High Active Alkyldimethylamine Oxides

K.R. Smith*, J.E. Borland, R.J. Corona and J.D. Sauer
Ethyl Corporation, Baton Rouge, LA 70820

A recently developed, high active, alkyldimethylamine oxide powder now permits the use of this valuable surfactant in water-sensitive formulations such as bar soaps. Study of the various amine oxide homologs in key performance properties of soap bars showed them to be effective foam modifiers, plasticizers, and synergistic lime soap dispersants. The solid amine oxides were found to be a versatile additive which could readily be formulated into a wide variety of personal care bars.

KEY WORDS: Amine oxides, lather, lime soap dispersant, plasticizer, slough, soap bus.

Alkyldimethylamine oxides (ADAO) are a well-known class of nonionic surfactant which have been commercially available since the 1960's (1). The applications in which these compounds are used varies with the size of the alkyl substituent. For example, the coco range ADAO serve as very effective foam boosters in light duty detergents and shampoos (2), while the higher stearyl amine oxides can be used as hair conditioners (3).

ADAO is prepared *via* the exothermic oxidation of alkyldimethylamine with hydrogen peroxide.

$$RMe_2N + H_2O_2 \rightarrow RMe_2N{\rightarrow}O + H_2O \qquad [1]$$

During the course of the oxidation, dilution water must be added to avoid gelling of the reaction mass (4,5). This results in a final product which is 20–40% active. The high water content not only contributes to shipping costs but also tends to limit the type of application in which these surfactants can be used.

To date, no cost efficient means of manufacturing concentrated ADAO has been reported in the chemical literature. Most of the reported efforts involve either the energy-intensive removal of water (6–9) or the addition of desiccant salts (10–12), which cannot be separated from the amide oxide. The difficulty in obtaining a concentrated, easily handled product of high purity can be ascribed to the relatively low thermal stability of these surfactants and also to their superior foaming ability.

Lutton (13) reported the isolation of neat ADAO as the crystalline monohydrate (~6–7% water) and as the anhydrous material. Both of these forms of ADAO have proven to be very hygroscopic and susceptible to gelling when exposed to moist air. Unexpectedly, however, the ADAO dihydrate (~13% water) has proven to be essentially nonhygroscopic.

A practical, cost-efficient procedure for the production of high purity ADAO dihydrate has recently been developed (14). Thus, the formulation limitations associated with dilute liquid amine oxides can now be circumvented. In this publication, the utility of alkyldimethylamine oxide dihydrates in bar soaps, a particularly water-sensitive application, is addressed.

*To whom correspondence should be addressed at Ethyl Corp., 8000 GSRI St., Baton Rouge, LA 70820.

EXPERIMENTAL PROCEDURES

A series of ADAO homologs was synthesized using a proprietary procedure.

The physical properties of ADAO were measured using a Fisher-Johns Melting point apparatus (Fisher Scientific, Pittsburgh, PA) and a Brookfield viscometer (Brookfield Engineering Labs, Stoughton, MA). Thermal stability, heat capacity, and latent heat were determined (Dupont, Boston, MA).

The following procedure was used for a comparison of the lime soap dispersing efficiency of compounds. A known amount of dispersing agent was added to a 10-mL portion of a 1% Ca stearate slurry. This sample and a control without lime soap dispersant were then shaken in test tubes and compared for complete dispersion of the calcium salt after standing 2 min. The results reflect the amount of material required to fully disperse 100 g of calcium stearate.

The foam profile of the test systems was measured as follows. A solution of 100 mL of the desired concentration of surfactants was prepared using water of either 50 or 200 ppm as $CaCO_3$ hardness (3 Ca/2 Mg). A 30-mL aliquot of the solution was then added to a 100-mL graduated cylinder and the stoppered cylinder inverted ten times. The initial volume of foam (flash foam) and the volume of foam remaining after 5 min were recorded. This procedure was run in triplicate and the results averaged.

RESULTS AND DISCUSSION

ADAO dihydrates. As shown in Table 1, ADAO dihydrates are low-melting solids with melting points ranging from 15–65°C for the C_8–C_{18} alkyl groups. Mixtures of carbon numbers will give a system with a melting point depressed approximately 5°C below that of the lowest melting component. When molten, the viscosity of the ADAO is such that it behaves as a gel rather than a liquid. For example, the viscosity of tetradecyldimethylamine oxide dihydrate at 75°C is 77,000 cp. Table 2 compares tetradecyldimethylamine oxide dihydrate with the corresponding 30% solution. The two forms of amine oxide differ in terms of physical state, concentration, and thermal stability.

