TITLE: Optimizing Metalworking Performance with Primary and tertiary Amines

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Extended Abstract:

The reformulation of emulsion lubricants (e.g., metalworking fluids) can be time consuming. The use of formulation constraints in the reformulation process can make the process more efficient. There are always the constraints of economics, as are typically considered in real time by maintaining a spreadsheet with the calculated base cost of ingredients for a gallon of concentrate (see example for semi-synthetic fluid below):

Component	Price per kg as purchased	Concentration as purchased (% wt./wt.)	Amount needed per gallon concentrate (kg as purchased)	Base cost (gallon of concentrate)
100 SUS Naphthenic Oil	0.9	100	1	0.90
25R4 nonionic surfactant	2.65	100	0.25	0.66
“synthetic” sulfonate emulsifier	1.15	60	0.8	1.53
C12 dicarboxylic acid	3	100	0.4	1.20
MDEA	2.2	100	0.4	0.88
Synergex LA	5.2	100	0.1	0.52
Total				5.70

The “cost” sheet will always place limits on the freedom of the formulator. Additional formulation limits can be added and accounted for in real time via the use of Excel. For instance, the sheet blow shows an original formulation (top) and revised formulation (bottom) wherein the ratio of base value to acid value is kept the same (bases with blue background, acids with yellow background):

Component	Description	%BW	Base value	Weight equivalent	Base eq. total
Water	Water	52.20			
TEA 99 LFG	Amine	17.50	327	57.23	
MEA	Amine	9.00	918	82.62	147.95
45% KOH	Amine	1.80	450	8.1	
			Acid value		**Acid eq. total**
Boric acid	Acid	7.00	905	63.35	
Corfree M1	Acid	8.50	509	43.27	118.82
Isononanoic acid	Acid	3.00	355	10.65	
Dover EM 706	Acidic	1.00	155	1.55	
					B/A ratio
Total		100.00%			1.25
Modified formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	56.30			
Amietol M12	Amine	8.00	471	37.68	
Synergex LA	Amine	6.00	324	19.44	148.92
MEA	Amine	10.00	918	91.8	
			Acid value		**Acid eq. total**
Boric acid	Acid	7.00	905	63.35	
Sebacic acid	Acid	6.60	555	36.63	119.64
Isononanoic Acid	Acid	5.10	355	18.11	
Dover EM 706	Acidic	1.00	155	1.55	
					B/A ratio
Total		100.00%			1.25

The acid/base sheet is easily prepared by input of the weight % of acidic or basic material (as purchased) used in the concentrate. The base or acid value of the component (as added) is multiplied by the weight % of the material in the concentrate to obtain a "weight equivalent" acid or base value. The sum of the "weight equivalent" acid and base values is tabulated and then the ratio of the "weight equivalent" base value to "weight equivalent" acid value is calculated. The same calculation runs in the portion of the sheet for the revised formulation wherein changes in acidic components can be immediately compensated for via an appropriate change in basic components (and vice versa).

The reason for changing acidic/basic components in a fluid might be:

1) Loss of supply of a raw material
2) Wish for use of a newly recommended ingredient
3) Need to improve stability of formula by switching to biostable materials

Maintaining a functional and economically competitive product requires keeping an open mind with respect to replacing ingredients and flexibility with respect to incorporating functional new ingredients into existing formulations. A recent development in biostable fluids has been the use of combinations of hydrophilic primary amines (e.g., MIPA) with hydrophobic tertiary and/or secondary amines. The selection of the right hydrophobic tertiary amine can be challenging in that there are so many possibilities to choose from. This talk will describe the use of formulation constraints in the reformulation of amine packages used in full synthetic metalworking fluids. Guidelines for the selection of optimal tertiary amines will be discussed, and new ideas concerning tertiary amine chemistry as it relates to amine partitioning between the oil and water phase will be introduced. The use of Excel spreadsheets as an integral part of reformulation efforts will be highlighted.