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Fig. 14.11.	M. J. Schick, *J. Colloid Sci.*, **17**, 801 (1962) (Fig. 1).
Fig. 14.13.	*Ibid.*, **18**, 378 (1963) (Fig. 3).
Fig. 15.6.	P. Becher, *ibid.*, **16**, 49 (1961) (Fig. 1).
Fig. 15.8.	*Ibid.*, **17**, 325 (1962) (Fig. 2).
Fig. 17.1.	K. Shinoda, T. Nakagawa, B. Tamamuchi, and T. Isemura, *Colloidal Surfactants*, 1963, p. 140 (Fig. 2.27).
Fig. 17.2.	*Ibid.*, p. 141 (Fig. 2.28).
Fig. 17.3.	M. E. L. McBain and E. Hutchinson, *Solubilization and Related Phenomena*, 1955, p. 169 (Fig. 5.14).
Fig. 17.4.	B. A. Mulley and A. D. Metcalf, *J. Colloid Sci.*, **17**, 525 (1962) (Fig. 2).
Fig. 17.5.	*Ibid.*, **17**, 526 (1962) (Fig. 3).
Fig. 17.7.	K. Shinoda, T. Nakagawa, B. Tamamuchi, and T. Isemura, *Colloidal Surfactants*, 1963, p. 142 (Fig. 2.29).
Fig. 17.8.	T. Nakagawa, K. Kuriyama, and H. Inoue, *J. Colloid Sci.*, **15**, 275 (1960) (Fig. 5).
Fig. 17.9.	W. N. Maclay, *ibid.*, **11**, 281 (1956) (Fig. 6).
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Fig. 17.11.	W. N. Maclay, *ibid.*, **11**, 277 (1956) (Fig. 4).
Fig. 17.28.	B. A. Mulley and A. D. Metcalf, *ibid.*, **19**, 508 (1964) (Fig. 6).
Fig. 17.29.	*Ibid.*, **19**, 504 (1964) (Fig. 2).
Fig. 17.30.	S. Ross, *ibid.*, **6**, 502-504 (1951) (Figs. 1-3).
Fig. 19.12.	E. Mackor, *ibid.*, **6**, 492 (1951) (Fig. 1).
Fig. 19.14.	E. Mackor and J. H. van der Waals, *ibid.*, **7**, 535 (1952) (Figs. 3 and 4).
Fig. 21.2.	J. F. Danielli, K. G. A. Pankhurst, and A. C. Riddiford, *Recent Progress in Surface Science*, 1964, p. 61 (Fig. 2).
Table 17.3.	T. Nakagawa, K. Kuriyama, and H. Inoue, *J. Colloid Sci.*, **15**, 270 (1960) (Table II).
Table 17.9.	A. M. Mankowich, *ibid.*, **14**, 133 (1959) (Table II).
Table 17.12.	S. Ross, *ibid.*, **6**, 500 (1951) (Table II).
Table 21.1.	A. G. Brown, W. C. Thuman, and J. W. McBain, *ibid.*, **8**, 502 (1953) (Table I).

Acta Chemica Scandinavica, Stockholm, Sweden

Fig. 2.10.	B. Weibull and B. Nycander, *Acta Chemica Scandinavica*, **8**, 847 (1954) (Fig. 1).

American Chemical Society, Washington, D.C.

Fig. 2.5.	W. B. Satkowski and C. G. Hsu, *Ind. Eng. Chem.*, **49**, 1875 (1957) (Fig. 2).
Fig. 2.6.	*Ibid.*, **49**, 1875 (1957) (Fig. 4.)
Fig. 2.7.	*Ibid.*, **49**, 1875 (1957) (Fig. 5).
Fig. 17.6.	S. Ross and J. P. Olivier, *J. Phys. Chem.*, **63**, 1673 (1959) (Fig. 2).
Fig. 17.26.	S. S. Marsden and J. W. McBain, *ibid.*, **52**, 121 (1948) (Fig. 9).
Fig. 18.3.	K. Shinoda and H. Arai, *ibid.*, **68**, 3485 (1964) (Fig. 1).
Fig. 18.4.	*Ibid.*, **68**, 3485 (1964) (Fig. 3).
Fig. 18.5.	*Ibid.*, **68**, 3485 (1964) (Fig. 5).
Fig. 18.6.	*Ibid.*, **68**, 3485 (1964) (Fig. 9).
Fig. 18.7.	*Ibid.*, **68**, 3485 (1964) (Fig. 10).
Fig. 19.23.	H. Lange, *ibid.*, **64**, 538 (1960) (Fig. 5).
Fig. 21.6.	P. Becher and A. J. Del Vecchio, *ibid.*, **68**, 3511 (1964) (Fig. 1).
Fig. 21.7.	S. Ross and R. Haak, *ibid.*, **62**, 1260 (1958) (Fig. 1).
Fig. 23.1.	F. E. Bailey, Jr., G. M. Powell, and K. L. Smith, *Ind. Eng. Chem.*, **50**, 8 (1958) (Fig. 1).
Fig. 23.11.	*Ibid.*, **50**, 8 (1958) (Fig. 4*a*).
Fig. 23.12.	*Ibid.*, **50**, 8 (1958) (Fig. 4*c*).
Fig. 23.13.	*Ibid.*, **50**, 8 (1958) (Fig. 7).
Fig. 27.1.	H. G. Nadeau, D. Oaks, W. A. Nichols, and L. P. Carr, *Anal. Chem.*, **36**, 1915 (1964) (Fig. 1).
Table 8.8.	G. F. D'Alelio and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 111 (1937) (Table I).
Table 8.9.	*Ibid.*, **59**, 111 (1937) (Table II).
Table 21.4.	M. J. Schick and F. M. Fowkes, *J. Phys. Chem.*, **61**, 1064 (1957) (Table VI).
Table 25.3.	L. Gatewood, Jr., and H. D. Graham, *Anal. Chem.*, **33**, 1395 (1961) (Table I).
Table 26.5.	H. Schott, *J. Phys. Chem.*, **68**, 3612 (1964) (Table II).
Table 27.3.	M. J. Rosen, *Anal. Chem.*, **29**, 1676 (1957) (Table II).
Table 27.5.	M. E. Ginn, C. L. Church, and J. C. Harris, *ibid.*, **33**, 145 (1961) (Table I).
Table 27.9.	T. Nakagawa, H. Inoue, and K. Kuriyama, *ibid.*, **33**, 1525 (1961) (Table I).
Table 27.10.	H. G. Nadeau, D. Oaks, W. A. Nichols, and L. P. Carr, *ibid.*, **36**, 1915 (1964) (Table I).
Table 27.11.	*Ibid.*, **36**, 1915 (1964) (Table II).
Table 27.12.	*Ibid.*, **36**, 1915 (1964) (Table III).
Section 25.3.	P. W. Morgan, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 500 (1946).
Section 27.3.	C. J. Kelly and H. L. Greenwald, *J. Phys. Chem.*, **62**, 1096 (1958).

American Institute of Physics, New York, N. Y.

Fig. 22.22.	L. Mandelkern, F. A. Quinn, and P. Flory, *J. Appl. Phys.*, **25**, 830 (1954) (Fig. 2).

American Oil Chemists' Society, Chicago, Ill.

Fig. 2.3.	A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, **34**, 40 (1957) (Fig. 2).
Fig. 5.2.	E. M. Stoltz, A. T. Ballun, H. J. Ferlin, and J. V. Karabinos, *ibid.*, **30**, 271 (1953) (Fig. 1).
Fig. 5.3.	A. N. Wrigley, F. D. Smith, and A. J. Stirton, *ibid*,. **34**, 39 (1957) (Fig. 5).
Fig. 5.4.	*Ibid.*, **34**, 39 (1957) (Fig. 3).
Fig. 8.1.	H. Kroll and H. Nadeau, *ibid.*, **34**, 323 (1957) (Fig. 1).
Fig. 12.5.	D. B. Lake and G. L. Hoh, *ibid.*, **40**, 628 (1963) (Fig. 1).
Fig. 12.6.	*Ibid.*, **40**, 628 (1963) (Fig. 2).
Fig. 20.3.	J. C. Harris, R. M. Anderson, and J. Satanek, *ibid.*, **38**, 123 (1961) (Fig. 1).
Fig. 20.4.	*Ibid.*, **38**, 123 (1961) (Fig. 2).
Fig. 20.5.	*Ibid.*, **38**, 123 (1961) (Fig. 7).

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Fig. 20.6.	*Ibid.*, **38**, 123 (1961) (Fig. 5).
Fig. 20.7.	G. E. Barker and H. J. Ranauto, *ibid.*, **32**, 249 (1955) (Fig. 3).
Fig. 20.8.	L. I. Osipow and F. D. Snell, *ibid.*, **38**, 184 (1961) (Fig. 3).
Fig. 20.9.	J. C. Harris, R. M. Anderson, and J. Satanek, *ibid.*, **38**, 123 (1961) (Fig. 8).
Fig. 20.10.	*Ibid.*, **38**, 123 (1961) (Fig. 9).
Fig. 20.11.	W. Kling and H. Lange, *ibid.*, **37**, 30 (1960) (Fig. 1).
Fig. 20.12.	R. M. Anderson, J. Satanek, and J. C. Harris, *ibid.*, **36**, 286 (1959) (Fig. 4).
Fig. 20.13.	*Ibid.*, **36**, 286 (1959) (Fig. 14).
Fig. 20.14.	*Ibid.*, **37**, 119 (1960) (Fig. 3).
Fig. 20.15.	J. C. Harris and J. Satanek, *ibid.*, **38**, 169 (1961) (Fig. 2).
Fig. 20.16.	*Ibid.*, **38**, 169 (1961) (Fig. 4).
Fig. 20.17.	*Ibid.*, **38**, 169 (1961) (Fig. 9).
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Fig. 20.19.	*Ibid.*, **38**, 244 (1961) (Fig. 3).
Fig. 21.3.	E. H. Crook, D. B. Fordyce, and G. F. Trebbi, *ibid.*, **41**, 231 (1964) (Fig. 1).
Fig. 21.4.	*Ibid.*, **41**, 231 (1964) (Fig. 4).
Fig. 21.5.	M. J. Schick and E. A. Beyer, *ibid.*, **40**, 66 (1963) (Fig. 1).
Fig. 21.9.	T. P. Matson, *ibid.*, **40**, 640 (1963) (Fig. 1).
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Fig. 26.15.	R. A. Greff, Jr., and P. W. Flanagan, *ibid.*, **40**, 118 (1963) (Fig. 1).
Fig. 27.2.	P. Becher and R. L. Birkmeier, *ibid.*, **41**, 170 (1964) (Fig. 3).
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Fig. 29.2.	*Ibid.*, **40**, 648 (1963) (Fig. 3).
Fig. 29.3.	*Ibid.*, **40**, 648 (1963) (Fig. 4).
Fig. 29.5.	C. D. Frazee, Q. W. Osburn, and R. O. Crisler, *ibid.*, **41**, 808 (1964) (Fig. 4).
Fig. 29.7.	E. C. Steinle, R. C. Myerly, and C. A. Vath, *ibid.*, **41**, 804 (1964) (Fig. 4).
Fig. 29.8.	*Ibid.*, **41**, 804 (1964) (Fig. 5).
Fig. 29.14.	J. K. Weil and A. J. Stirton, *ibid.*, **41**, 355 (1964) (Fig. 6).
Fig. 29.15.	L. J. Garrison and R. D. Matson, *ibid.*, **41**, 799 (1964) (Fig. 5).
Fig. 29.17.	*Ibid.*, **41**, 799 (1964) (Fig. 4).
Table 5.6.	A. N. Wrigley, F. D. Smith, and A. J. Stirton, *ibid.*, **34**, 40 (1957) (Table II).
Table 5.7.	E. M. Stoltz, A T. Ballun, H. J. Ferlin, and J. V. Karabinos, *ibid.*, **30**, 271 (1953) (Table I).
Table 8.10.	J. Kritchevsky, *ibid.*, **34**, 178 (1957) (Table I).
Table 20.4.	V. R. Gaertner, *ibid.*, **38**, 410 (1961) (Table I).
Table 20.6.	G. E. Barker and H. J. Ranauto, *ibid.*, **32**, 249 (1955) (Table II).
Table 20.8.	T. H. Vaughn, H. R. Suter, L. G. Lundsted, and M. G. Kramer, *ibid.*, **28**, 294 (1951) (Table II).
Table 20.9.	J. Kritchevsky, *ibid.*, **34**, 178 (1957) (Table III).
Table 20.10.	G. E. Barker, *ibid.*, **26**, 304 (1949) (Tables I-III).
Table 20.13.	M. E. Ginn, F. B. Kinney, and J. C. Harris, *ibid.*, **38**, 138 (1961) (Table VII).
Table 20.14.	M. E. Ginn, E. L. Brown, and J. C. Harris, *ibid.*, **38**, 361 (1961) (Table II).
Table 20.15.	M. E. Ginn and J. C. Harris, *ibid.*, **38**, 605 (1961) (Table V).
Table 20.16.	A. M. Mankowich, *ibid.*, **38**, 589 (1960) (Table III).
Table 20.17.	M. E. Ginn and J. C. Harris, *ibid.*, **38**, 605 (1961) (Table IV).
Table 20.19.	R. M. Anderson, J. Satanek, and J. C. Harris, *ibid.*, **36**, 286 (1959) (Table I).
Table 20.20.	*Ibid.*, **37**, 119 (1960) (Table II).
Table 21.3.	M. J. Schick and E. A. Beyer, *ibid.*, **40**, 66 (1963) (Table I).
Table 21.5.	J. H. McFarland and P. R. Kinkel, *ibid.*, **41**, 742 (1964) (Table VI).
Table 24.1.	C. Kortland and H. F. Dammers, *ibid.*, **32**, 63 (1955) (Table IV).
Table 25.1.	L. E. Weeks, J. T. Lewis, and M. E. Ginn, *ibid.*, **35**, 149 (1958) (Table III).
Table 25.2.	*Ibid.*, **35**, 149 (1958) (Table V).
Table 25.5.	H. Kroll and H. Nadeau, *ibid.*, **34**, 323 (1957) (Table I).
Table 26.6.	R. A. Greff, Jr., and P. W. Flanagan, *ibid.*, **40**, 118 (1963) (Table I).
Table 29.2.	L. H. Smithson, 39th Meeting, American Oil Chemists' Society, Cincinnati, Ohio, 1965.

Table 29.4.	R. L. Huddleston and R. C. Allred, *J. Am. Oil Chemists' Soc.*, **42**, 983 (1965) (Table VI).
Sect. 25.3.1.	L. E. Weeks, J. T. Lewis, and M. E. Ginn, *ibid.*, **35**, 149 (1958) (Methods).

The Chemical Society, London, England

Table 2.2.	G. Gee, W. C. E. Higginson, P. Levesley, and K. J. Taylor, *J. Chem. Soc.*, **1959**, 1339 (Table 1).
Table 2.3.	G. Gee, W. C. E. Higginson, and G. T. Merrall, *J. Chem. Soc.*, **1959**, 1350 (Table 2).

Deutscher Ausschuss für Grenzflächenaktive Stoffe im Verband der Chemischen Industrie, Bonn, West Germany (Verlag Universitäts-druckerei, Mainz, West Germany)

Fig. 2.11.	G. Tischbirek, *Vorträge Originalfassung Intern. Kongr. Grenzflächenaktive Stoffe, 3, Cologne, 1960* (*Proc. Intern. Congr. Surface Activity, 3rd, Cologne, 1960*), **1**, 126 (1960) (Fig. 1).
Fig. 2.12.	*Ibid.*, **1**, 126 (1960) (Fig. 8).
Fig. 17.31.	H. Wedell, *ibid.*, **4**, 220 (1960) (Fig. 7).
Table 17.1.	H. Lange, *ibid.*, **1**, 279 (1960) (Table 2).
Table 17.2.	T. Nakagawa, *ibid.*, **2**, 636 (1960) (Table 1).

The Dow Chemical Company, Midland, Mich.

Fig. 12.1.	*Alkanolamines Handbook.*
Fig. 12.2.	*Ibid.*
Fig. 12.3.	*Ibid.*
Fig. 12.4.	*Ibid.*
Sect. 27.3.B.	N. E. Skelly and W. B. Crummet, paper presented at Anachem Conference, Wayne State University, Detroit, Mich,

The Faraday Society, London, England

Fig. 19.2.	J. M. Corkill, J. F. Goodman, and J. R. Tate, *Trans. Faraday Soc.*, **62**, 979 (1966) (Figs. 1-4).
Fig. 19.4.	K. G. Mathai and R. H. Ottewill, *ibid.*, **62**, 750 (1966) (Fig. 5).
Fig. 19.9.	*Ibid.*, **62**, 759 (1966) (Fig. 7).
Fig. 19.18.	*Ibid.*, **62**, 750 (1966) (Fig. 6).
Fig. 19.19.	*Ibid.*, **62**, 750 (1966) (Fig. 1).
Fig. 19.20.	*Ibid.*, **62**, 750 (1966) (Fig. 2*c*).
Fig. 19.21.	*Ibid.*, **62**, 750 (1966) (Fig. 3*c*).
Fig. 19.22.	*Ibid.*, **62**, 750 (1966) (Fig. 4).
Fig. 19.26.	*Ibid.*, **62**, 759 (1966) (Fig. 1*c*).
Fig. 19.27.	*Ibid.*, **62**, 759 (1966) (Fig. 6).
Fig. 19.30.	*Ibid.*, **62**, 759 (1966) (Fig. 5).
Fig. 19.31.	*Ibid.*, **62**, 759 (1966) (Fig. 8).
Fig. 21.1.	F. Van Voorst Vader, T. F. Erkens, and M. Van den Tempel, *ibid.*, **60**, 1170 (1963) (Fig. 2).

Fette, Seifen, Anstrichmittel, Münster, Germany

Fig. 14.15.	H. Lange, *Fette, Seifen, Anstrichmittel*, **64**, 459 (1962) (Fig. 4).
Fig. 22.8.	M. Rösch, *ibid.*, **59**, 1, 80 (1957) (Fig. 1).
Fig. 22.11.	M. Rösch, *ibid.*, **59**, 1, 80 (1957) (Fig. 4).
Fig. 22.12.	M. Rösch, *ibid.*, **59**, 1, 80 (1957) (Fig. 5,6).

Gauthier-Villars Editeur, Paris, France

Fig. 17.21.	M. Cohen, *Compt. Rend.*, **229**, 1075 (1949) (Fig. 1).
Fig. 17.22.	*Ibid.*, **229**, 1075 (1949) (Fig. 2).

Japanese Chemical Society, Tokyo, Japan

Fig. 17.12.	T. Sugano, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **84**, 521 (1963) (Fig. 1).
Fig. 17.19.	*Ibid.*, **84**, 521 (1963) (Fig. 4).
Fig. 17.20.	*Ibid.*, **84**, 521 (1963) (Fig. 6).

Macmillan & Co., Ltd., London, England

Fig. 15.2.	P. Becher, *Nature*, **206**, 611 (1965) (Fig. 1).

MacNair-Dorland Co., Inc., New York, N. Y.

Fig. 21.8.	T. P. Matson, *Soap Chem. Specialties*, **39**, (11), 53 (1963) (Fig. 1).
Fig. 25.1.	A. B. Steele and L. D. Berger, Jr., *ibid.*, **32**, (2), 48 (1956) (Fig. 1).
Fig. 29.6.	F. A. Blankenship and V. M. Piccolini, *ibid.*, **39**, (12), 75 (1963) (Fig. 7).
Fig. 29.9.	*Ibid.*, **39**, (12), 75 (1963) (Fig. 4).
Fig. 29.10.	*Ibid.*, **39**, (12), 75 (1963) (Fig. 5).
Fig. 29.11.	*Ibid.*, **39**, (12), 75 (1963) (Fig. 6).
Fig. 29.12.	R. C. Myerle, J. M. Rector, E. C. Steinle, C. A. Vath, and H. T. Zika, *ibid.*, **40**, (5), 78 (1964) (Fig. 6).
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Table 24.2.	E. J. Quinn and J. V. Karabinos, *ibid.*, **32**, (11), 39 (1956) (Table 2).
Table 25.4.	J. V. Karabinos, G. E. Kapella, and G. E. Bartels, *ibid.*, **30**, (6), 41 (1959) (Table 1).

Manufacturing Chemist and Aerosol News, London, England

Table 8.5.	A. T. Pugh, *Mfg. Chemist*, **28**, 557 (1957).

Melliand Textilberichte KG., Heidelberg, Germany

Fig. 22.10.	M. Kehren and M. Rösch, *Melliand Textilber.*, **38**, 191, 319 (1957) (Fig. 12).

Pennsalt Chemicals Corporation, Philadelphia, Pa.

Table 6.1.	*Pennsalt Nonic 218.*
Table 6.7.	*Ibid.*
Table 6.8.	*Ibid.*

Sadtler Research Laboratories, Inc., Philadelphia, Pa.

Fig. 26.3.- 26.14.	*Spectra* 2945, B 1006, B 1023, C 567, C 335, C 792, C 791, C 25, C 23, C 1654, C 917, C 920, C 216, C 58.

The Science Reports of the Saitama University, Japan

Fig. 17.25.	K. Fukuda and Y. Taniyama, *Sci. Rept. Saitama Univ.*, **A3**, 27 (1958) (Fig. 4).