Soap bar performance. The "ideal" soap bar is mild and performs well under a broad range of conditions. The contributions of ADAO to a broad range of soap bar properties are as follows: Mildness to skin, rich lather, superior hard water performance, minimal soap scum, conditions skin, hard bar, and good slough resistance.

One key property of amine oxides is the ability to lessen the skin irritation of anionic surfactants. For example, Pittz and Smerbeck reported that only 0.25% lauryldimethylamine oxide is needed to fully protect guinea pig skin against both a 0.25% solution of sodium alkylbenzene sulfonate and sodium lauryl sulfate (14). A glycerine level of 20% was required to achieve the same

TABLE 1

ADAO Dihydrate Melting Points

Carbon number distribution, wt %						
C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	M.P. (°C)
100	—	—	—	—	—	~15
—	100	—	—	—	—	22–23
—	—	100	—	—	—	30–31
—	—	—	100	—	—	41–42
—	—	—	—	100	—	49–50
—	—	—	—	—	100	61–62
—	—	36	64	—	—	paste
—	—	51	49	—	—	paste
—	—	67	33	—	—	paste
—	—	40	50	10	—	paste
—	—	60	25	15	—	paste
—	—	65	—	35	—	25–35
—	—	—	65	35	—	27–38

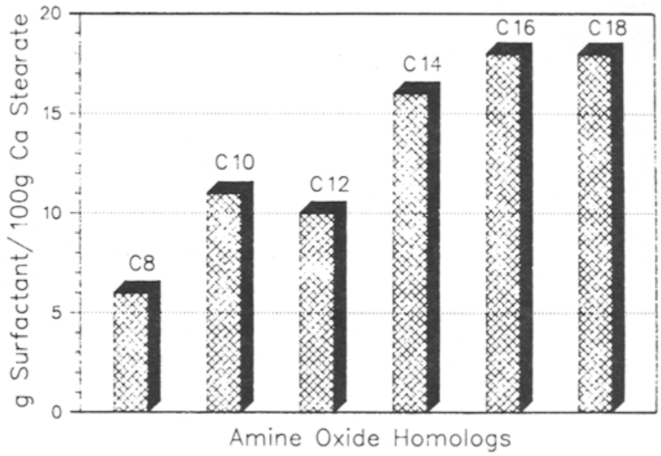

FIG. 1. ADAO homologs as lime soap dispersants (containing minimum AO/Ca stearate ratio needed to disperse 1 wt% Ca stearate). C12, C14, C16 and C18; with g ADAO/100 g Ca stearate: 6, 11, 10, 16, 18 and 18, respectively. Conditions: 35°C deionized waer.

TABLE 2

Comparison of Forms of Tetradecyldimethylamine Oxide

Property	Dihydrate	30% Solution
Physical state	Powder or pellets	Liquid or gel
Wt% active tested	85%	30%
Decomp. pt. (°C)	⩾ 135	⩾ 100
Viscosity (cp):		
50°C	130,000	557
75°C	77,000	101
100°C	41,000	—
Heat capacity (g/cal):		
75°C	0.579	0.699
100°C	0.597	—
Latent Heat (cal/g)	28.9	—

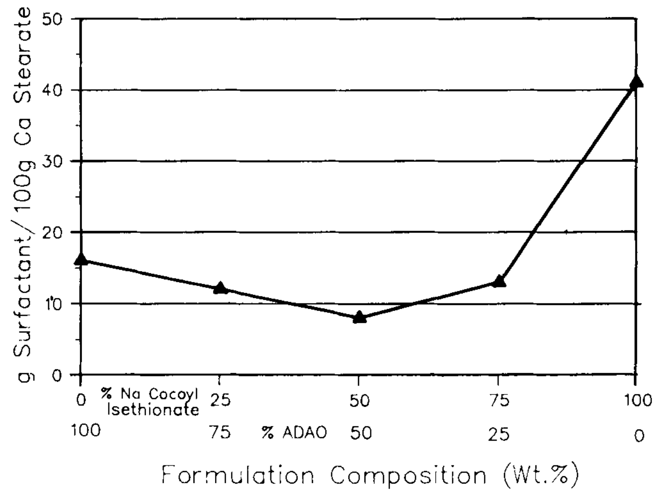

FIG. 2. ADAO/sodium cocoyl isethionate blends as dispersants. g Dispersant/100 g Ca stearate: C_{14} amine oxide, 16, none, 4, 9 and 4; with Na cocoyl isethionate, none, 41, 4, 3 and 9, respectively.

effect. While we do not yet have data on the effect of amine oxides on soap irritancy, the parallel is clear.

