approval to be used in some metalworking formulations. Huntsman is pursuing the TSCA and other registrations for several salts of BHEMA. The CAS numbers of the first group of products is listed in Figure 6.

The interaction of amines and several metals has been investigated. The interaction of BHEMA and cobalt is presented in Figure 7. The leaching tendency of BHEMA is much lower than triethanolamine or monoethanolamine and many other amines, especially at pH 9.5. This suggests that BHEMA will not adversely affect the life of carbide tooling or contribute to the metals loading in the effluent of metalworking facilities. Similar data exists for copper/amine interactions. This data displayed in Figure 8 shows that BHEMA is likely to affect the machining of yellow metals or weaken tooling using brazed carbide inserts.

Of particular note is the performance of BHEMA in aluminum machining. Aluminum is particularly susceptible to corrosion, especially at higher pH. When aluminum alloys were exposed to solutions of different amines, BHEMA proved to have about one-tenth of the corrosion rate of triethanolamine as determined by dissolved aluminum using ICP (See Figure 9). For instance, the aluminum level observed on 7075 alloy was 155 ppm with TEA and 7 ppm with BHEMA. Triethanolamine is often used in aluminum machining formulations. Its corrosion tendency is tamed by the use of fatty acids. In a separate experiment the same amines were mixed with isonionic acid and exposed to the same aluminum alloys. The pH of each sample was adjusted to 8.8 with KOH (see Figure 10). In this experiment the dissolved aluminum observed was much lower. On 7075 alloy the observed soluble aluminum was 40 ppm for TEA. The level of dissolved aluminum for the BHEMA salt was much lower (16 ppm) as well. This data suggests that BHEMA is an excellent choice for aluminum machining formulations.

In order to evaluate the performance of BHEMA in a formulation and to demonstrate the single amine concept, we formulated a simple synthetic fluid that could form the basis of a grinding or cutting fluid. The fluid was formulated using commonly used metalworking fluid components available from Huntsman and other suppliers. This formulation was evaluated using the Cast Iron Chip Test. A break point was demonstrated at a 40:1 dilution, which in this case equates to 25-3% fatty acid content. Previous work in our laboratory indicates that good corrosion protection on ferrous metals generally requires about 25% fatty acid in this test. Falex pin and vee tests were run at a 10:1 and 50:1 dilution. The data shown in Figure 11 indicates that formulations based on BHEMA are comparable in terms of wear and lubricity to those of other commercially employed amines.

Conclusions

We have shown that BHEMA, a unique tertiary amine, has a very desirable ecological and worker impact profile. This product also has a very desirable profile of performance in terms of interaction with metals like aluminum and cobalt. Additionally it appears that BHEMA can provide the right blend of pH and reserve alkalinity to allow the formulation of “single amine” products.