Seifen-Oele-Fette-Wachse, Augsburg, Germany

Fig. 22.20.	M. Kehren and M. Rösch, *Seifen-Oele-Fette-Wachse*, **82**, 567, 600 (1956) (Fig. 4).

Society of Chemical Industry, London, England

Fig. 17.26.	P. A. Winsor, *Chem. Ind. London*, **1960**, 637 (Fig. 10).
Fig. 17.27.	*Ibid.*, **1960**, 638 (Fig. 12).

Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany

Fig. 14.2.	H. Lange, *Kolloid-Z.*, **182**, 123 (1962) (Fig. 11).
Fig. 14.4.	*Ibid.*, **182**, 123 (1962) (Fig. 13).
Fig. 14.5.	*Ibid.*, **201**, 131 (1965) (Fig. 2).
Fig. 14.6.	*Ibid.*, **201**, 131 (1965) (Fig. 3).
Fig. 14.12.	*Ibid.*, **201**, 131 (1965) (Fig. 1).
Fig. 14.17.	*Ibid.*, **201**, 131 (1965) (Fig. 4).

Fig. 17.13.	T. Nakagawa and K. Tori, *ibid.*, **168**, 135 (1960) (Fig. 4).
Fig. 17.14.	*Ibid.*, **168**, 135 (1960) (Fig. 8).
Fig. 17.15.	*Ibid.*, **168**, 136 (1960) (Fig. 11).
Fig. 17.16.	*Ibid.*, **168**, 136 (1960) (Fig. 14).
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Fig. 17.18.	*Ibid.*, **180**, 63 (1962) (Fig. 15).
Fig. 19.1.	H. Kuno and R. Abe, *ibid.*, **181**, 70 (1962) (Fig. 1).
Fig. 19.7.	A. F. Watanabe, F. Tsuji, and S. Ueda, *ibid.*, **193**, 39 (1963) (Fig. 1).
Fig. 19.28.	A. Watanabe and R. Gotoh, *ibid.*, **191**, 36 (1963) (Fig. 4).
Fig. 19.29.	A. Watanabe, M. Matsumato, and R. Gotoh, *ibid.*, **201**, 147 (1965) (Fig. 3).
Fig. 22.14.	M. Rösch, *ibid.*, **150**, 153 (1957) (Fig. 1).
Table 17.5.	T. Nakagawa and K. Tori, *ibid.*, **168**, 138 (1960) (Table 4).
Table 17.6.	K. Kuriyama, *ibid.*, **180**, 58, 61 (1962) (Tables 1 and 3).
Table 17.7.	*Ibid.*, **180**, 59 (1962) (Table 2).
Table 17.8.	*Ibid.*, **180**, 61 (1962) (Table 3).
Table 17.10.	T. Nakagawa and K. Tori, *ibid.*, **168**, 136 (1960) (Table 3).
Table 19.1.	R. Abe and H. Kuno, *ibid.*, **181**, 70 (1962) (Table 1); H. Kuno and R. Abe, *ibid.*, **177**, 40 (1961) (Table 1); H. Kuno, R. Abe, and S. Tahara, *ibid.*, **198**, 77 (1964) (Table 3).
Table 23.6.	G. Müh, *ibid.*, **196**, 140 (1964) (Table 3).

John Wiley & Sons, Inc., New York, N. Y.

Fig. 2.4.	F. Patat, E. Cremer, and O. Bobletter, *J. Polymer Sci.*, **12**, 489 (1954) (Fig. 1).
Fig. 22.24.	F. P. Price and R. W. Kilb, *ibid.*, **57**, 398 (1962) (Fig. 4).
Fig. 23.2.	F. E. Bailey, Jr., and R. W. Callard, *J. Appl. Polymer Sci.*, **1**, (1), 56 (1959) (Fig. 3).
Fig. 23.3.	*Ibid.*, **1**, (1), 56 (1959) (Fig. 5).
Fig. 23.4.	*Ibid.*, **1**, (1), 56 (1959) (Fig. 6).
Fig. 23.7.	*Ibid.*, **1**, (1), 56 (1959) (Fig. 7).
Fig. 23.8.	*Ibid.*, **1**, (1), 56 (1959) (Fig. 8).
Fig. 23.14.	*Ibid.*, **1**, (1), 56 (1959) (Fig. 11).
Table 23.1.	*Ibid.*, **1**, (1) 56 (1959) (Table II).
Table 26.3.	D. Hummel, *Identification and Analysis of Surface-Active Agents by Infrared and Chemical Methods*, Vol. I, 1962, p. 141.

Wyandotte Chemicals Corporation, Wyandotte, Mich.

Fig. 26.2.	R. D. Ring, "A Near Infrared Spectrophotometric Differential Method for the Determination of Oxypropylene Groups in Polyoxypropylene Glycols," paper presented at the 7th Anachem Conference, Wayne State University, Detroit, Mich., 1952 (Figs. 1, 2, and 3).
Table 26.2.	*Ibid.*

CHAPTER **1**

INTRODUCTION

M. J. Schick

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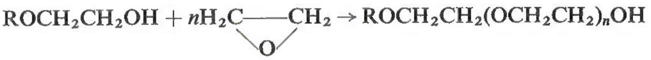
EDGEWATER, NEW JERSEY

The first surface-active condensation products of polyoxyethylene glycols with oleic and stearic acids were prepared by C. Schöller at the Badische Aniline and Soda Fabrik in Ludwigshafen, Germany, in September 1930. This invention led to the first patents in the field of nonionic surfactants, with priorities of November 30, 1930. In the years since Schöller's discovery a large-scale industrial development in the manufacture of nonionic surfactants has taken place. These surfactants now constitute a sizable fraction of the total production of surfactants. In 1964, 215,000,000 pounds of ethylene oxide, which forms the major raw material, were used for the production of polyoxyethylene-type surfactants in the U.S. At present, nonionic surfactants are the subject of intensive research and development efforts with continuously growing fields of applications.

The term nonionic surfactants refers chiefly to polyoxyethylene and polyoxypropylene derivatives, but other surfactants are also included in this category, such as anhydrohexitol derivatives, sugar esters, fatty alkanolamides, and fatty amine oxides. Nonionic surfactants are usually prepared by the addition of ethylene oxide to compounds containing one or more active hydrogen atoms, such as alkylphenols, fatty alcohols, fatty acids, fatty mercaptans, fatty amines, fatty amides, and polyols. In this reaction (1.1) ethylene oxide adds to hydroxyl



$$ROCH_2CH_2OH + nH_2C\underset{O}{—}CH_2 \rightarrow ROCH_2CH_2(OCH_2CH_2)_nOH \qquad (1.1)$$

radicals by ring cleavage with regeneration of the hydroxyl group. This reaction is an addition without termination. In a mechanism of this kind, the growth of all the ethylene oxide adducts proceeds under conditions affording equal opportunities for all the hydroxyl groups to react and the resulting distributions are extremely narrow. Further modification of the ethylene oxide adducts may be carried out by reaction of the terminal hydroxyl groups with propylene oxide, inorganic acids, etc.

Because nonionic surfactants do not ionize in aqueous solution, they have many advantages as detergents, emulsifiers, and for chemical studies. The inverse temperature-solubility relation of polyoxyethylene surfactants indicates that the over-all solubility of these materials depends on the extent of hydration of the hydrophilic moiety. The water molecules are affixed to the ether oxygens by hydrogen bonding. Consequently, depending on the nature of the hydrophobic group, at least four to six ethylene oxide units per molecule are required to produce a water-soluble surfactant. Wide ranges of polyoxyethylene surfactants are being produced for a multitude of purposes, ranging from additives for drilling muds to pharmaceutical preparations, in which their wetting, foaming, dispersing, or emulsifying properties are utilized. In the last decade nonionic surfactants have gained important commercial success as actives in low-sudsing heavy-duty detergent formulations and in the form of their sulfated derivatives in light-duty dishwashing liquids. The latter use was prompted by the mildness of these products to the skin. The most recent requirement of ready biodegradability of all household detergent formulations has caused significant changes in the manufacture of the hydrophobes. In contrast, the hydrophobes of nonionic surfactants for industrial applications have remained unchanged.

A number of processes have been developed for the preparation of biodegradable nonionic surfactants. The biodegradability of these products is due to use of straight-chain α olefins as starting materials. In the initial process phenol was alkylated with straight-chain α olefins with subsequent oxyethylation. Other processes are being used for the preparation of highly effective intermediates, such as random secondary alcohols, Ziegler alcohols, and oxo primary alcohols. A detailed account of these processes is given in Chapter 4.

The contents of this book are organized into four parts, each representing a different discipline. Part I covers the organic chemistry of nonionic surfactants, including preparative procedures, physical properties, and applications. In the years since the initial synthesis of nonionic surfactants, a considerable amount of technical and patent literature has appeared, supplemented by a great number of technical bulletins indicative of the multitude of manufacturers and applications of these surfactants. Ample reference to this literature is made in Part I. The physical chemistry of nonionic surfactants, including the discussion of important theoretical aspects of colloid chemistry, is covered in Part II. In Parts III and IV methods of analysis and biological aspects of nonionic surfactants are reviewed.

Chapter 2 deals with the mechanism of ethylene oxide condensation. The kinetics of this reaction as a function of catalyst type and the resulting ethylene oxide chain-length distribution functions are demonstrated. The following ten chapters cover the preparation, physical properties, and applications of the principal commercially produced nonionic surfactants. Of these, Chapters 3 to 9 deal with ethylene oxide adducts with hydrophobes containing one or more active hydrogen atoms, such as alkylphenols, fatty alcohols, fatty acids, fatty mercaptans, fatty amines, fatty amides, and polyols, whereas Chapters 10 to 12, and also partly 9, deal with other types of nonionic surfactants. The preparation of the hydrophilic intermediate is given in Chapter 3 and that of the hydrophobic intermediates in each of the individual chapters.

Polyoxyethylene alkylphenols (Chapter 3) comprise the largest production volume among nonionic surfactants, with a wide scope of applications in both household and industrial products. In view of the growing importance of biodegradable nonionic surfactants in household products, the volume of production of polyoxyethylene alcohols (Chapter 4), in particular those based on straight-chain hydrophobes, is rapidly increasing. The use of natural products as intermediates has led to the development of a large number of inexpensive polyoxyethylene esters of fatty acids (Chapter 5), which have found many industrial applications. In contrast, polyoxyethylene mercaptans have found only a limited field of application (Chapter 6). Polyoxyethylene alkylamines are cationic in nature, but, on increasing the length of the ethylene oxide chain, acquire the properties of nonionic surfactants (Chapter 7). The alkanolamides are the simplest members of the polyoxyethylene alkylamides (Chapter 8). Fatty alkanolamides are presently the most important suds boosters for formulations containing anionic detergent actives and may be classified among the surfactants with the largest volume of production. Polyol surfactants include fatty acid esters of anhydrohexitols and their reaction products with ethylene oxide (Chapter 9), which constitute one of the most important class of emulsifiers. A major development in the field of nonionic surfactants has been the discovery that gradual variation of hydrophobicity can be brought about by the use of polyoxypropylene and polyoxybutylene "blocks." This has found practical application in the preparation of polyalkylene oxide block copolymers (Chapter 10). The functionality of these block copolymers depends on the initial starting material. Countless combinations and variations in composition of these polyalkylene oxide block copolymers are possible.

Nonionic surfactants may also be utilized as intermediates for the synthesis of ionic surfactants (Chapter 11). Depending on the length of the ethylene oxide chain, the nature of these compounds varies from that of an ionic to that of a nonionic surfactant. Miscellaneous nonionic surfactants of the polyoxyethylene and of other types, which have not been covered among the major commercial products in Chapters 3 to 11, are discussed in Chapter 12. This is followed by a treatment of the synthesis of homogeneous nonionic surfactants (Chapter 13). These well-defined compounds are of great importance in physicochemical investigations, as shown in Part II. For example, homogeneous samples of *n*-alkyl polyoxyethylene monoethers have been prepared by means of the Williamson ether synthesis, wherein *n*-alkyl bromide was reacted with the monosodium salt of the appropriate homogeneous polyoxyethylene glycol (1.2).

$$\mathrm{RBr} + \mathrm{NaO(CH_2CH_2O)_6H} \rightarrow \mathrm{RO(CH_2CH_2O)_6H} + \mathrm{NaBr} \qquad (1.2)$$

Papers pertaining to the physicochemical properties of nonionic surfactants began to appear in the literature only in the mid-1950s, in contrast to the much earlier start of the corresponding studies with ionic surfactants. This delay in exploring a field of growing industrial importance must be attributed to the fact that monodisperse materials are difficult to prepare. Their synthesis by the

Williamson synthesis has been reported for a chain length of one to six ethylene oxide units (Chapter 13). However, the preparation of homogeneous compounds with longer ethylene oxide chains involves considerable experimental difficulty. To cover a wide range of molecular structures, polydisperse nonionic surfactants have been used mainly since the mid-1950s to elucidate the physicochemical properties of nonionic surfactants in aqueous solution. In many instances, these samples were molecularly distilled to remove unreacted components and reduce the width of the molecular-weight distribution. Since 1960, papers discussing the use of homogeneous nonionic surfactants have also appeared in the literature. Furthermore, it has been demonstrated that the properties of a polydisperse material are close to those of a homogeneous compound having the composition of the mean.

Part II covers the physicochemical properties of both homogeneous and polydisperse nonionic surfactants. Data on the interfacial, solution, and bulk properties are examined. The characteristic properties of surfactants in solution, which render possible their practical applications, depend on the tendency of these compounds to be adsorbed at interfaces between the solution and the adjacent gaseous, liquid, or solid phases. Therefore, it appeared appropriate to discuss the properties of interfacial films of nonionic surfactants at the air/water, oil/water, and solid/water interfaces (Chapters 14, 18, and 19). Chapter 14 deals with spread and adsorbed films. The kinetics of film formation by adsorption is reviewed. The following three chapters cover micellar properties. The phenomenological aspects of micelle formation are discussed in Chapter 15, whereas the theoretical aspects are covered in Chapter 16. Critical micelle concentration and micellar size and shape are examined in terms of the nonionic surfactant structure, additives, and temperature (Chapter 15). Recent results pertaining to the effect of additives on changing the nature of the water structure, which is reflected in changes in micellar properties, are presented. The thermodynamics of noninteracting small systems recently developed by T. L. Hill has been applied to micelle formation of nonionic surfactants (Chapter 16). Hill's treatment has been extended to a consideration of mixed micellar systems. The relationship among the concentration of free molecules and micelles, the mean aggregation number and its temperature dependence, and the heats of micellization have been established. Finally, investigations of the micellar properties in ternary systems of nonionic surfactant, solvent, and solubilizate are reviewed in Chapter 17. A quantitative theory of solubilization is presented.

Some phenomena that are closely related to the interfacial properties of nonionic surfactants are discussed in Chapters 18 to 21. These are emulsification, dispersing, detergency, and foaming. One of the main applications of nonionic surfactants is in emulsion technology, where these surfactants now form the largest and fastest growing group of emulsifiers. The HLB (hydrophile-lipophile balance) system for the selection of nonionic emulsifiers for a specific system is explained in Chapter 18. The mechanism of detergency of nonionic surfactants is based principally on two phenomena: solubilization and dispersing.

Therefore, Chapter 20 on detergency is preceded by chapters on solubilization and on the stability of dispersions (Chapters 17 and 19). The factors determining the stabilization of solid dispersions by nonionic surfactants are discussed in terms of the adsorption at the solid/liquid interface, particle-particle interactions, and electrokinetic properties. Chapter 20 deals with "detergency values" of the various classes of nonionic surfactants, correlation between detergency and other factors, and some theoretical aspects of detergency. Nonionic surfactants as a class are usually considered low or moderate foamers, as shown in Chapter 21. Chapters 22 and 23 deal with the configuration of the ethylene oxide chain, which forms the hydrophilic moiety of most nonionic surfactants. Although polyoxyethylenes cannot be considered surfactants, their hydrodynamic studies provide background for current concepts of the configuration of the polyoxyethylene chain of nonionic surfactants in solution (Chapter 23). Our experimental knowledge of the configuration of the polyoxyethylene chain in bulk is based mainly on X-ray investigations (Chapter 22). Evidence is presented that, with increasing length, the original zig-zag configuration of the polyoxyethylene chain in nonionic surfactants acquires a large electrical moment in the coaxial direction, which may contract the main chain and transforms it to the meander configuration.

Part III covers the analytical chemistry of nonionic surfactants. In the initial chapter, 24, the reader is presented with an introduction to the subject. Methods of separating the nonionic surfactant from mixtures, classification, and, finally, quantitative determination are considered. The analysis of nonionic surfactants is discussed in terms of noninstrumental (Chapter 25), instrumental (Chapter 26), and separation methods (Chapter 27). Analytical procedures for the determination of trace quantities are included. Examples of structural characterization by instrumental methods, such as UV, IR, and NMR spectroscopy are cited. Among the separational methods, ion-exchange and chromatographic procedures are discussed. The latter include paper, thin-layer, gas, and gel-permeation chromatography.

In recent years nonionic surfactants have become increasingly important in pharmaceutical technology because of their well-known properties of solubilizing organic substances and of low toxicity. Similarly, nonionic surfactants have found wide applications as emulsifiers for food products. These applications require knowledge of the toxicity of these compounds, which is discussed in Part IV. This part covers the biology of nonionic surfactants, with Chapter 28 presenting a brief review of the entire field. Toxicological, metabolic, dermatological, and bacteriological aspects of nonionic surfactants are discussed. Finally, Chapter 29 deals with the biodegradability of nonionic surfactants. Relatively few papers on this topic have appeared so far in the literature, in contrast to the numerous papers published on ionic detergents. Thus, only a very brief summary of this subject could be given at the present time.

CHAPTER 4

POLYOXYETHYLENE ALCOHOLS

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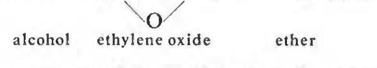
4.1. INTRODUCTION

Among the various types of nonionic surfactants of commercial importance, the products made by reacting an alcohol, particularly a straight-chain primary alcohol, with ethylene oxide have recently come to the forefront. This is the result of the recent emphasis on biodegradable surfactants, specifically nonionic surfactants. This chapter covers exclusively polyoxyethylene alcohols based on alcohols which are either straight- or branched-chain. A few polyoxyethylene alcohols based on other types of alcohols are discussed in Section 12.9.

The fundamental chemical reaction by which alcohols are converted to nonionic surfactants consists of adding ethylene oxide to the hydroxyl group of the alcohol to form an ether:



$$\underset{\text{alcohol}}{ROH} + \underset{\text{ethylene oxide}}{H_2C\!-\!\!\!\underset{O}{}\!\!-\!CH_2} \rightarrow \underset{\text{ether}}{ROC_2H_4OH} \qquad (4.1)$$

One mole of this ether as expressed in (4.1) is then further reacted with additional ethylene oxide to produce polyoxethylene ethers, as shown in (4.2),

$$ROC_2H_4OH + nH_2C\!-\!\!\!\underset{O}{}\!\!-\!CH_2 \rightarrow RO(C_2H_4O)_nC_2H_4OH \qquad (4.2)$$

where $n + 1$ is the average number of moles of ethylene oxide added to 1 mole of a given alcohol. In Chapter 2, as well as later on in this chapter, further details on the kinetics of the reaction are given.

The synthesis of the hydrophobic intermediates, i.e., the relevant primary and secondary alcohols, is considered in Section 4.2, followed by that of the corresponding polyoxyalkylene alcohols in Section 4.3. The synthesis of the hydrophilic intermediates, i.e., ethylene or propylene oxide, has been given in Chapter 3. In addition, the properties and application of the polyoxyethylene alcohols are discussed in Sections 4.4 and 4.5. The growing commercial importance of these nonionic surfactants may be assessed from the large number of products now being marketed and listed in Section 4.4,B.

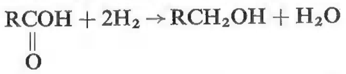
4.2. SYNTHESIS OF THE HYDROPHOBIC INTERMEDIATES

A. Primary Alcohols

1. Natural Sources

The surface-active properties of primary straight-chain fatty alcohols derived from animal and vegetable oils have established a definite and sizeable market for these alcohols in the preparation of synthetic detergents. Although there are numerous routes for obtaining alcohols from natural sources, only two reduction processes are commercially being used: (a) hydrogenolysis of either fats or fatty acids and (b) reduction of fatty esters with an alcohol and an alkali metal (*1–4*). The two processes give somewhat different properties, depending upon the starting raw material and the purity of alcohol desired. The two processes can be considered competitive only over a rather narrow range of application.

Hydrogenolysis is the reduction of a fatty acid, anhydride, ester of fatty acid or metallic salt of fatty acid to yield a fatty alcohol. This reaction is carried out at high temperatures (50 to 350°C) and pressures (10 to 200 atm) in the presence of a catalyst. The equation for the reaction is



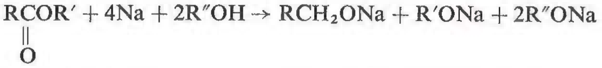
$$\underset{\underset{\displaystyle O}{\|}}{RCOH} + 2H_2 \rightarrow RCH_2OH + H_2O \qquad (4.3)$$

The hydrogenolysis of fatty acids and their derivatives was first described in 1930 by Adkins et al. (*5,6*). Copper chromite catalysts were used initially; however, at present, the catalyst combinations are too numerous to discuss here (*7–40*).