Amine oxides are also very substantive towards skin (15). This behavior may partially explain the conditioning activity of amine oxides in bar soap formulations. Pittz and Smerbeck's (14) observation that ADAO retards moisture loss from the skin may also contribute to the conditioning effect. Our panel tests have shown that 5% tetradecyldimethylamine oxide in a bar soap is sufficient to impart skin conditioning. In this test, all panelists selected a bar containing 5% tetradecyldimethylamine oxide over a "pure" soap bar as the formulation giving the best skin after-feel. Descriptions of the after-feel imparted by the system included "soft", "moist", and "not greasy".

Amine oxides also serve as lime soap dispersants (16). Marmer and Linfield (17) reported a LSDR of 9 for lauryldimethylamine oxide and 10 for stearyldimethylamine oxide, using the Borghetty-Bergman procedure with sodium oleate (18). To put these values into perspective, sodium cocoyl isethionate, a well-known lime soap dispersant, has a reported value of 15–20 for its LSDR.

During the course of this study, a closer look was taken at the relative efficacy of amine oxide homologs as lime soap dispersants. Our more rigorous test procedure was a modification of the Borghetty-Bergman method in which the dispersing action of ADAO on calcium stearate was evaluated. As Figure 1 shows, octyldimethylamine oxide was found to be the most effective of the C_8-C_{18} homologs. Further, mixtures of ADAO and sodium cocoyl isethionate were found to be mutually synergistic as lime soap dispersants. Figure 2 illustrates the effect of ADAO/sodium cocoyl isethionate blend composition on the amount of dispersing agent required for full disper-

TABLE 3

Effect of Amine Oxide on Foaming of Soap[a]

	Foam volume[b] (mL)			
	t=0 min		t=5 min	
Amine oxide	No soil	Soil	No soil	Soil
None	3	0	0	0
C_8	4	0	0	0
C_{10}	5	0	0	0
C_{12}	9	6	4	3
C_{14}	13	7	11	5
C_{16}	3	1	2	0
C_{18}	4	1	1	0
C_{1214}	10	4	8	3

[a]Conditions: 35°C, 200 ppm as $CaCO_3$ water hardness (3 Ca/2 Mg), 30 mL test solution, 0.10% soap, 0.02% amine oxide (active basis), and 0.2 mL olive oil as soil.

[b]Average of three runs; standard deviation ± 1 mL.

TABLE 4

Recommended Moisture Levels in Amine Oxide/Soap Bars

% ADAO	% Total water	
	C_{14}	C_{18}
5		
10	10–14	10–14
20	≤ 7	10–14

TABLE 5

Prototype Soap Bar Formulations

Component	1	2	3	4
Soap (80/20)	82	82	10	34
$C_{14}H_{29}Me_2NO$	10	10	45	10
Na cocoyl isethionate	0	10	15	0
Stearic acid	0	0	20	10
Triethanolamine	0	0	0	30
Water (total)	8	8	10	16

sion of calcium stearate. Blends of tetradecyldimethylamine oxide and sodium cocoyl isethionate were clearly more efficient dispersants than either material alone, achieving maximum effectiveness at a 1:1 weight ratio.

Additionally, ADAO can be used to both boost and stabilize the foam of anionic surfactants, including soap. Using a standard cylinder test, it was found that C_{14} ADAO is the optimum single carbon number to improve the foam profile of 80 tallow/20 coco soap (Table 3). This improvement is evident in both hard and soft water. Closer examination revealed that the maximum effect on foam occurs at a 4:1 ratio of soap to tetradecyldimethylamine oxide. However, discernable improvement in foam volume and density was noted even at 1% C_{14} ADAO.

ADAO is moderately active as an antimicrobial in its own right (19) and also has been used as a potentiator of more potent antimicrobials such as quaternary ammonium salts (20). Cheng *et al.* (21) describe amine oxides as a means of enhancing the antibacterial properties of deodorant bars.

Soap bar formulations. Based on the properties discussed above, ADAO is a multifunctional surfactant which we believe would be a valuable component of soap bars. Several efforts to introduce ADAO into personal care bars are reported in the literature (21–25). However, the high water content of amine oxides heretofore available has hindered the preparation of soap bars with significant ADAO content. Use of the alkyldimethylamine oxide dihydrates avoids this problem.