In general, the conditions for hydrogenolysis vary from 100 to 200 atm at 200 to 350°C, although above 300°C the major products are hydrocarbons (*41*). The DeNora hydrogenolysis process is now in commercial use (*42*). This process uses copper chromite as a catalyst, and fatty acids are the feed stock normally used.

The sodium reduction process is more versatile and simpler than hydrogenolysis. Both saturated and unsaturated esters are reduced to the corresponding alcohols without modifying the basic process. Sodium reduction is specific for the ester grouping in the presence of unsaturation, except in the case of α,β-unsaturated esters.

Sodium reductions are conducted at atmospheric pressure in conventional mild-steel equipment and involve simply the addition of a solution of dry and neutral ester, alcohol, and solvent to a stirred dispersion or suspension of metallic sodium in an inert solvent. At the completion of this rapid and exothermic reaction, the resulting mixture is quenched or hydrolyzed by adding it to water. The over-all reaction can be elucidated by the equations



$$R\underset{\overset{\|}{O}}{C}OR' + 4Na + 2R''OH \rightarrow RCH_2ONa + R'ONa + 2R''ONa \qquad (4.4)$$

$$RCH_2ONa + R'ONa + 2R''ONa + 4H_2O \rightarrow RCH_2OH + R'OH + 2R''OH + 4NaOH \qquad (4.5)$$

Details on this reduction technique are given by Hansley (*43*) and Kastens and Peddicord (*44*).

The sodium reduction process is limited to esters of fatty acids but not necessarily to glyceride esters. The reduction of glyceride esters yields by-product glycerol in the form of a caustic-glycerol solution. Fortunately, other esters are suitable for reduction and can be prepared readily from glycerides.

2. Synthetic Sources

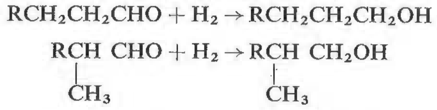
a. Oxo Process

The oxo process is an outgrowth of the Fisher-Tropsch catalytic synthesis of higher hydrocarbons and oxygenated compounds from carbon monoxide and hydrogen. The oxo reaction involves the addition of carbon monoxide and hydrogen to an olefin in the presence of a cobalt catalyst to produce an aldehyde containing one carbon atom more than the starting compound. The general equation may be represented as

$$\begin{aligned} RCH{=}CH_2 + CO + H_2 &\rightarrow RCH_2CH_2CHO \\ RCH{=}CH_2 + CO + H_2 &\rightarrow RCH(CHO)CH_3 \end{aligned} \qquad (4.6)$$

The reaction may be considered the addition of a hydrogen atom and a formyl group across the double bond. This reaction is properly called hydroformylation.

The oxo reaction for the synthesis of alcohols is usually a two-step process (*45*). The second step consists of the hydrogenation of the aldehyde made in the first step [Eq. (4.6)] according to the reaction



$$\begin{aligned} RCH_2CH_2CHO + H_2 &\rightarrow RCH_2CH_2CH_2OH \\ \underset{\overset{|}{CH_3}}{RCH}\ CHO + H_2 &\rightarrow \underset{\overset{|}{CH_3}}{RCH}\ CH_2OH \end{aligned} \qquad (4.7)$$

Hydroformylation takes place at superatmospheric pressures. The carbon monoxide and hydrogen are usually supplied as "synthesis gas" (*46*) in a 1:1 mole ratio. The conditions for the reaction vary widely, depending on the results desired and the olefinic molecule used. Three fundamental concepts govern the specific conditions—catalyst stability, reaction rate required, and products or isomers desired. The reaction can occur from room temperature to 220°C and from slightly above atmospheric pressures to about 10,000 psi. Most commercial units operate in the range of 150 to 200°C and from 2500 to 6500 psi.

Compounds of cobalt are the usual hydroformylation catalysts. There are numerous patent references to the use of cobalt carbonyl compounds as well as other carbonyl compounds. Several excellent reviews of the kinetics and mechanism of cobalt carbonyl have been published (*47–50, 188–191*).

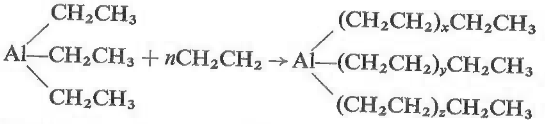
Oxo products have been used as industrial chemicals since the 1950s. Mixtures of isomeric alcohols are sold under the generic terms of "primary amyl alcohol," "isohexanol," "isodecanol," "tridecanol," and "hexadecyl alcohol" (*51,52*). The last three are of great importance to the surfactant industry, since they can be used as building blocks for the preparation of nonionic surfactants.

Most of the information reported in the literature deals with the use of a branched-chain olefin as the raw material for reaction with carbon monoxide and hydrogen (*51,52*). However, with the great emphasis on biodegradable detergents, commercialization of straight-chain primary alcohols based on α olefins appears to be a reality (*53,54*).

b. Ziegler Process

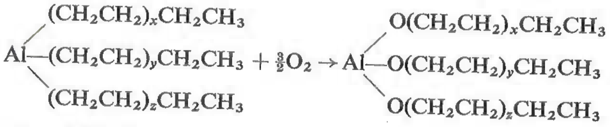
A new method of producing straight-chain alcohols on a commercial basis was recently instituted by Continental Oil Company (*55*). This process is based on the finding of K. Ziegler, the pioneer of organic aluminum chemistry.

The first step in the Ziegler process (*56–62*) is the reaction of ethylene with triethyl aluminum under controlled conditions of about 100°C and 800 to 1200 psi to obtain a high-molecular-weight trialkyl aluminum product. This is represented by (4.8). The alkyl aluminum is then oxidized with air forming an



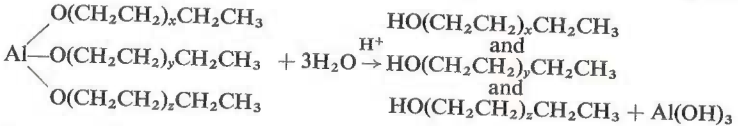
$$\mathrm{Al}\left<\begin{array}{l}\mathrm{CH_2CH_3}\\ \mathrm{CH_2CH_3}\\ \mathrm{CH_2CH_3}\end{array}\right. + n\mathrm{CH_2CH_2} \rightarrow \mathrm{Al}\left<\begin{array}{l}\mathrm{(CH_2CH_2)_xCH_2CH_3}\\ \mathrm{(CH_2CH_2)_yCH_2CH_3}\\ \mathrm{(CH_2CH_2)_zCH_2CH_3}\end{array}\right. \tag{4.8}$$

alcoholate (4.9). This aluminum alcoholate is then hydrolyzed with a dilute



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{(CH_2CH_2)_xCH_2CH_3}\\ \mathrm{(CH_2CH_2)_yCH_2CH_3}\\ \mathrm{(CH_2CH_2)_zCH_2CH_3}\end{array}\right. + \tfrac{3}{2}\mathrm{O_2} \rightarrow \mathrm{Al}\left<\begin{array}{l}\mathrm{O(CH_2CH_2)_xCH_2CH_3}\\ \mathrm{O(CH_2CH_2)_yCH_2CH_3}\\ \mathrm{O(CH_2CH_2)_zCH_2CH_3}\end{array}\right. \tag{4.9}$$

acid, H_2SO_4, to yield the straight-chain primary alcohol according to (4.10).



$$\mathrm{Al}\left<\begin{array}{l}\mathrm{O(CH_2CH_2)_xCH_2CH_3}\\ \mathrm{O(CH_2CH_2)_yCH_2CH_3}\\ \mathrm{O(CH_2CH_2)_zCH_2CH_3}\end{array}\right. + 3\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \begin{array}{c}\mathrm{HO(CH_2CH_2)_xCH_2CH_3}\\ \text{and}\\ \mathrm{HO(CH_2CH_2)_yCH_2CH_3}\\ \text{and}\\ \mathrm{HO(CH_2CH_2)_zCH_2CH_3} + \mathrm{Al(OH)_3}\end{array} \tag{4.10}$$

A Poisson mathematical relationship governs the distribution of the straight-chain alcohols made via the above route. However, proper adjustment of reaction conditions easily shifts the alcohol-chain-length distribution to a higher or lower peak (*59*).

The lower alcohols ($C_6H_{13}OH$ through $C_{10}H_{21}OH$) go into the manufacture of phthalate and adipate esters for use as plasticizers. The higher alcohols ($C_{12}H_{25}OH$ through $C_{20}H_{41}OH$) are being used in the detergent industry. Normally, these alcohols are not sold as a single-carbon-number fraction but rather as a blend of several alcohols (*55,59,63*).

c. *Hydrolysis of Alkyl Halides*

Although it is not known that the manufacture of primary alcohols via the hydrolysis of alkyl bromides has been commercially exploited, the literature contains several references (*64–68*) on this reaction which is anti-Markownikoff's rule [(4.11) and (4.12)]. This reaction is carried out in the presence of a catalyst, either peroxides or ultraviolet light. Also, the hydrohalogenation only works with HBr and not with HCl.

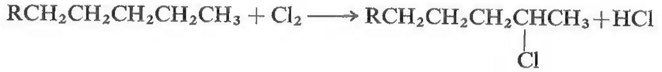
$$\mathrm{RCH{=}CH_2 + HBr \longrightarrow RCH_2CH_2Br} \tag{4.11}$$

$$\mathrm{RCH_2CH_2Br \xrightarrow{H_2O} RCH_2CH_2OH + HBr} \tag{4.12}$$

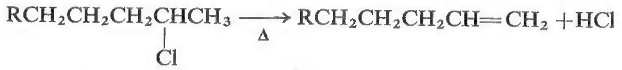
B. Secondary Alcohols

1. Hydration of α Olefins

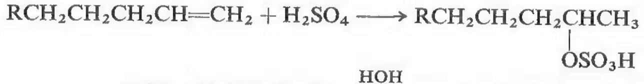
Considerable work has been reported (*69–74*) on preparing alcohols by hydration of α olefins. The olefin for reaction can be obtained by dehydrochlorination of chloroparaffins, which one obtains from the chlorination of normal paraffins. The following equations illustrate this procedure:



$$\mathrm{RCH_2CH_2CH_2CH_2CH_3 + Cl_2 \longrightarrow RCH_2CH_2CH_2\underset{\underset{Cl}{|}}{C}HCH_3 + HCl} \tag{4.13}$$



$$\mathrm{RCH_2CH_2CH_2\underset{\underset{Cl}{|}}{C}HCH_3 \xrightarrow[\Delta]{} RCH_2CH_2CH_2CH{=}CH_2 + HCl} \tag{4.14}$$



$$\mathrm{RCH_2CH_2CH_2CH{=}CH_2 + H_2SO_4 \longrightarrow RCH_2CH_2CH_2\underset{\underset{OSO_3H}{|}}{C}HCH_3} \tag{4.15}$$

$$\mathrm{RCH_2CH_2CH_2\underset{\underset{OSO_3H}{|}}{C}HCH_3 \xrightarrow{HOH} RCH_2CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3 + H_2SO_4} \tag{4.16}$$

In (4.13) the chlorine actually adds itself to any carbon atom rather than just the α and β carbon used for illustration purposes. Therefore, as shown in (4.14), one also obtains unsaturation along the entire carbon length. Thus, in (4.16) the hydroxyl group may be attached to any of the non-terminal carbon atoms.

One method of obtaining the hydroxyl group on the second carbon atom is to use an α olefin as illustrated in Eq. (4.15). These α olefins are now being produced commercially by the thermal cracking of petroleum waxes (*53*).

2. Oxidation of Paraffins

The oxidation of paraffins has been referred to in the literature a number of times (*75,76*). A simplification of the reaction is

$$RH + (O) \rightarrow ROH \qquad (4.17)$$

With this process one obtains a mixture of secondary alcohols, and the distribution of these alcohols is based on the kinetic equilibrium of the reaction. Also, if the rate of oxidation is uncontrolled, the formation of by-products (e.g., acids and esters) results. A ready source of raw materials are paraffins separated from kerosene by the molecular-sieve process (*53*).

3. Other Routes

Several other possible routes for making secondary alcohols are worth mentioning.

a. Halogenation of Paraffins and Hydrolysis of Halides

$$RH + \underset{(Cl_2)}{X_2} \rightarrow RX + HX\uparrow \qquad (4.18)$$

$$RX + HOH \rightarrow ROH + HX\uparrow \qquad (4.19)$$

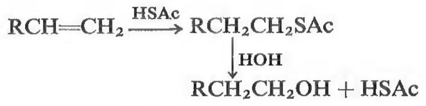
This route gives predominantly a mixture of secondary alcohols because of the difficulty in controlling the reaction. As discussed previously, to obtain the 1-alkylhalide it is necessary to react HBr with an α olefin in the presence of a catalyst (*69,70*).

b. Direct Hydration of Olefins

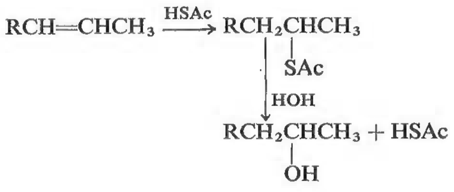
Olefins in the C_2 to C_4 chain length have been hydrated directly with water at high temperatures (300 to 500°C) and high pressures (up to 1000 atm) over silica and aluminum (*77*).

c. Addition of Thioacetic Acid to Olefin and Hydrolysis

A recent publication (*78*) showed that the addition of thioacetic acid to an olefin using ultraviolet light as a catalyst gave a primary alcohol if the olefin had the double bond in the 1-2 position and a secondary alcohol if it were an internal olefin. Equations (4.20) and (4.21) illustrate this method of synthesis.



$$RCH{=}CH_2 \xrightarrow{HSAc} RCH_2CH_2SAc \xrightarrow{HOH} RCH_2CH_2OH + HSAc \qquad (4.20)$$



$$RCH{=}CHCH_3 \xrightarrow{HSAc} RCH_2\underset{SAc}{CH}CH_3 \xrightarrow{HOH} RCH_2\underset{OH}{CH}CH_3 + HSAc \qquad (4.21)$$

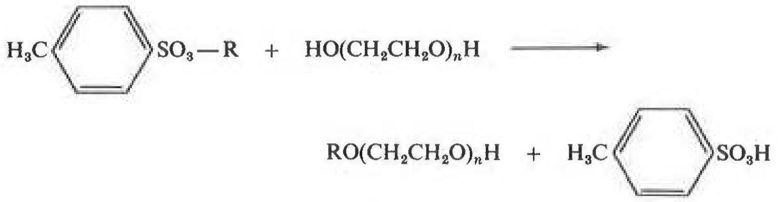
4.3. PREPARATION OF POLYOXYETHYLENE ALCOHOLS

Polyoxyethylene alcohols have been prepared by the following methods:

1. Etherification by reaction of alkyl bromide and monosodium salt of polyethylene glycol, commonly known as the Williamson synthesis (*79–83*):

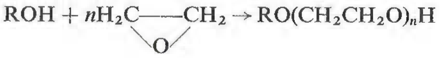
$$RBr + NaO(CH_2CH_2O)_nH \rightarrow NaBr + RO(CH_2CH_2O)_nH \qquad (4.22)$$

2. Etherification by reaction of alkyl-*p*-toluene sulfonate and polyethylene glycol (*84,85*):



(4.23)

3. Etherification by reaction of alcohol and ethylene oxide (*86–88*):



$$ROH + nH_2\underset{\diagdown O \diagup}{C\text{——}C}H_2 \rightarrow RO(CH_2CH_2O)_nH \qquad (4.24)$$

Methods 1 and 2 were usually used for the synthesis of alkyl polyoxyethylene alcohols of homogeneous ethylene oxide chain-length distribution. A detailed account of both these methods is given in Chapter 13. For commercial production of nonionic surfactants, method 3 is much more widely used because of the low cost and availability of the raw materials, alcohol and ethylene oxide, and the relative simplicity in processing. Therefore, most of the investigations reported in the literature have been devoted to the study of the reaction of an alcohol with ethylene oxide.

A. Ethylene Oxide Condensation

The oxyethylation of an alcohol was first reported by a group of chemists in I.G. Farbenindustrie (*89*), who condensed methanol, ethanol, propanol, and isobutanol with ethylene oxide using an acidic or basic catalyst. Later Schoeller and Wittwer (*90*) also successfully achieved reaction between a long-chain alcohol such as octadecyl alcohol and ethylene oxide. Since then, a number of patents have been issued concerning this reaction, both in this country and abroad. Recently, the development of the biodegradable nonionic surfactants further enhanced interests in polyoxyethylene linear alcohols because of their favorable biodegradability.

In spite of the findings that the addition of alcohols and ethylene oxide can be carried out in the presence of either an acidic catalyst or a basic catalyst (*86–88, 91,92*) the base-catalyzed addition of ethylene oxide to alcohol is by far the most commonly used method for the manufacture of polyoxyethylene alcohols.

1. Catalyst

The rate of reaction of tridecyl alcohol, a branched-chain primary alcohol obtained from oxo process, and ethylene oxide was studied extensively by

Satkowski and Hsu (*92*). Tridecanol does not react with ethylene oxide by itself at 195 to 200°C under a slight positive pressure (9 to 40 cm Hg). In the presence of potassium hydroxide, sodium hydroxide, sodium methoxide, sodium ethoxide, or sodium, tridecyl alcohol condenses smoothly with ethylene oxide. The rate of the addition of ethylene oxide was found to be practically the same at 195 to 200°C for all the catalysts mentioned (Figure 4.1). However, at a lower temperature, 135 to 140°C, there is a difference in the rate of addition of ethylene oxide among these catalysts (Figure 2.5). It was shown that the increased effectiveness of basic catalysis increases with increased basicity of the catalyst (see Section 2.4,B,3,b). Sodium hydroxide was less effective than the other catalysts (Figure 2.6). Also, potassium hydroxide shows a slightly delayed action at the beginning

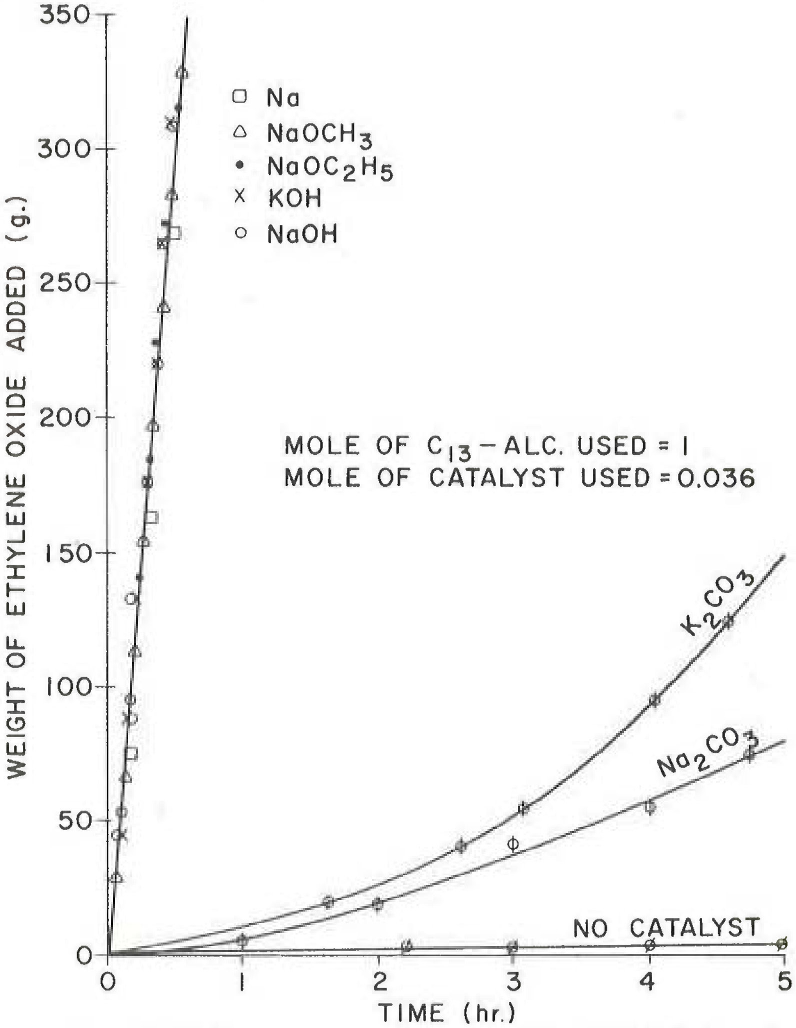
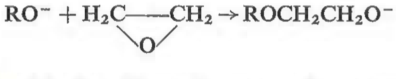


Fig. 4.1. Effect of catalyst on the rate of polyoxyethylation (195 to 200°C) (*92*).

of the reaction. These phenomena led the authors to believe that the first step of the oxyethylation of alcohol is similar to that in the oxyethylation of phenols postulated by Boyd and Marle (*93*), namely, the reaction between the ethylene oxide and the alkoxide ion, RO^-. This postulate was also accepted by Schechter and Wynstra (*94*) in their study of glycidyl ether reactions:



$$RO^- + H_2C\underset{O}{\overline{\quad}}CH_2 \rightarrow ROCH_2CH_2O^- \qquad (4.25)$$

The formation of alkoxide ion from these catalysts can be presented by the equations

$$ROH + R'OM \rightleftharpoons ROM + R'OH \qquad (4.26)$$

$$ROM \rightleftharpoons RO^- + M^+ \qquad (4.27)$$

$$R' = H, CH_3, C_2H_5; \quad M = Na, K$$

Equations (4.26) and (4.27) are considered to be reversible (*95*). Thus, (4.26) can be shifted to its right by a complete removal of R'OH. Since methanol and ethanol have a lower boiling point than water, they can be more easily removed at a moderate temperature. Also, because of the greater basicity of CH_3O^- and $C_2H_5O^-$ in comparison with HO^-, reaction (4.26) will go faster and further to completion. Therefore, the concentration of ROM will then be expected to be lower in the case of sodium hydroxide than in sodium methoxide or sodium ethoxide. This is shown in Figures 2.5, 2.6, and 4.2. At the high reaction temperature this difference between the various catalysts becomes less important and they will be expected to act similarly. In comparing potassium hydroxide and sodium hydroxide according to Richards and Rowe (*96*), the first compound (KOH) has a higher basicity than the second (NaOH). Hence, at a lower temperature the ionization of ROM will be expected to go further toward completion for the potassium salt than for the sodium salt. Also, the reversible reaction between potassium hydroxide and tridecyl alcohol explains the delay in the reaction at the beginning of the oxyethylation. As the tridecoxide ions are slowly reacted with ethylene oxide, the equilibrium of this reversible reaction maintains the concentration of tridecoxide ions substantially constant while the concentration of the oxyethylated tridecoxide ions is increasing. Because of this increase in the total concentration of reactive ions (tridecoxide ion and oxyethylated tridecoxide ion), the rate of condensation increases rapidly. Similarly, this phenomenon was also observed with sodium hydroxide.

Potassium carbonate has been applied successfully as a catalyst for the oxyethylation of acids (*97*). However, it was found to be unsatisfactory in catalyzing the oxyethylation of tridecyl alcohol. Karabinos et al. (*86*) also found this same result in the oxyethylation of other alcohols. This is to be expected because the reaction between alcohol and potassium carbonate or sodium carbonate will not readily form the desired alkali alkoxide, since the alkoxide ion is more basic than the carbonate ion.

To further substantiate the necessity of the tridecoxide ion in this oxyethylation reaction, metallic sodium was tried instead of sodium hydroxide. Ethylene oxide was introduced into the alcohol solution after all the metallic sodium was reacted and the hydrogen had been vented out of the system. The rate of the reaction was found to be the same as the others. The only products formed from the reaction of metallic sodium and tridecyl alcohol are sodium tridecoxide and hydrogen, which was liberated from the system before oxyethylation. Therefore, the tridecoxide ion is the important reacting species in the oxyethylation, according to the equations

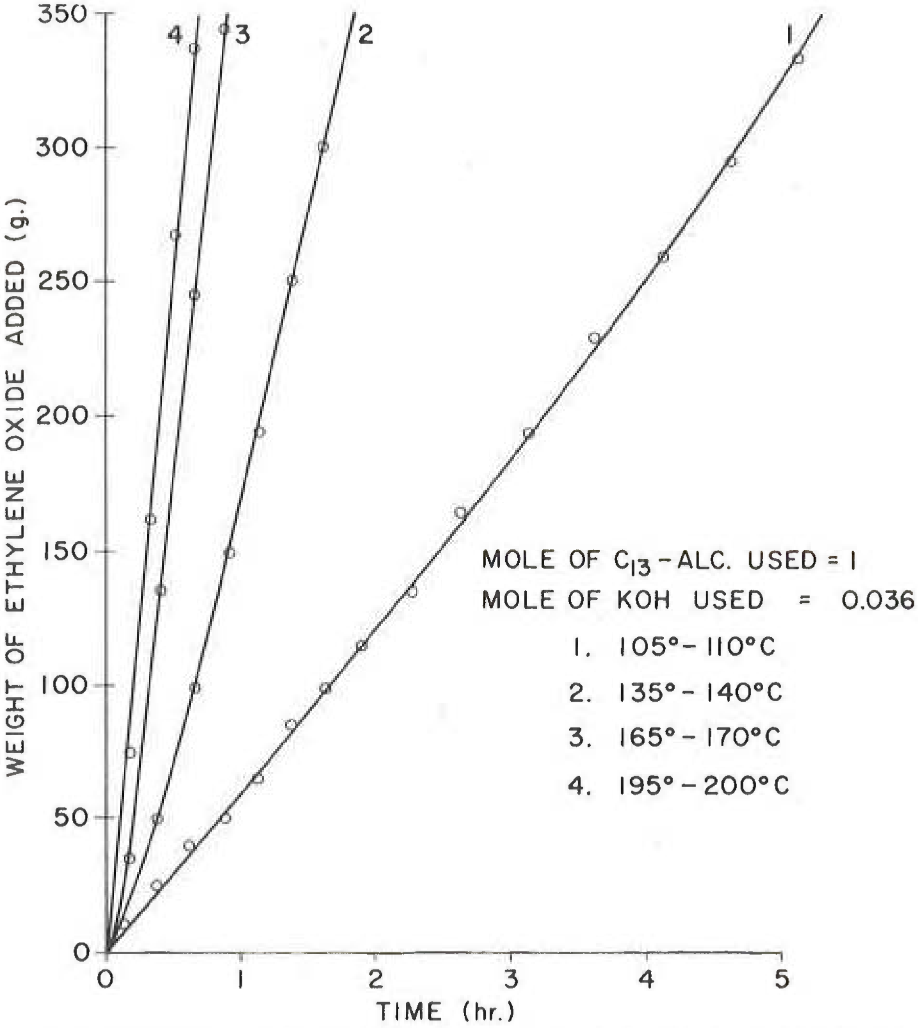


Fig. 4.2. Effect of temperature (with KOH as catalyst) on the rate of polyoxyethylation (*92*).

$$2C_{13}H_{27}OH + 2Na \rightarrow 2C_{13}H_{27}ONa + H_2 \qquad (4.28)$$

$$C_{13}H_{27}ONa \rightleftharpoons C_{13}H_{27}O^- + Na^+ \qquad (4.29)$$

2. Catalyst Concentration

The concentration of catalyst plays an important role. The rate of the reaction increases with the catalyst concentration (Figure 2.7). However, as the concentration of potassium hydroxide was progressively doubled from 1.8 mole per cent to 3.6, 7.2, and 14.3 mole per cent, the rate of the reaction did not increase accordingly. It increased more at low concentrations than at high concentrations. This indicates that the ethylene oxide molecule reacts with alkoxide ion rather than the nonionized metallic alkoxide, because the degree of ionization of metallic alkoxide is higher at lower concentration compared with that at higher concentration.

3. Temperature

Since the temperature of the reaction was an important factor in the rate of the addition of ethylene oxide, several temperatures were examined with different catalysts. The results are shown in Figures 2.5 and 4.2. The rate of the addition of ethylene oxide increases with the reaction temperature. However, the relationship is not linear. The rate of the addition of ethylene oxide at the same temperature increment is greater at higher temperatures than at lower temperatures. The disappearance of the initial delayed reaction when potassium hydroxide and sodium hydroxide were used at high temperature can be explained by the findings of Engel, Lescoeur, Williams, and Bost (*98*)—that the reaction between alcohol and potassium or sodium hydroxide is completed more rapidly at high temperatures.

4. Pressure

According to the mass-action law, one will expect that the pressure of ethylene oxide will have some effect on the rate of the reaction because the pressure of ethylene oxide is directly proportional to the concentration of ethylene oxide present in the system. However, in this low-pressure study it was found not to be large. As shown in Figure 4.3 there is not much difference in the reaction rate at 135 to 140°C between 7.5 and 15 cm of mercury. The speed of the reaction definitely increases as the pressure is raised to 30 and 45 cm Hg. However, in higher-pressure studies it was found that the rate of the addition of ethylene oxide increases considerably with the increasing of ethylene oxide pressure.

5. Structure

It has been pointed out that the initial reaction species is believed to be alkoxide ion. Therefore, the structure of the alkoxide ion will have some effect on the rate of oxyethylation. In other words, one will expect a difference in reaction rate between two different alcohols. From the results shown in Figures 4.4 and 4.5, a generalization about the effect of alcohol structure can be drawn. That is, in a homologous series the rate of the oxyethylation of an alcohol decreases as the carbon-chain length in the alcohol increases. For isomeric alcohols under the alkali-catalyzed conditions, the rate of oxyethylation is in the order, primary > secondary > tertiary alcohol. The effect of the position of attachment of the hydroxyl group of alcohol on the reactivity with ethylene oxide was more pronounced than that from changes in the size of the alkyl group or the introduction of branched chains other than those on the α carbon (*91,99*).

The product from the reaction of alcohol and ethylene oxide is a mixture of monoalkylpolyethylene glycol ethers of various ethylene oxide chain lengths. It is of interest to observe the effect of the difference in reactivities of the starting

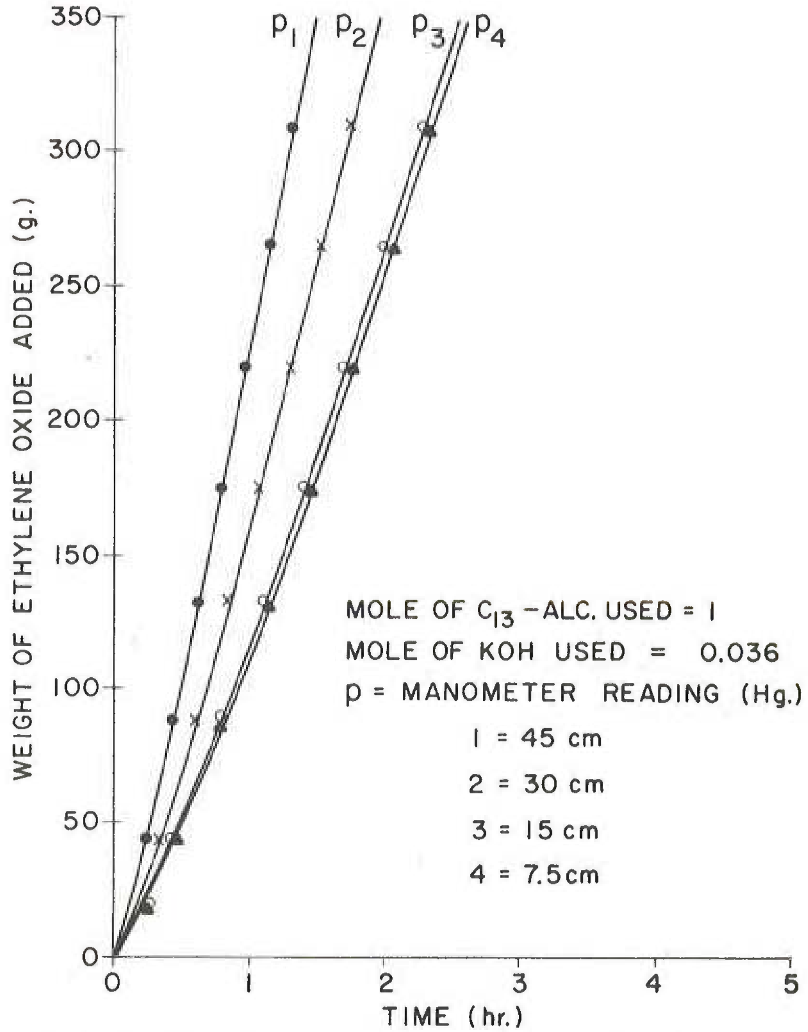


Fig. 4.3. Effect of ethylene oxide pressure on the rate of polyoxyethylation (135 to 140°C) (*92*).

alcohol and its monoglycol ether during the base-catalyzed oxyethylation on the distribution of product (*91,100,101*). After one or more units of oxyethylene have been added to the alcohol molecule or alkoxide ion, the close environment around the reacting center (—OH or —O$^-$) becomes very similar. The reactivity of these molecules or ions should then be approximately the same. This was confirmed experimentally. Figure 4.6 shows that the ethylene oxide consumption (g/min) became constant after 8 or 9 moles of ethylene oxide per mole of alcohol was introduced. The low consumption at the beginning of the reaction is due to the existence of the less-active unreacted alcohol.

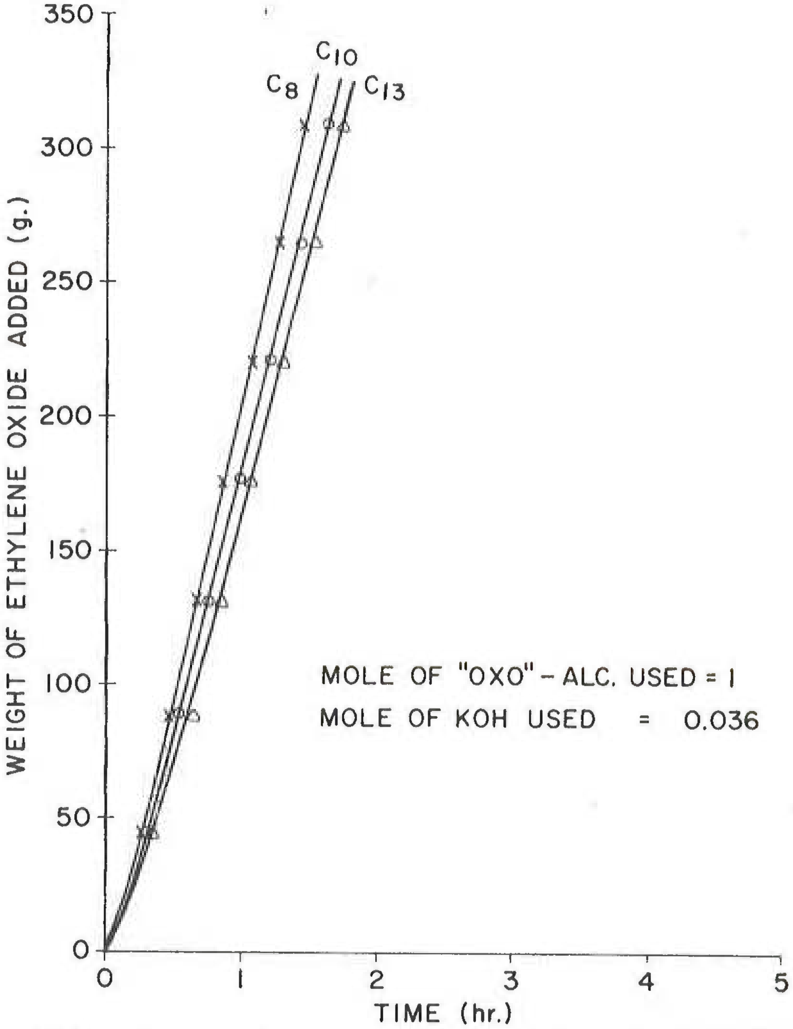


Fig. 4.4. Effect of oxo alcohols on the rate of polyoxyethylation (135 to 140°C) (*92*).

For the oxyethylation of the secondary and tertiary alcohols using alkali catalyst, the product contains a much wider distribution of the ethylene oxide chain length than that from the primary alcohol because of the considerable difference in reactivities of the secondary and tertiary alcohols and their respective ethylene oxide adducts.

As has been shown in Chapter 2, the composition of the ethylene oxide adducts resulting from the base-catalyzed oxyethylation of alcohol approaches the distribution predicted by Wrigley et al. (*101*), Weibull and Nycander (*102*), Puthoff and Benedict (*103*), and by Karabinos and Quinn (*104*).

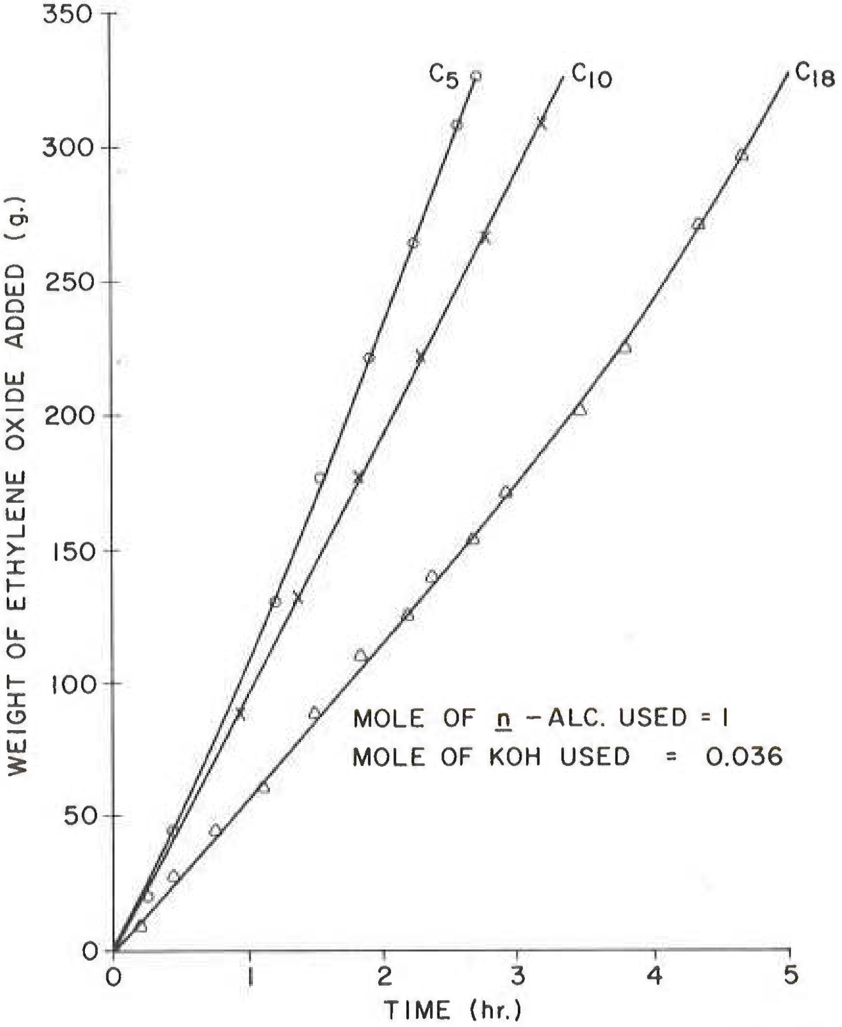


Fig. 4.5. Effect of *n*-alcohols on the rate of polyoxyethylation (105 to 110°C) (*92*).

For acid-catalyzed oxyethylation of primary alcohol, which proceeds by different mechanism from the base-catalyzed reaction, the product composition follows approximately the Flory-Poisson distribution (*91,105–108*).

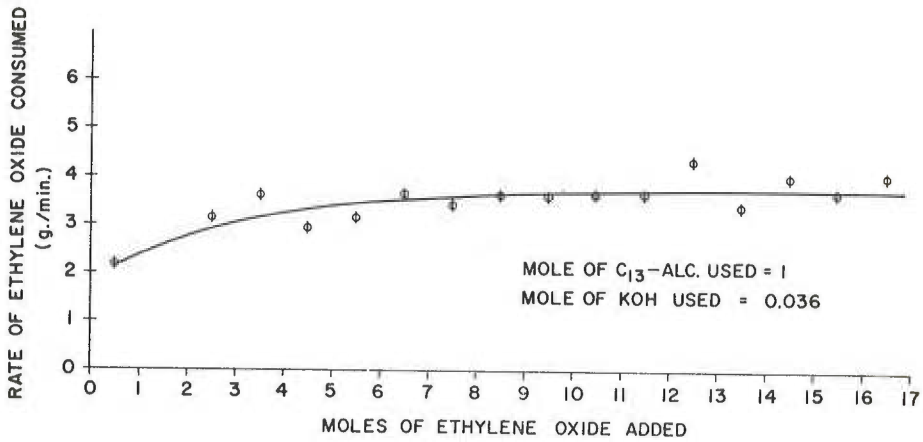


Fig. 4.6. Rate of ethylene oxide consumption (135 to 140°C) (*92*).

B. Production of Polyoxyethylene Alcohols

The important raw material ethylene oxide is flammable, toxic, and forms explosive mixtures with air. It can undergo exothermic decomposition (see Chapters 3 and 28). Therefore, safety precautions in handling it should be strictly observed (*109–112*).

Because of the ease of controlling the reaction and the consequent product composition, and the ease of adapting the various starting hydrophobes for oxyethylation, batch operation rather than continuous operation is generally preferred for the commercial production of monoalkylpolyethylene glycol ethers (*113–119*).

All equipment is explosion-proof and properly grounded to prevent the creation of static electricity. The reaction system is usually constructed from stainless steel, or glass-lined steel if the product color is important. Otherwise, low-cost carbon-steel equipment can be used. Temperature and pressure of the reactor are usually controlled automatically. Other instrumentation is designed so that the temperature and pressure controllers are interlocked with the ethylene oxide-feeding system. In case the temperature or the pressure exceeds a preset figure, the ethylene oxide feed valves are closed automatically. Check valves are provided in the feeding line to prevent back flow from the reactor to the ethylene oxide supply tank, wherein an uncontrolled reaction, which is extremely hazardous, can take place. The reaction of alcohol and ethylene oxide is highly exothermic; thus adequate cooling should be provided for the reaction system.

Mixing, heating, and cooling of the reaction mixture may be accomplished by using a multiimpeller agitative system to promote reaction rate by intimate contact of the liquid phase and the ethylene oxide-vapor phase and to increase the heat transfer by circulating the reaction mixture around cooling and heating coils. Patent literature (*120*) also shows that the intimate contact of liquid reaction phase with the gaseous ethylene oxide phase can be achieved by spraying the liquid in finely divided state into an absorption zone of the reactor which is continuously supplied with ethylene oxide at a rate to maintain a constant pressure in the reactor. Removal of the heat of reaction is accomplished by circulating the reaction mixtures through an external heat exchanger and then recycling back to the absorption zone of the reactor.