For bars comprised of only ADAO and 80/20 soap, it was found that the amine oxide acts as a plasticizer, making the total water content of the bar critical. This effect varies with both the alkyl length of the ADAO and the amount of amine oxide present. As Table 4 shows, 6–10% water is recommended for a bar containing 10% tetradecyldimethylamine oxide (on the basis of bar hardness). When 10% octadecyldimethylamine oxide is used, a water level of 10–14% is recommended. Calculations reveal that if a 30% active solution of tetradecyldimethylamine oxide is used as the amine oxide source too much water will be present, affording a very soft bar. No odor other than that of the soap base was detectable in any of these unfragranced bars.

ADAO dihydrate can also be formulated into other types of bars. Table 5 shows prototype formulations for several systems. A detailed study of the performance, clinical, and mechanical properties of these formulations is in progress and will be reported shortly.

Toxicology. The physical (26) and toxicological properties of alkyldimethylamine oxides are reported in the literature. ADAO can be classified as a nontoxic surfactant (27) which is readily metabolized (28) and which is also nonmutagenic (29). Cardin *et al.* (30) reported the results of a two year chronic feeding and dermal study of ADAO. Skin irritancy studies also have been described (31–33). Perhaps the most important facet of ADAO safety, though, is its decades-long history of use as a significant component of detergents involving intimate consumer contact.

REFERENCES

1. Devinsky, F., *Acta Facultatis Pharm. 40*:63 (1986).
2. British Pat. 942,870 (1963).
3. Gerstein, T., U.S. Pat. 4,033,985 (1977).
4. Hoh, G.L., D.O. Barlow, A.F. Chadwick, D.B. Lake and S. Sheeran, *J. Am. Oil Chem. Soc. 40*:268 (1963).
5. Shapiro, S.H., *Amine Oxides*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edn., 1970, p. 259.
6. Mitchell, L.C., and T.H. Coffield, U.S. Pat. 3,332,999 (1967).
7. Shulman, G.P., U.S. Pat. 3,336,388 (1967).
8. Kennedy, E.F., and D.E. Harwell, U.S. Patent, 3,330,327 (1967).
9. Stalioraitis, J.S., and C.S. Wilhelmly, U.S. Pat. 3,558,710.
10. Starks, C.M., and L.E. Harwell, U.S. Pat. 3,316,236 (1967).
11. Inamorato, J.T., and G.F. Marlon, U.S. Pat. 3,489,687 (1970).
12. Japanese Pat. 59/167558 A2 (1984).
13. Lutton, E.S., *J. Am. Oil Chem. 43*:28 (1966).
14. Pittz, E.P., and R.V. Smerbeck, European Patent Appl. 186,453 (1986).
15. Ginn, M.E., S.C. Dunn and E. Jungermann, *J. Am. Oil Chem. Soc. 47*:83 (1970).
16. Marsh, B.E., *Am. Perfum. Cos. 84*:37 (1969).
17. Marmer, W.N., and W.M. Linfield, *J. Am. Oil Chem. Soc. 53*:69 (1976).

18. Borghetty, H.C., and C.A. Bergman, *Ibid.* *27*:88 (1950).
19. Babu, H., P.K. Sarawathyamma, S.V. Rao and K.T. Achaya, Indian Pat. 105,080 (1969).
20. Findlan, J.C., R.P. Sorrentino and R.L. Wakeman, U.S. Pat. 3,484,523 (1969).
21. Cheng, W.M., J.F. Davies and B.A. Pethica, U.S. Pat. 3,835,057 (1974).
22. Japanese Pat. 57/74397 (1982).
23. Cheng, M.W., N.M. Barnes, T. Rikards, D.A. Rosser and P. Thurairajan, British Pat. 1,296,351 (1972).
24. Poper, M., and E. Jungermann, U.S. Pat. 4,290904 (1981).
25. Japanese Pat. 56/62897 (1981).
26. Devinsky, F., *Acta Facultatis Pharm.* *39*:173 (1985).
27. Devinsky, F., *Ibid.* *39*:197 (1985).
28. Turan, T.S., and W.B. Gibson, *Xenobiotica* *11*:447 (1981).
29. Anon., *Food Cosmet. Toxicol.* *18*:289 (1980).
30. Cardin, C.W., B.E. Domeyer and L. Bjorkquist, *Fundamental and Applied Toxicology* *5*:869 (1985).
31. Like, B., R. Sorrentino and A. Petrocci, *J. Soc. Cosmet. Chem.* *26*:155 (1975).
32. Smith, G.J., *Seifen, Ole, Fette, Wachse* *105*:319 (1979).
33. Devinsky, F., Ph.D. Thesis, Comenius University, Bratslavia, 1980.

[Received June 26, 1990; accepted April 26, 1991]