The procedure for the commercial production of polyoxyethylene alcohols by batch operation generally consists of the following steps.

1. Preparation of Alcohol-Catalyst Mixture

The alcohol and the alkali catalyst are transferred to a weigh tank, where they are weighed, heated, and dried. The catalyst usage is ranged from 0.1 to 2 per cent by weight of the alcohol charge.

2. Reaction of Alcohol and Ethylene Oxide

The weighed charge of the alcohol-catalyst mixture is transferred to the reactor. The reactor is evacuated and purged thoroughly with an inert gas such as nitrogen. Nitrogen pressure is kept in the reactor at all times. The partial pressures are adjusted so that the explosive limits of the gas mixture are not exceeded (*109–112*).

The alcohol-catalyst mixture is heated to the reaction temperature in the range of 120 to 200°C. Ethylene oxide supplied from a weigh tank is admitted slowly to the reactor until the desired pressure is reached, usually in a range of 20 to 100 psig. Initiation of the reaction is indicated by a rise in temperature, and cooling is provided to control the reaction temperature. If there is over-cooling, the reaction can stop and lead to absorption of ethylene oxide without reaction. Such an occurrence constitutes a safety hazard, as the concentration of ethylene oxide is built up in the reactor and sudden rapid reaction with excessive heating can occur. The reaction temperature and pressure are controlled until the desired weight of ethylene oxide is added. Then, the ethylene oxide supply to the reactor is discontinued. After the reaction is completed as indicated by the dropping of the pressure to a constant level, the batch is cooled.

3. Removal of Catalyst

The batch from the reactor is transferred to a treatment tank, where the catalyst may be converted to salts by using organic or inorganic acids (*121,122*) and removed by filtration. Also, decolorization treatment of the product may be incorporated at this stage if required (*121,123,124*).

The finished product is then drummed or loaded to tank cars for shipment.

The analyses generally used for the quality and process controls of the polyoxyethylene alcohols are the determination of hydroxyl number, color, pH, ash content, water content, and cloud point.

C. Propylene Oxide Condensation

The reaction conditions for preparing the propylene oxide adduct of an alcohol will vary from one commercial unit or commercial product to another. However, basically, all the processes known to the art are quite similar. An excellent review of commercial production units is given by Malkemus (*113*). In addition, operating procedures initially used in Germany are found in a series of PB and BIOS reports (*114–118,125*). Another review article on a versatile commercial unit is given by Gushee and Scherr (*126*). Additional references are cited (*111,127–132*).

There have been several references on continuous processes for propylene oxide reactions (*119,133,134*). However, the standard procedure is to make these adducts by batch operations to ensure a finished product of the desired composition.

In most commercial units, the alcohol plus the catalyst (alkaline earths or alcoholic alkali) are heated to the desired reaction temperature. The propylene oxide is then added to the hydrophobic base plus catalyst at a rate dependent upon the heat-exchanger capacity of the unit, since the reaction with propylene oxide is exothermic (approximately 20 kcal/g-mole). The addition of the propylene oxide is continued until the proper ratio of propylene oxide to the alcohol is obtained.

As with ethylene oxide, all the equipment which handles propylene oxide should be explosion-proof and adequately grounded (*109–111,127*). The normal operating temperature for the reaction is 150 to 200°C, and the reaction pressure is normally 25 to 75 psig.

After the reaction with propylene oxide is completed, the catalyst used for the condensation is normally removed. The common mineral acids such as H_2SO_4, HCl, and $HC_2H_3O_2$ are used for catalyst removal (*121,122,133,135*).

4.4 PROPERTIES OF POLYOXYETHYLENE ALCOHOLS

A. Alcohol Structure and Surface Properties

1. Straight-Chain Primary and Branched-Chain Secondary Alcohols

In a fundamental study the chemical structure of normal straight chain and branched chain alcohols has been related to detergency of their EO adducts, and the results are given in Figures 4.7 to 4.10 (*136*). The following straight-chain alcohols in order of their increasing molecular weight

n-octanol (*n*-C_8)
n-decanol (*n*-C_{10})
n-dodecanol (*n*-C_{12})
n-tetradecanol (*n*-C_{14})
n-octadecanol (*n*-C_{18})

and the following branched-chain secondary alcohols in order of their increasing molecular weight

5-ethylnonanol-2 (*sec*-C_{11})
2,5,8-trimethylnonanol-4 (*sec*-C_{12})
2-methyl-7-ethylundecanol-4 (*sec*-C_{14})
3,9-diethyltridecanol-6 (*sec*-C_{17})

were investigated.

Detergency data of the straight-chain alcohol-EO adducts on an active basis are given in Figure 4.7. The solid lines represent cotton detergency expressed as per cent GARDINOL WA (DUPONOL WA, trademark of E. I. du Pont de Nemours & Co.) in 300-ppm water hardness, 0.2 per cent concentration as determined in a Launder-Ometer at 60°C by eight replicate swatches (*137*). The dotted lines in Figure 4.7 represent cotton detergency expressed as per cent GARDINOL WA in 50-ppm water hardness, 0.2 per cent concentration as determined in Launder-Ometer at 60°C by eight replicate swatches.

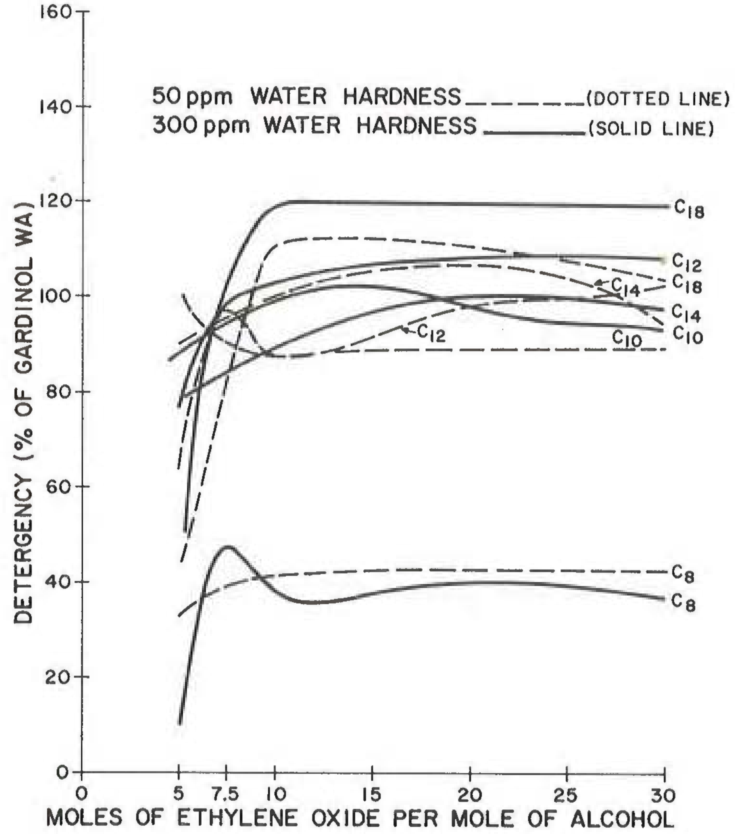


Fig. 4.7. Detergency of oxyethylated straight-chain alcohols on active basis at 0.2% concentration in hard water (*136*).

From Figure 4.7 it is evident that the poorest detergents for cotton are the *n*-octanol-EO adducts which have the lowest-molecular-weight alcohol as a starting raw material. From this figure it may also be deduced that the best detergents are based on *n*-octadecanol-EO adducts, which are the highest-molecular-weight alcohols used in this study. These trends are not only true for detergency in 50 but also in 300-ppm. No significant difference between the EO adducts of C_{10}, C_{12}, and C_{14} alcohols has been observed except that the C_{12} adduct appears to increase slightly with EO addition, whereas the C_{10} and C_{14} alcohol adducts level off at 10 moles of ethylene oxide in line with the general behavior of nonionic surfactants shown in Chapter 20.

In general, it can be seen from Figure 4.7 that, once a maximum in detergency is obtained, the further addition of ethylene oxide has little effect on the detergency values; in short, a plateau has been reached.

Figure 4.8 shows the detergency data of branched-chain alcohols on an active

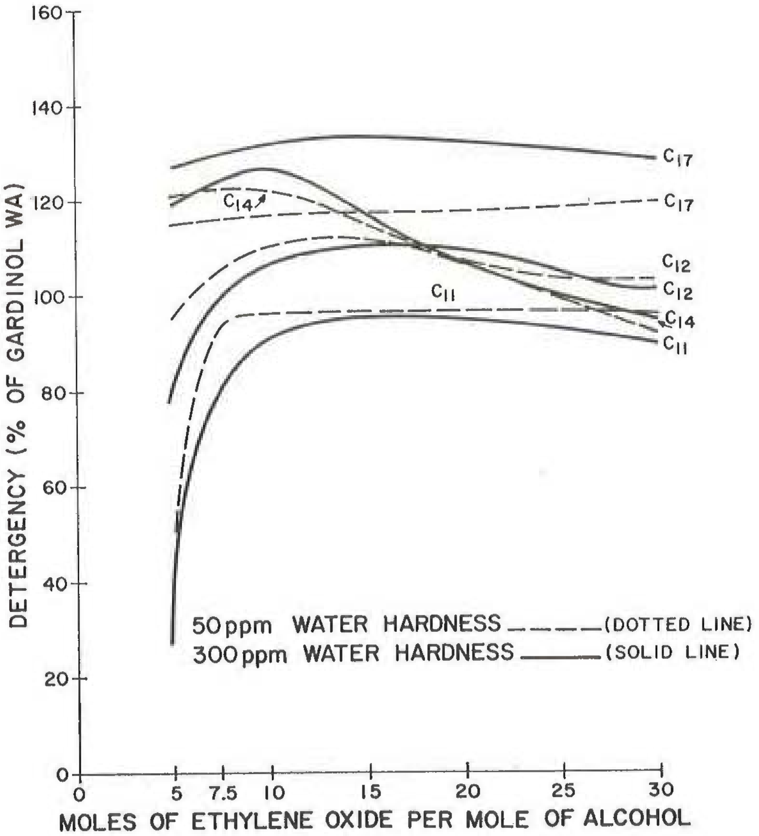


Fig. 4.8. Detergency of oxyethylated branched-chain alcohols on active basis at 0.2% concentration in hard water (*136*).

basis. The solid lines represent cotton detergency expressed as per cent GARDINOL WA in 300-ppm water hardness and 0.2 per cent concentration as determined in the Launder-Ometer at 60°C by eight replicate swatches. The dotted lines express detergency as per cent GARDINOL WA in 50-ppm and 0.2 per cent concentration under same test conditions as above.

It is shown in Figure 4.8 that the poorest detergents for cotton are based on *sec*-C_{11}-alcohol-EO adducts. This alcohol is also the lowest-molecular-weight member of the secondary alcohol series. Also, the best detergents are based on *sec*-C_{17}-alcohol-EO adduct. *Sec*-C_{17}-alcohol is the highest-molecular-weight alcohol of this series studied.

Again, as in the case of the straight-chain alcohols, once a maximum detergency is obtained, the further addition of ethylene oxide does not change the detergency much except in the case of the *sec*-C_{14}-alcohol-EO adducts.

As shown in Figures 4.7 and 4.8, in 50-ppm hard water the branched-chain alcohol has a higher detergency value than a straight-chain alcohol with the same number of carbon atoms in the molecule or with a slightly lower number of carbon atoms in the molecule. One exception to this is the *sec*-C_{14}-alcohol adduct which has high detergency with 5 to 10 moles of ethylene oxide, but the further addition of ethylene oxide reduces the detergency enormously. It has also been found that in 300-ppm hard water the difference between the branched- and straight-chain alcohol-EO adducts is not quite so pronounced as the difference exhibited in 50-ppm. The adducts of *sec*-C_{17}-alcohol are definitely better than those of *n*-C_{18}-alcohol. However, *sec*-C_{14}-alcohol adducts have high detergency with 5 to 10 moles of EO but then drop off rapidly with further addition of EO, so that initially these adducts have higher detergency than those of the straight-chain C_{14}-alcohol. The same trend applies to the *sec*-C_{12}-alcohol adducts which have higher detergency values than the normal C_{12}-alcohol adducts in the range of shorter EO-chain length.

As shown by these curves, the detergency of the alcohol-EO adducts is influenced by (a) the structure of the alcohols (straight- or branched-chain) and (b) the carbon numbers or molecular weight of the alcohols.

Figures 4.9 and 4.10 show the cotton detergency of the previously discussed normal-straight- and branched-chain alcohols when formulated with builders. Detergency is expressed as per cent GARDINOL WA, 0.2 per cent concentration, as determined under the standard conditions previously given. Figure 4.9 represents cotton detergency in 50-ppm hard water, and Figure 4.10 represents detergency in 300-ppm hard water.

Again, as has been shown in Figures 4.7 and 4.8, the branched-chain alcohol-EO adducts have a higher detergency value than the straight-chain alcohol of higher molecular weight. Similarly, the detergency of alcohol-EO adducts is influenced by the structure and molecular weight of the alcohol.

Curves of wetting time (Draves) (*137*) of these straight- and branched-chain alcohol-ethylene oxide adducts versus ethylene oxide content are shown in

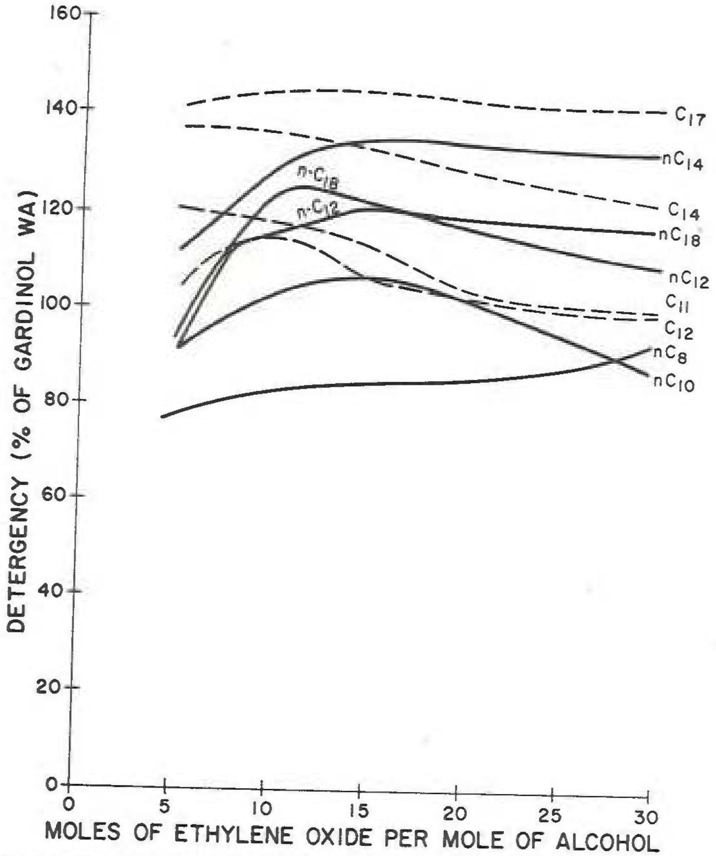


Fig. 4.9. Detergency of oxyethylated straight- and branched-chain alcohols on built basis at 0.2% concentration in 50-ppm hard water (*136*).

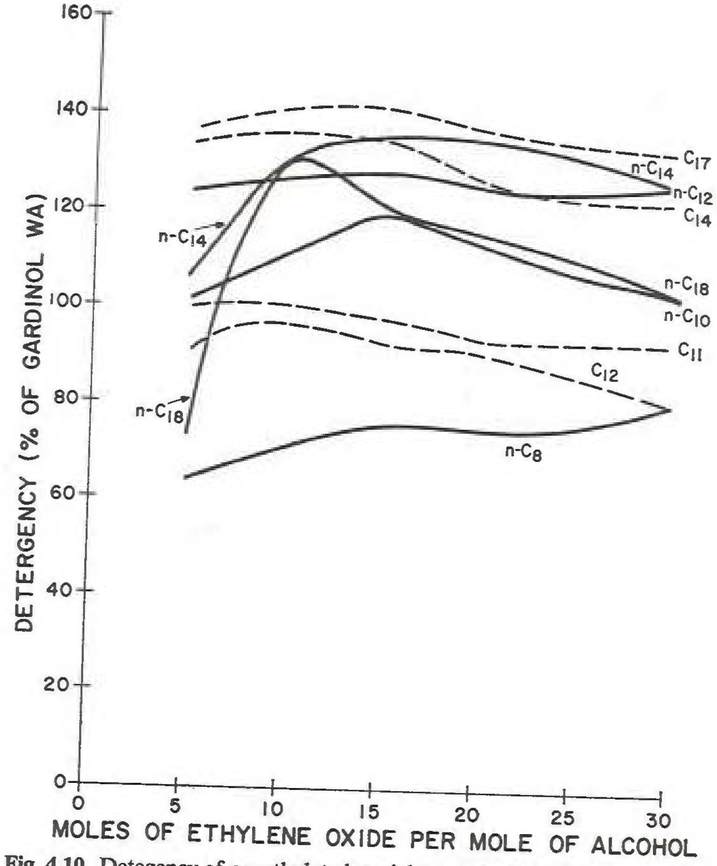


Fig. 4.10. Detegency of oxyethylated straight- and branched-chain alcohols on built basis at 0.2% concentration in 300-ppm hard water (*136*).

Figure 4.11. This test was run at 0.125 per cent concentration of nonionic surfactant in water of 0-ppm hardness at room temperature.

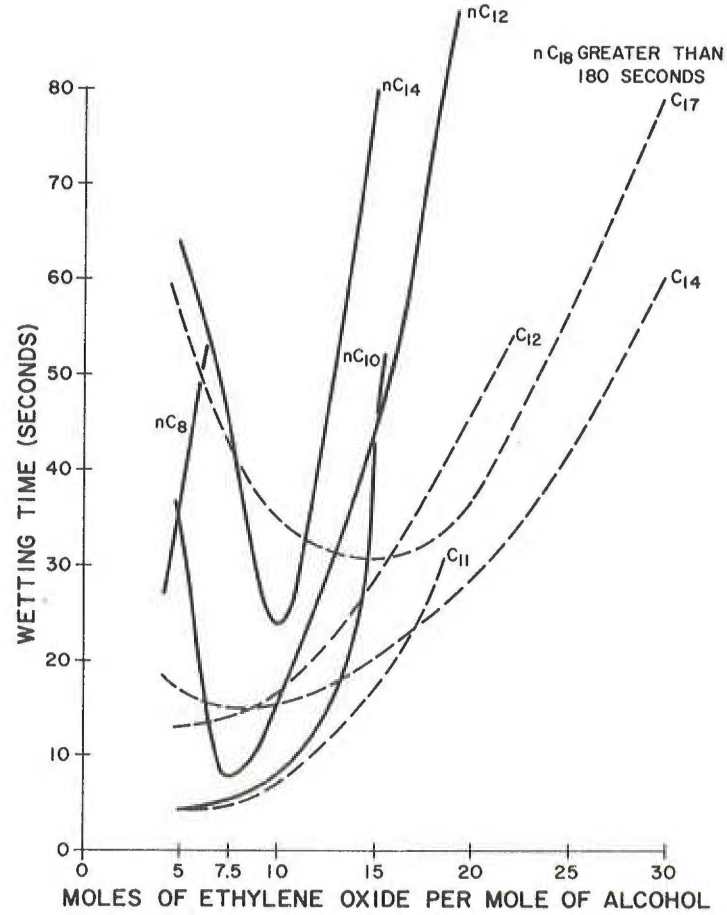


Fig. 4.11. Wetting time of oxyethylated straight- and branched-chain alcohols at 0.125% concentration in 0-ppm hard water and at room temperature (*136*).

From these curves it is noted that, for the lowest-molecular-weight hydrophobe alcohol (n-C_8), there is a rapid increase in wetting time with increasing amounts of ethylene oxide. All the other compounds exhibit a minimum wetting time. It is interesting to observe that, as the molecular weight of the alcohol is increased, the minimum wetting time of the compound is increased, and that as the molecular weight increases, the number of moles of ethylene oxide required to give the minimum wetting time also increases.

In general, the branched-chain alcohol-EO adducts have better wetting properties than those derived from a straight-chain alcohol of the same molecular weight.

The foam values of these normal alcohol and branched-chain alcohol-based ethylene oxide adducts were determined by the Ross-Miles foam test (*137*) at 50°C with a 0.1 per cent nonionic surfactant in 0- and 300-ppm hard water. These foam values versus ethylene oxide content are presented in Figures 4.12, 4.13, 4.14, and 4.15. As shown by these figures, the following generalizations are made.

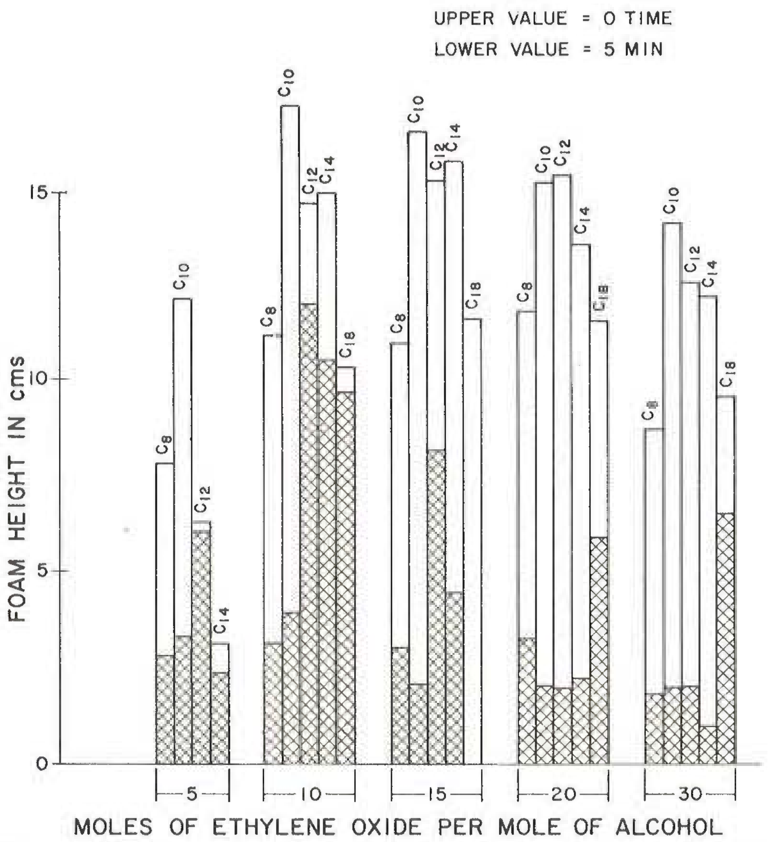


Fig. 4.12. Ross-Miles lather values of oxyethylated straight-chain alcohols at 0.1% concentration in 0-ppm hard water and at 50°C (*136*).

1. For a given alcohol, there is generally an ethylene oxide content which corresponds to an adduct of maximum foam value.

2. Of the alcohols studied, the ethylene oxide adducts derived from the normal alcohol usually have higher foam values than those derived from the branched-chain alcohols.

3. Foam from ethylene oxide adducts derived from the low-molecular-weight alcohol is generally less stable than that derived from the high-molecular-weight alcohol.

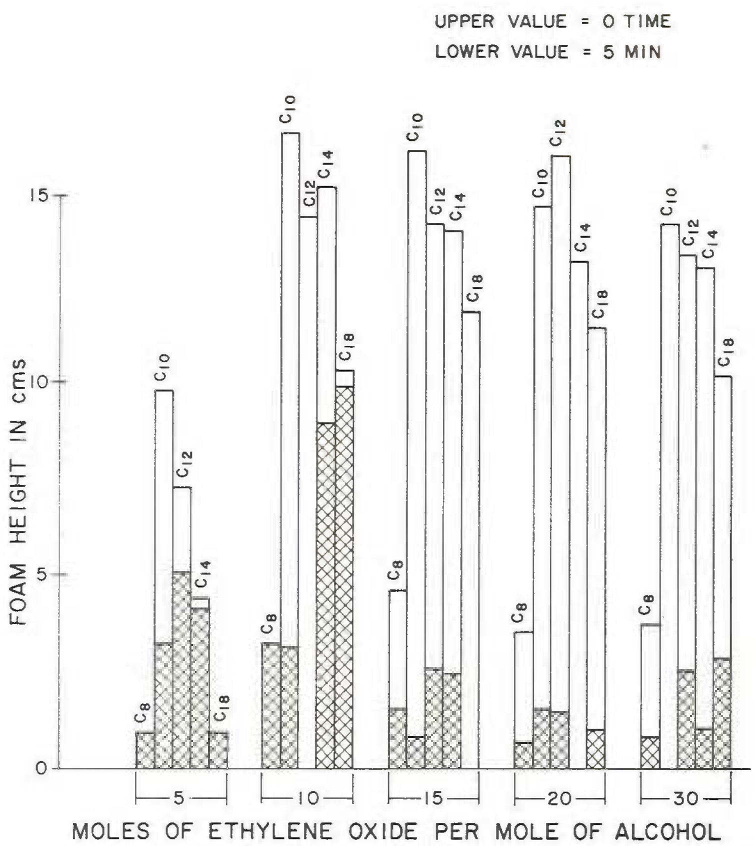


Fig. 4.13. Ross-Miles lather values of oxyethylated straight-chain alcohols at 0.1% concentration in 300-ppm hard water and at 50°C (*136*).

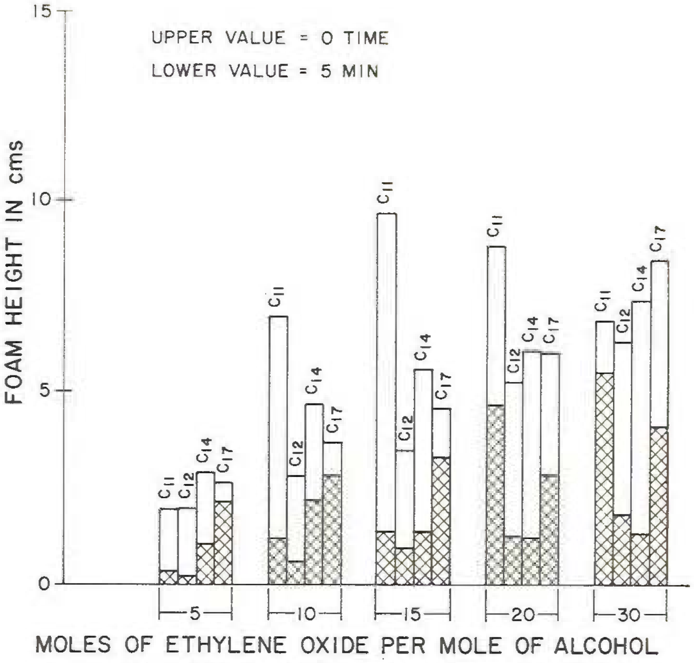


Fig. 4.14. Ross-Miles lather values of oxyethylated branched-chain alcohols at 0.1% concentration in 0-ppm hard water and at 50°C (*136*).

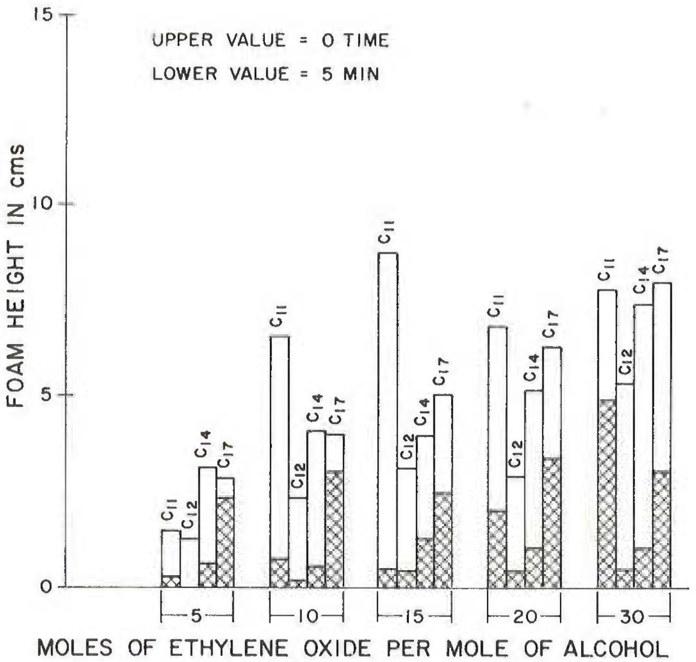


Fig. 4.15. Ross-Miles lather values of oxyethylated branched-chain alcohols at 0.1% concentration in 300-ppm hard water and at 50°C (*136*).

4. Water hardness affects appreciably the foam stability but not the initial foam value of these alcohol-ethylene oxide adducts.

Surface-tension and interfacial-tension measurements of these alcohol-based nonionics were made at 25°C and 1.0 per cent of surfactant in redistilled water by the du Nouy ring-tensiometer method (*137*).

Figures 4.16, 4.17, 4.18, and 4.19 give the surface tension versus ethylene oxide content and interfacial tension versus ethylene oxide content for the two series of alcohol-ethylene oxide adducts. In general, the surface and interfacial tensions increase with the increasing ethylene oxide content. In case of the straight-chain alcohol-ethylene oxide adducts the rate of increase of surface tension with respect to the ethylene oxide content is much higher than that of branched-chain alcohol-ethylene oxide adducts.

2. Oxo Alcohols

Another series of alcohols which are known in the trade as "oxo" process alcohols were investigated (*136*). The manufacture of these alcohols was discussed in Section 4.2A, 2a. By varying the molecular weight and structures of the olefin feed, one can obtain alcohols of various molecular weights and structures. The alcohols used for this study are branched-chain primary alcohols ranging from C_8 to C_{16}.

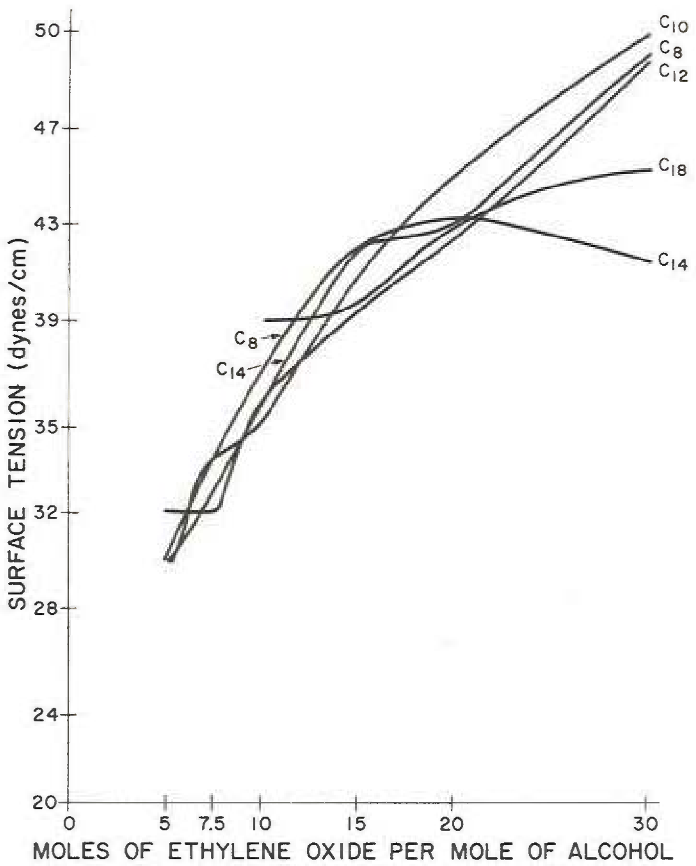


Fig. 4.16. Surface tension of oxyethylated straight-chain alcohols at 1.0% concentration and 25°C (*136*).

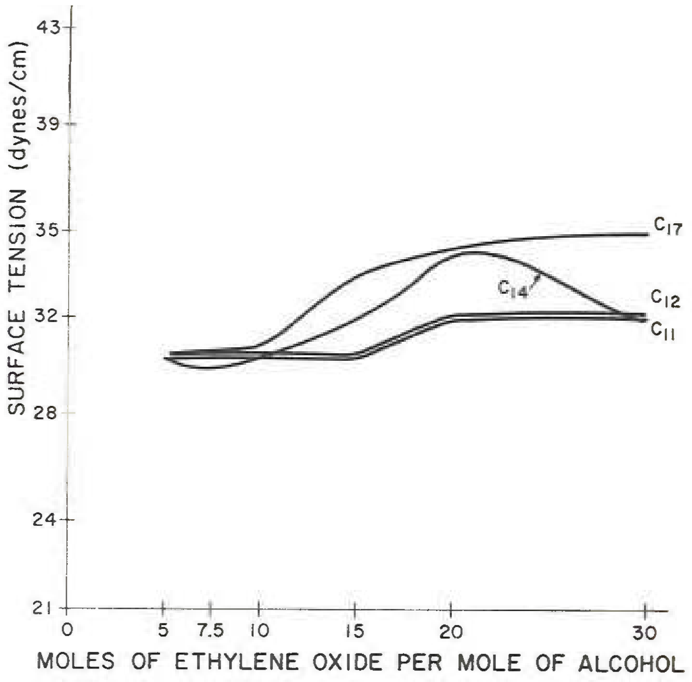


Fig. 4.17. Surface tension of oxyethylated branched-chain alcohols at 1.0% concentration and 25°C (*136*).

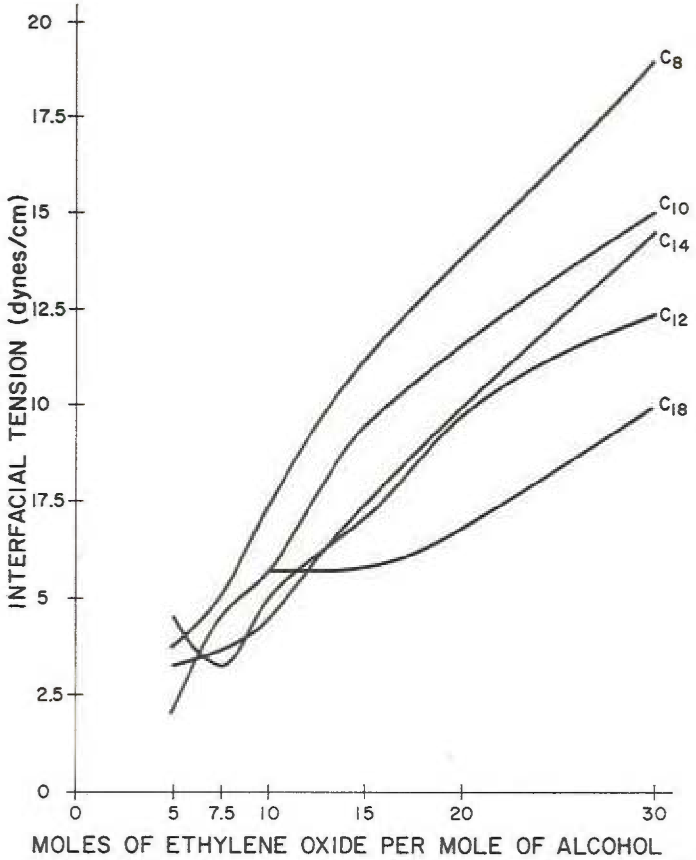


Fig. 4.18. Interfacial tension of oxyethylated straight-chain alcohols at 1.0% concentration and 25°C (*136*).

Fig. 4.19. Interfacial tension of oxyethylated branched-chain alcohols at 1.0% concentration and 25°C (*136*).

a. Ethylene Oxide Adducts

Figure 4.20 shows the detergency of these oxo alcohol-ethylene oxide adducts. Detergency, again, is expressed as per cent GARDINOL WA. The concentration of the detergent used was 0.2 per cent and water hardness was 300 ppm. Also the same equipment and test conditions previously used were employed. From this figure it is evident that, as the molecular weight of the oxo process alcohol was increased, the detergency also increased.

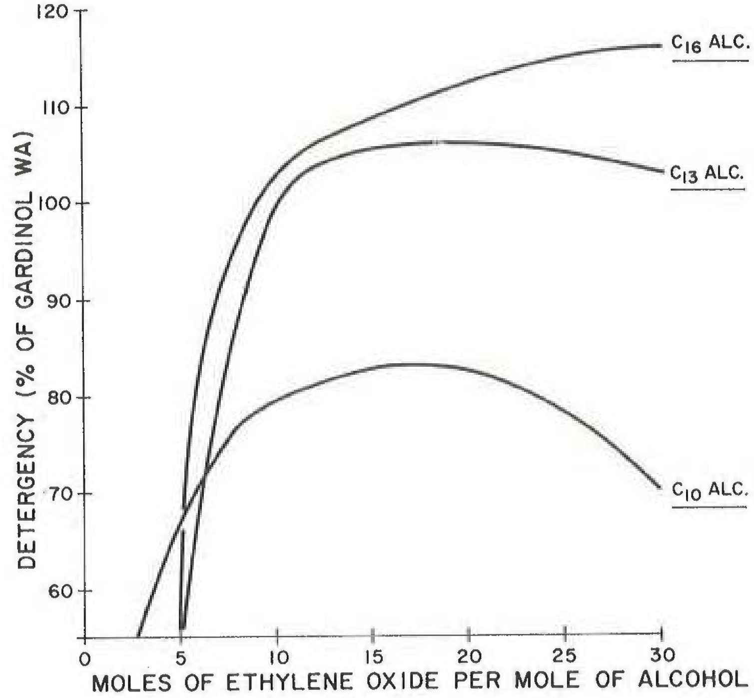


Fig. 4.20. Detergency of oxyethylated oxo alcohols on active basis at 0.2% concentration in 300-ppm hard water (*136*).

Figures 4.21 and 4.22 represent the detergency of these oxo process alcohols when formulated with builders in 50- and 300-ppm hardness. Again the cotton detergency is expressed as per cent GARDINOL WA and it was determined under the same conditions previously described.

From these two figures it is again shown that the low molecular weight oxo alcohol EO adduct, that is, C_{10}-EO, is a poor detergent even with the help of builders. However, the tridecanol-EO adducts and hexadecanol-EO adducts have good detersive properties.

Figure 4.23 gives the wetting time of these oxo alcohol-ethylene oxide adducts at 0.125 per cent concentration. It is readily noted that the isooctyl alcohol-EO adduct is a poor wetting agent. Although isodecanol-EO adduct has a very low

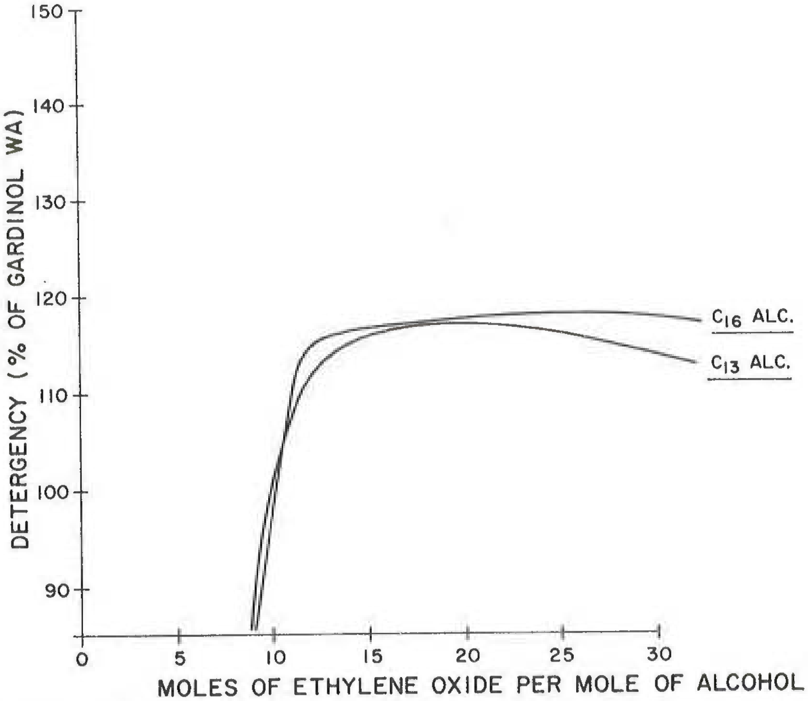


Fig. 4.21. Detergency of oxyethylated oxo alcohols on built basis at 0.2% concentration in 50-ppm hard water (*136*).

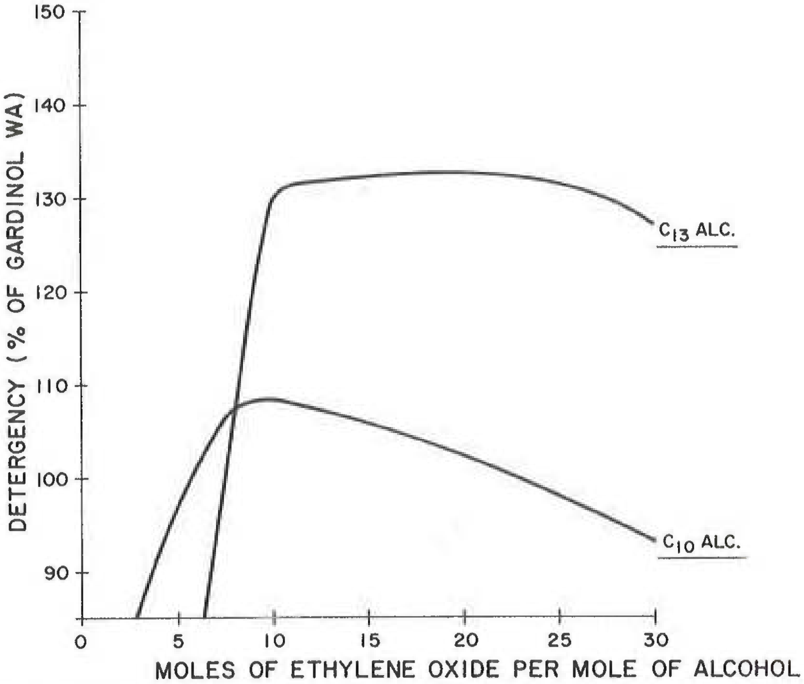


Fig. 4.22. Detergency of oxyethylated oxo alcohols on built basis at 0.2% concentration in 300-ppm hard water (136).

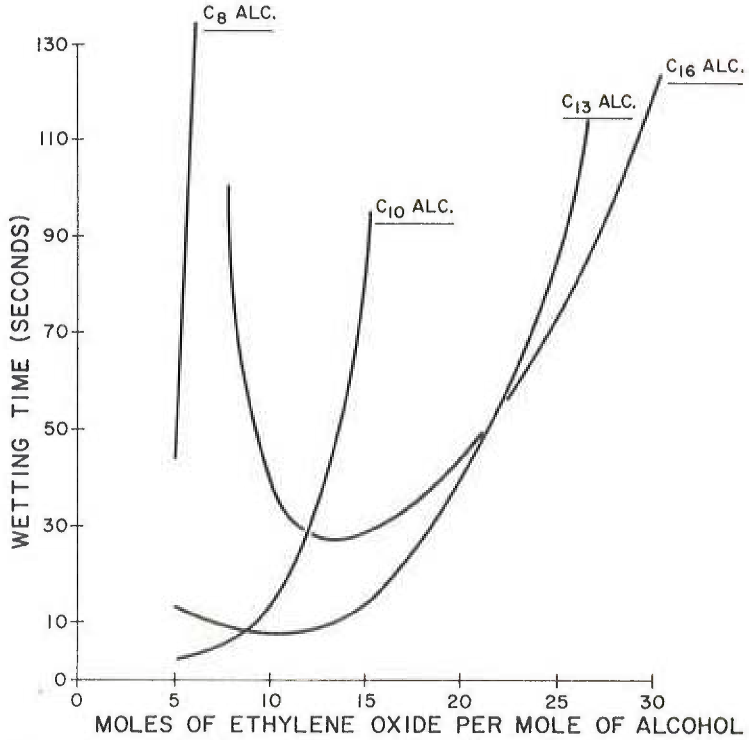


Fig. 4.23. Wetting time of oxyethylated oxo alcohols at 0.125% concentration in distilled water (*136*).

wetting time with low EO content, its wetting characteristics are rapidly changed with a slight increase in ethylene oxide content. Tridecanol-EO adducts give good wetting properties.

As shown in Figure 4.23, the molecular weight of alcohol has a great effect on wetting properties of its ethylene oxide adducts. Also, as the molecular weight of the alcohol is increased, the number of moles of ethylene oxide required for good wetting properties is increased.

The foam values of these oxo alcohol-ethylene oxide adducts were determined by the Ross-Miles foam test at 50°C with 0.1 per cent of surfactant at 50- and 300-ppm. Figures 4.24 and 4.25 give the foam values versus ethylene oxide content. From these figures, the following generalizations can be made:

1. For a given alcohol, there is an ethylene oxide content which corresponds to an adduct of maximum foam value.
2. The initial foam value and the foam stability of C_{13}-alcohol-EO adducts are better than those from C_8 and C_{10} alcohols.
3. Water hardness affects the foam stability much more than the initial foam value.

Figures 4.26 and 4.27 show the surface and interfacial tension versus ethylene oxide content of the oxo alcohol-derived nonionics.

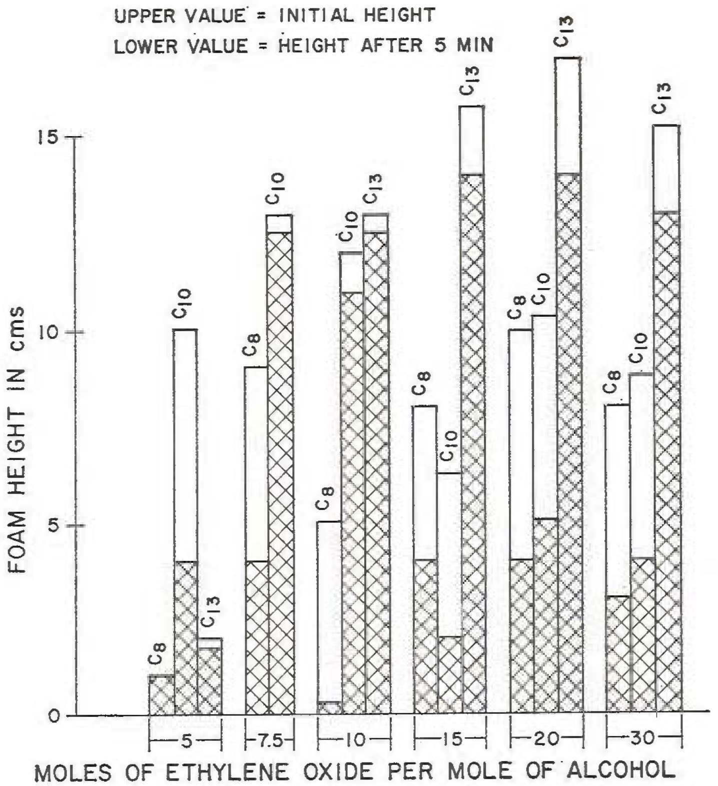


Fig. 4.24. Ross-Miles lather values of oxyethylated oxo alcohols at 0.1% concentration in 50-ppm hard water and at 50°C (*136*).

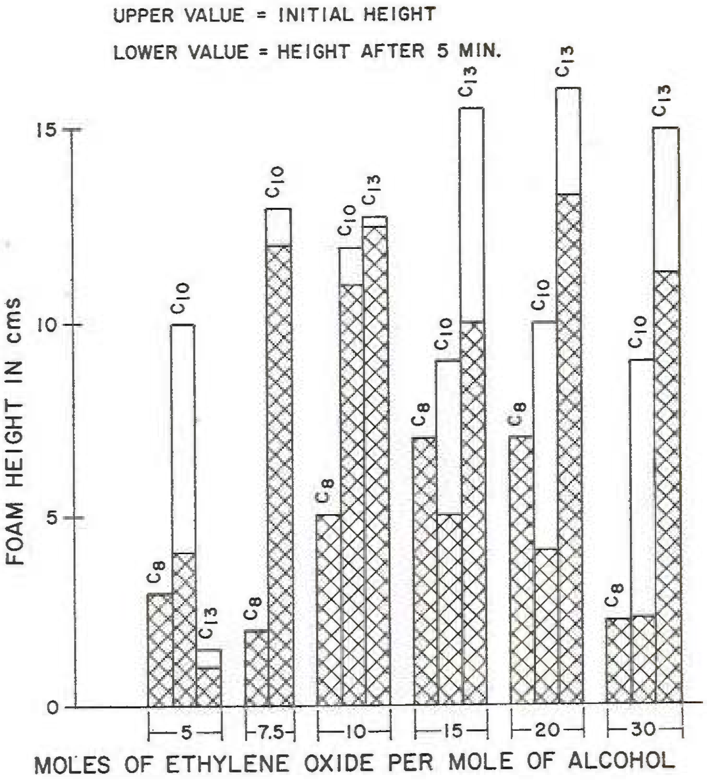


Fig. 4.25. Ross-Miles lather values of oxyethylated oxo alcohols at 0.1% concentration in 300-ppm hard water and at 50°C (*136*).

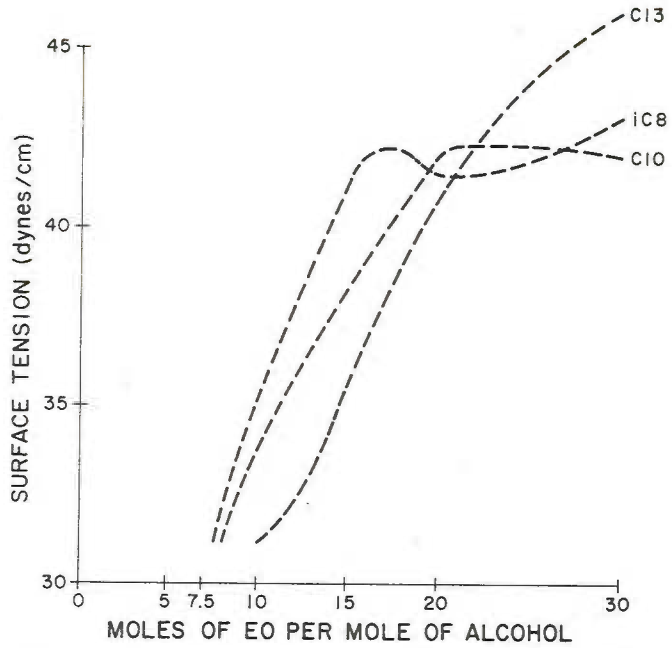


Fig. 4.26. Surface tension of oxyethylated oxo alcohols at 25°C and 1.0% concentration (*136*).

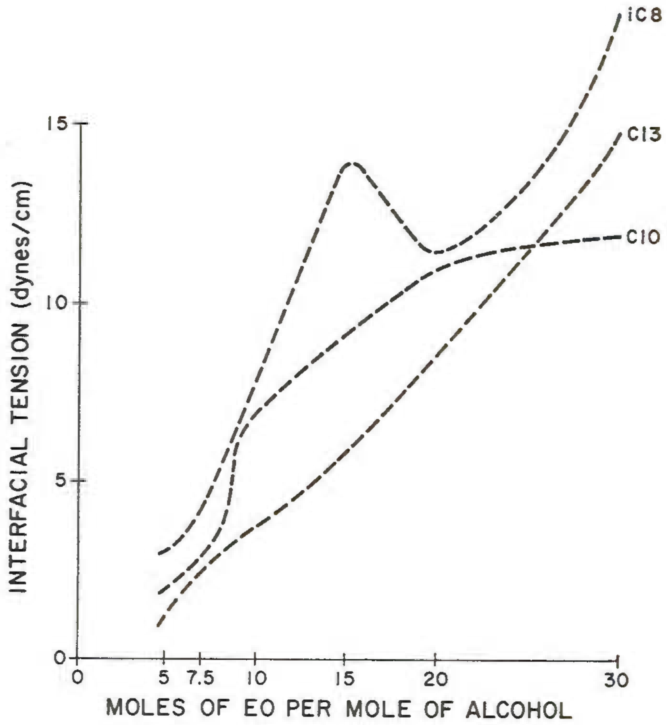


Fig. 4.27. Interfacial tension of oxyethylated oxo alcohols at 25°C and 1.0% concentration (*136*).

The surface and interfacial tension are determined by the du Nouy ring-tensiometer method at 25°C and 1.0 per cent concentration of nonionic surfactant.

In general, the surface and interfacial tension increase with the increasing ethylene oxide content.

b. Propylene Oxide-Ethylene Oxide Adducts

A third part of this fundamental study (*136*) covered the preparation of a series of compounds based on commercial iso-decyl alcohol, propylene oxide, and ethylene oxide.

The patent literature indicates that propylene oxide can be used to provide the hydrophobic polyoxyalkylene glycol units for nonionic surfactants (*138–143*). Also, propylene oxide does not appear to be used very much commercially except in the form of propylene glycol and polypropylene glycols. The use of propylene oxide permits almost unlimited variation in molecular weight and hydrophobic properties (see Chapters 10 and 11). Thus the compound greatly extends the ability to tailor-make nonionic surfactants for specific applications or for specific properties.

In this study a series of compounds based on oxo decyl alcohol, derived from tripropylene, with various amounts of propylene oxide and ethylene oxide were prepared. These compounds were evaluated for the following functional properties: detergency (active and built basis), wetting time, Ross Miles lather values, surface tension, interfacial tension, and spreading coefficient. The data obtained from these different evaluations were then subjected to statistical treatment, the analysis of variance.

To show separately the effect of propylene oxide and ethylene oxide content on the functional properties of the nonionic surfactant derived from them, the average values of the functional property, corresponding to a propylene oxide content at various ethylene oxide contents, were used to construct the functional property versus propylene oxide content curve. In the same manner, the average values of the functional property, corresponding to an ethylene oxide content at various propylene oxide contents were used to construct the functional property versus ethylene oxide content curve.

The first functional property studied in the three-component system of oxo decyl alcohol, propylene oxide, and ethylene oxide was detergency.

i. *Detergency*

All the compounds prepared were first given a detergency evaluation on an active basis, 0.2 per cent concentration in 300-ppm water hardness. Then only those compounds that had detergency values greater than 80 per cent GARDINOL WA were formulated with builders and then submitted for further evaluation.

Figure 4.28 represents the detergency data obtained from the evaluation of these compounds of oxo decyl alcohol, propylene oxide, and ethylene oxide in

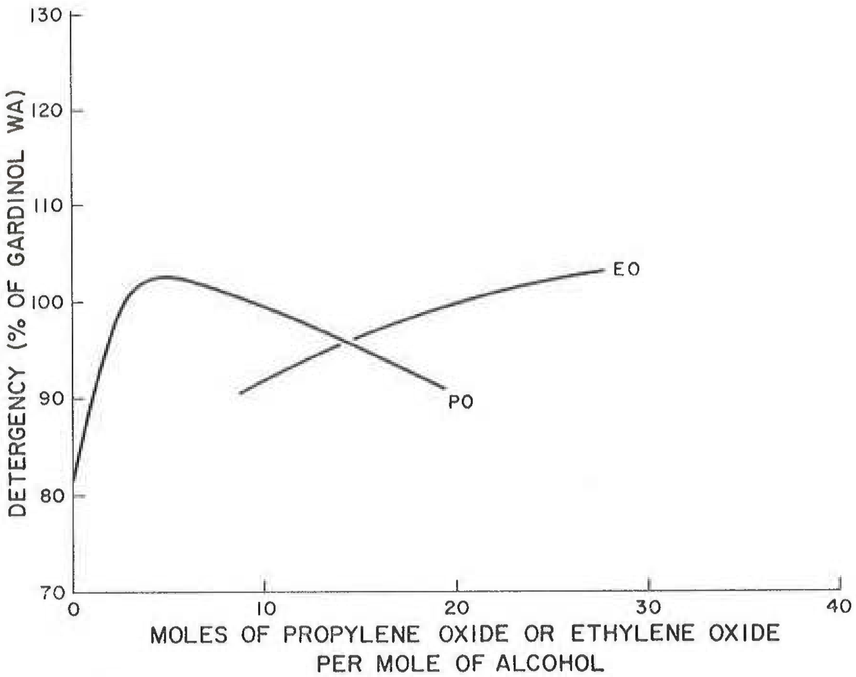


Fig. 4.28. Detergency of oxo alcohol-PO-EO adducts on active basis at 0.2% concentration in 300-ppm hard water (*136*).

300-ppm water hardness, 0.2 per cent concentration. It also shows that there is a maximum in the amount of propylene oxide that can be added for optimum detergency. This optimum occurs with 4 to 8 moles of PO. The EO curve shows no maximum or minimum and is fairly constant with a tendency to increase as the amount of EO is increased.

The effect of PO and EO on detergency when the compound is formulated with builders and then evaluated in 50-ppm water hardness is given in Figure 4.29. Again, it is shown that the EO content of the molecule has not affected the detergency greatly but that the PO content has and that a maximum in detergency occurs with 4 to 12 moles of PO.

Figure 4.30 shows the results obtained when the compound is built with inorganic builders and evaluated in 300-ppm hardness. The curves for PO and EO closely resemble those of Figure 4.29, in which the built compound was evaluated in 50-ppm. Again a peak or maximum in detergency is obtained when the PO content is from 6 to 12 moles, whereas the EO curve is fairly constant.

Therefore, the best detergent in this series would contain about 4 to 12 moles of propylene oxide and sufficient ethylene oxide to make the compound water soluble.

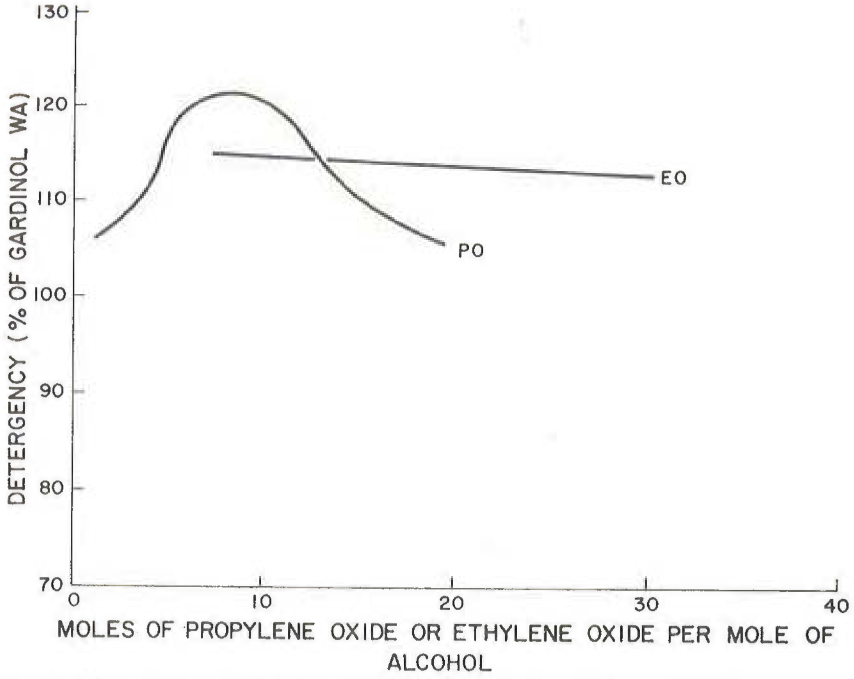


Fig. 4.29. Detergency of oxo alcohol-PO-EO adducts on built basis at 0.2% concentration in 50-ppm hard water (*136*).

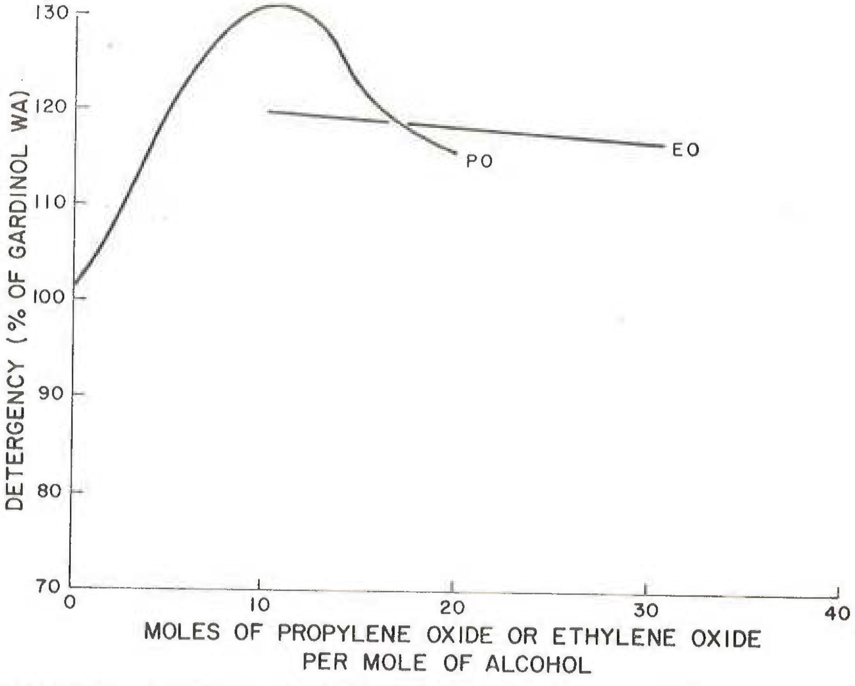


Fig. 4.30. Detergency of oxo alcohol-PO-EO adducts on built basis at 0.2% concentration in 300-ppm hard water (*136*).

ii. *Wetting*

The results of the Draves-Clarkson wetting test (neutral solution) at 0.125 per cent versus PO and EO content are plotted in Figure 4.31. From this curve

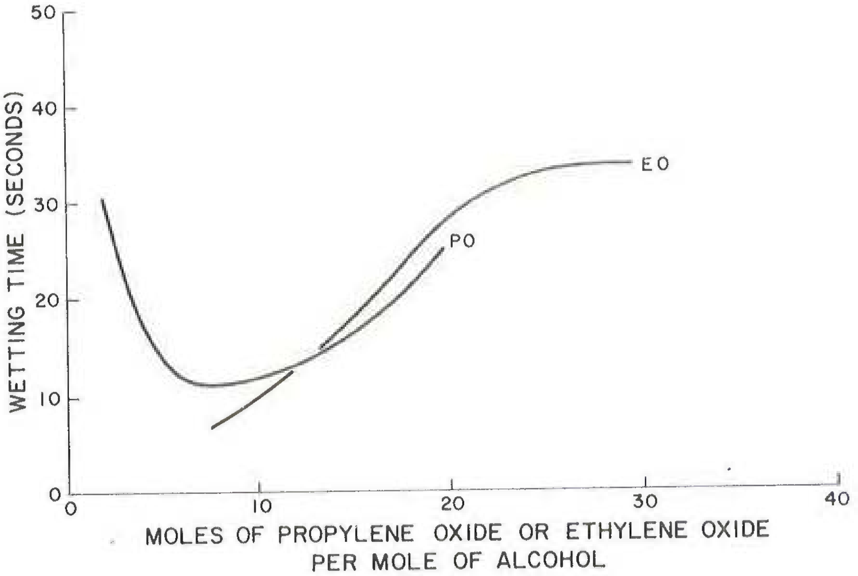


Fig. 4.31. Wetting time of oxo alcohol-PO-EO adducts at 0.125% concentration (*136*).

the effect opposite from detergency can readily be seen. In wetting, the amount of ethylene oxide has a larger effect on the wetting time than the amount of PO. The curves on Figure 4.31 also show that a minimum in wetting time occurs at about 6 to 10 moles of PO. The EO content curve indicates an increasing wetting time with increasing EO content.

The same trends are shown in Figure 4.32, which is a plot of wetting time versus PO and EO content of 0.50 per cent concentration.

Conclusion from the wetting-time data is that the compound containing 5 to 11 moles of PO, i.e., just sufficient EO to make it water soluble, renders maximum wetting.

iii. *Ross-Miles Foam*

These values were obtained in 0- and 300-ppm water hardness. Only the initial foam values were used to investigate the effect of PO and EO. These data are plotted in Figures 4.33 and 4.34.

From Figure 4.33 (0-ppm), it is evident that foam increases with EO content. Also, the foam tends to increase as the PO content is increased from 0 to 5 moles, and from there the foam decreases with increasing PO content.

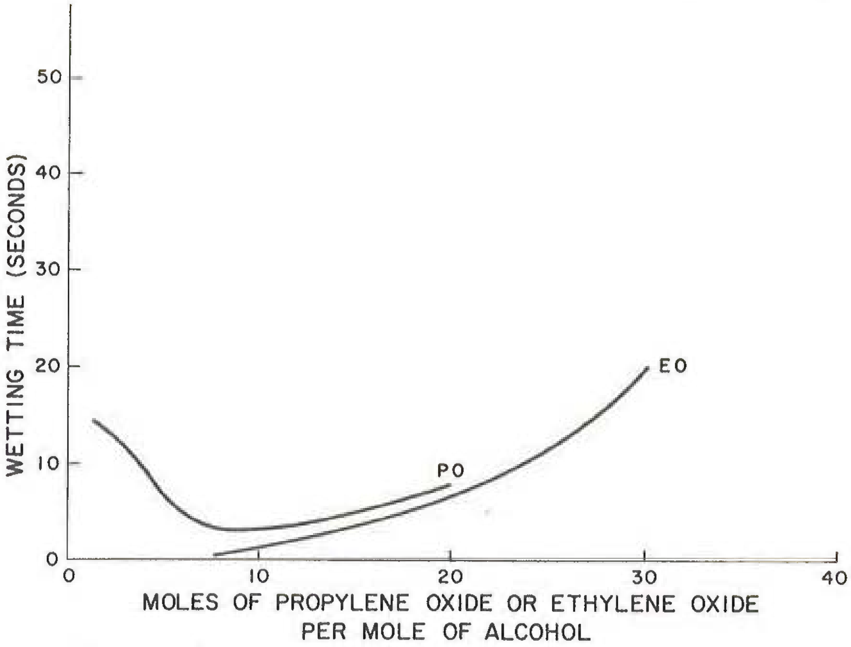


Fig. 4.32. Wetting time of oxo alcohol-PO-EO adducts at 0.50% concentration (*136*).

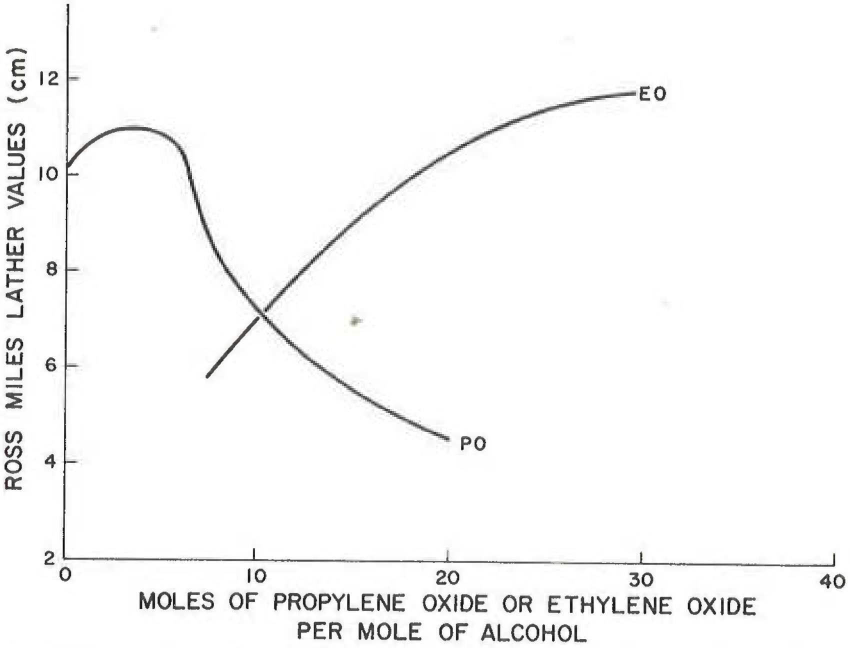


Fig. 4.33. Ross-Miles lather values of oxo alcohol-PO-EO adducts on active basis at 0 time and 0.1% in 0-ppm hard water and at 50°C (*136*).

Figure 4.34 represents 300-ppm water hardness. The same effect of PO and EO can be drawn. Since the PO and EO have independent effect on foam, to obtain a low foaming agent, it should have more than 5 moles PO and sufficient EO to render it water dispersible.

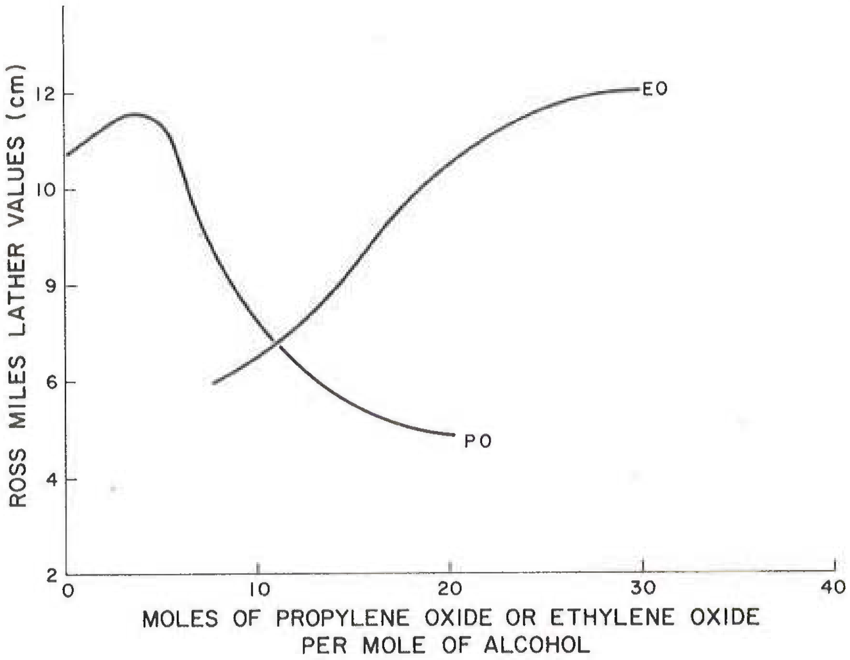


Fig. 4.34. Ross-Miles lather values of oxo alcohol-PO-EO adducts on active basis at 0 time and 0.1% concentration in 300-ppm hard water and at 50°C (*136*).

iv. ***Surface Activity***

Figure 4.35 gives the results of surface-tension data at 1.0 per cent concentration. These data indicate that the amount of EO has a much larger effect than the amount of PO. This figure also shows that the surface tension is fairly constant when the amount of PO is varied. However, the surface tension increases as the amount of EO is increased. Thus, to obtain a compound having low surface tension, the amount of PO is not critical, but the amount of EO should be sufficient to make the compound water dispersible.

Figure 4.36 gives the results of interfacial tension data at 1.0 per cent concentration. The curves for PO and EO are inversely proportional; as the amount of PO is increased, the interfacial tension decreases and as the amount of EO increases, the interfacial tension increases.

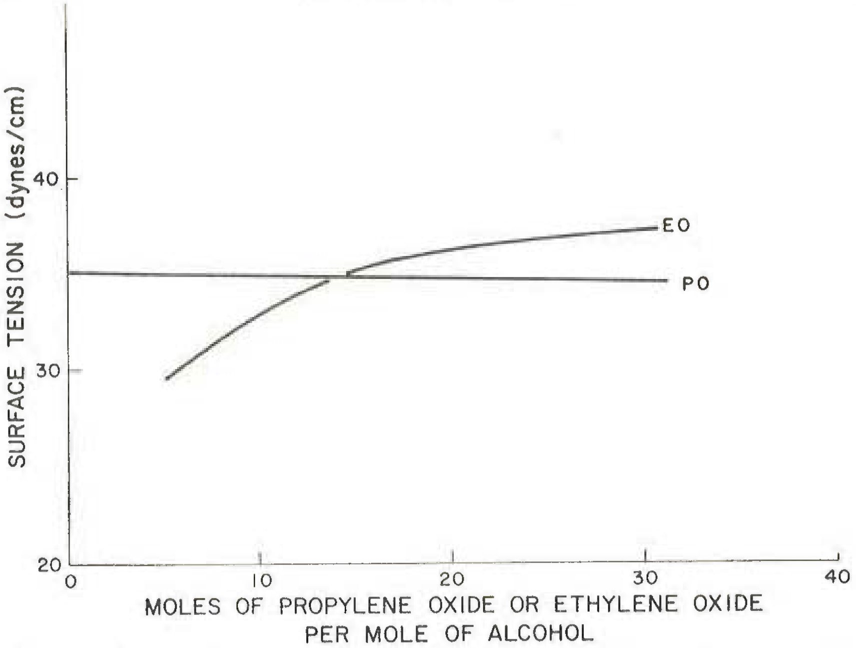


Fig. 4.35. Surface tension of oxo alcohol-PO-EO adducts at 25°C and 1.0% concentration (*136*).

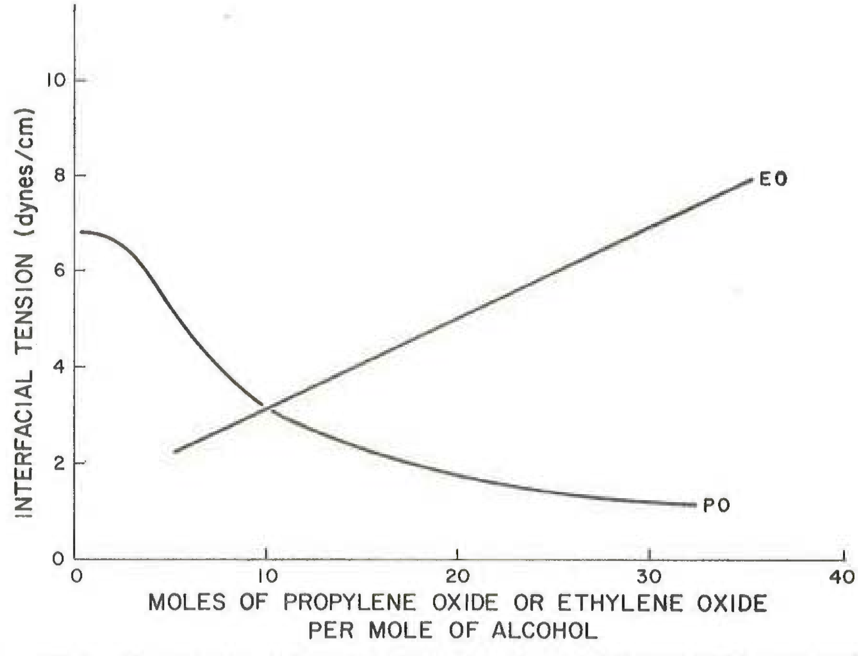


Fig. 4.36. Interfacial tension of oxo alcohol-PO-EO adducts at 25°C and 1.0% concentration (*136*).

Thus to have a compound in this three-component system of oxo decyl alcohol, propylene oxide, and ethylene oxide with a low interfacial tension, the hydrophobic group (propylene oxide) must be large compared with the hydrophilic group (ethylene oxide).

Since the value for spreading coefficient is calculated from surface-tension and interfacial-tension data, any trends that appear in either the surface tension or interfacial tension will also be reflected in the spreading coefficient. Thus, our results show that the spreading coefficient decreases with increasing amounts of EO, but increases with increasing amounts of PO. From this it follows that the preparation of a compound with a positive or low negative spreading coefficient requires a large hydrophobic group (PO) in comparison to the hydrophilic group (EO).

On the basis of the results of this study on nonionic surfactants made from oxo decyl alcohol, propylene oxide, and ethylene oxide, it can generally be concluded that:

1. The amount of propylene oxide in this three-component system has a great effect on the detersive properties of the compound. Ethylene oxide content has little effect on detergency efficiency.
2. Wetting time is greatly affected by the ethylene oxide content. As the number of moles of ethylene oxide increases, so does the wetting time. Also, for best wetting characteristics, the compound should have about 5 to 11 moles of PO.
3. The amounts of PO and EO have independent effects when it comes to foam. Maximum foam is reached with 1 to 5 moles PO and then falls off rapidly. Foam increases with increasing EO content.
4. The amount of ethylene oxide in this system is the controlling factor for surface tension. As the amount of ethylene oxide increases, so does the surface tension.
5. The number of moles of propylene oxide and number of moles of ethylene oxide have opposite effects on interfacial tension and spreading coefficients. Increase in ethylene oxide content increases interfacial tension and gives poorer spreading characteristics.

B. Commercial Products

A partial list of the commercially available nonionics derived from an alcohol and ethylene oxide is given in Table 4.1. A more complete listing of commercial products manufactured in the U.S. and abroad are in the literature (*144–146*).

Because of the favorable biodegradability of the linear alcohol ethylene oxide adducts, synthetic linear alcohol capacity is rapidly building up, in addition to the existing alcohols based on tallow and natural oils. Hence the supply of linear alcohol based nonionic surfactants is increasing.

TABLE 4.1

Product[a]	Alcohol type	Manufacturer
ALFONICS	Normal, primary (Ziegler process)	Continental Oil Co.
ALKANOL OA, OE, OJ	Normal, primary (natural source)	E. I. du Pont de Nemours & Co.
AROSURF EO-60 to EO-80	Normal, primary (natural source)	Archer Daniels Midland Co.
ATCONIL O	Normal, primary (natural source)	Metro-Atlantic, Inc.
BASOPHOR P, AF, O	Fatty alcohol	BASF Color & Chemicals Inc.
BIO-SOFT EA	Fatty alcohol	Stepan Chemical Co.
BRIJ 30, 35, 52, 56	Lauryl alcohol, cetyl alcohol	Atlas Chemical Industries
DEHYDOL 100	Fatty alcohol	Henkel International GmbH
DEPCONOL	Fatty alcohol	DePaul Chemical Co.
DIAZOPON AN	Fatty alcohol	General Aniline & Film Corp.
DISPERSOL A, VLX	Fatty alcohol	Imperial Chemical Industries Ltd.
EMPILAN K series	Fatty alcohols	Marchon Products Ltd.
EMULPHOGENE BC series	Oxo tridecanol	General Aniline & Film Corp.
ETHOSPERSE LA	Lauryl alcohol	Glyco Chemicals, Inc.
EUMULGIN 1000 NI	Fatty alcohols	Henkel International GmbH
LIPAL LA, MA, OA series	Fatty alcohols	Drew Chemical Corp.
LIPAL 3TD, 6TD, 10TD	Oxo tridecanol	Drew Chemical Corp.
LUBROL AL series	Oleyl/cetyl alcohol mixtures	Imperial Chemical House
PEREGAL O	Fatty alcohol	General Aniline & Film Corp.
PLURAFAC A & B series	Fatty alcohol	Wyandotte Chemicals Corp.
POLY TERGENT J series	Oxo tridecanol	Olin Mathieson Chemical Corp.
RENEX 30 series	Oxo tridecanol	Atlas Chemical Industries
RETZANOL BA series	Fatty alcohol	Retzloff Chemical Co.
SIPONIC series, E, L, Y	Fatty alcohol	Alcolac Chemical Corp.
SOLE-TERGE, LAE, OAE series	Lauryl alcohol, oleyl alcohol	Sole Chemical Corp.
STANDAMUL	Fatty alcohol	Standard Chemical Prod.
STAOL 10	Stearyl alcohol	Werner G. Smith, Inc.
STEROX AJ, AP	Oxo tridecanol	Monsanto Co.
SURFACTANT AD series	Hydroabietyl alcohol	Hercules Powder Co.
SURFONIC LR series	Fatty alcohol	Jefferson Chemical Co.
TELKANITE M	Fatty alcohol	Drexter Chemical Co.
TERGITOL 15-S series	Linear secondary alcohol	Union Carbide Corp., Chemicals Division
VOLPO series	Oleyl alcohol	Croda, Inc.
CIMAGAL O	Lauryl alcohol	Sapchim-Fournier-Cimog SA
ELFAN NC	Cocoalcohol	Chemische Fabrik Duren GmbH
NONION E-208	Oleyl alcohol	Nippon Oils & Fats Co.
NONIONIC 21, 22, 23	Lauryl alcohol	Sapchim-Fournier- Cimog SA

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[a] Trademarks of the respective manufacturers as listed under the manufacturers column in the above table.

1. Physical Properties

a. Solubility

The polyoxyethylene alcohol surfactants range in solubility from complete oil solubility to complete water solubility. This characteristic, as generally observed with nonionic surfactants, is dependent upon the number of moles of ethylene oxide added to a specific alcohol. It is a broad generality that the addition of 1 to 5 moles of ethylene oxide gives products that are oil soluble and in many cases completely soluble in hydrocarbons. As the mole ratio of ethylene oxide is increased to about 8 to 10 oxyethylene groups, water dispersibility and visual solubility begin (*147*). Table 4.2 gives solubility data on STEROX AJ-100 and STEROX AP-100 (trademarks of Monsanto Co.) in a number of salt solutions and in NaOH solutions. These two products are ethylene oxide adducts of tridecyl alcohol with 9.5 and 15.0 moles, respectively, and are manufactured by Monsanto Co. A marked increase in solubility with increasing number of ethylene oxide groups and a marked decrease in solubility with

TABLE 4.2

Solubility in Salt and NaOH Solutions

			Solubility, vol %	
Reagent	Concentration, %	Temp. °C	STEROX AJ-100	STEROX AP-100
Na_2CO_3	5	25	0.2	>15.0
		60	0.2	>15.0
	10	25	<0.2	0.4
		60	<0.2	0.2
NaCl	5	25	>15.0	>15.0
		60	0.2	>15.0
	10	25	<0.2	9.0
		60	<0.2	1.0
Na_2SO_4	5	25	0.4	>15.0
		60	0.2	>15.0
	10	25	<0.2	0.4
		60	<0.2	0.2
$Na_3PO_4 \cdot 12H_2O$	5	25	>15.0	>15.0
		60	0.2	>15.0
	10	25	<0.2	0.4
		60	<0.2	0.2
NaOH	5	25	0.2	>15.0
		60	0.2	>15.0
	10	25	<0.2	0.4
		60	<0.2	0.2

increasing temperature is evident from these solubility data in various salt solutions. This effect is most pronounced with salt solutions at 60°C (*136,148, 149*).

Table 4.3 gives cloud point data on STEROX AJ-100 and STEROX AP-100 in distilled water. Over the concentration range of 0.1 to 5.0 per cent, the cloud point is only slightly affected by the surfactant concentration level.

TABLE 4.3

Cloud Point, °C

Concentration, %	STEROX AJ-100	STEROX AP-100
5	40.5	97.0
1	40.0	98.5
0.5	40.0	98.5
0.1	40.5	>100.0

b. Specific Gravity

The dependence of the specific gravity on number of ethylene oxide units and temperature is illustrated in Table 4.4. Similarly, STEROX AJ-100 and STEROX AP-100 have been selected as examples. The specific gravity slightly increases with increasing number of ethylene oxide units, but decreases with increasing temperature.

TABLE 4.4

Specific Gravity Versus Temperature

Temp., °C	STEROX AJ-100	STEROX AP-100
25	Semisolid	Solid
40	1.003	1.030
60	0.998	1.013
80	0.983	0.998

c. Viscosity

In general, the viscosity of polyoxyethylene alcohol increases with increasing number of ethylene oxide units. In contrast, an increase in temperature results in a decrease of viscosity, as exemplified by the viscosity data of STEROX AJ-100 and STEROX AP-100 given in Table 4.5 (*136,148,149*).

It is evident from the plots of viscosity versus concentration of STEROX AJ-100 and STEROX AP-100 in Figures 4.37 and 4.38 that in line with other

TABLE 4.5

Viscosity versus Temperature

	Viscosity, centipoises	
Temp., °C	STEROX AJ-100	STEROX AP-100
25	Semisolid	Solid
40	40	56
60	22	25
80	16	17

nonionic surfactants a very viscous solution is formed at concentrations between 50 and 75 per cent of the anhydrous surfactant. In some cases a gel is formed, although STEROX AJ-100 does not generally set up in this fashion. It is also noted that the viscosity of STEROX AP-100 solutions above 70 per cent concentration is somewhat greater than that of the corresponding concentrations of STEROX AJ-100. This is presumably because of the greater degree of hydration and the higher molecular weight of STEROX AP-100.

2. Surface Properties

Surface properties such as detergency, wetting, foaming, surface tension, and interfacial tension for some representative polyoxyethylene alcohols are listed below. More comprehensive performance information is available from the suppliers' technical literature (*148–151*).

a. Detergency

Tables 4.6 and 4.7 contain data on the detersive efficiency of three different types of alcohol-ethylene oxide adducts. No direct comparison can be made on the three different types, since test methods are different for each set of conditions.

TABLE 4.6

Detersive Efficiency[a] (*148,149*)

	Water hardness, ppm	
	50	300
Active basis		
STEROX AP-100	115	105
STEROX AJ-100	121	111
Built basis		
STEROX AP-100	117	132
STEROX AJ-100	119	126

[a] 0.20% conc.; 140°F; sodium lauryl sulfate = 100. Eight replicates, 95% confidence limits ±4.

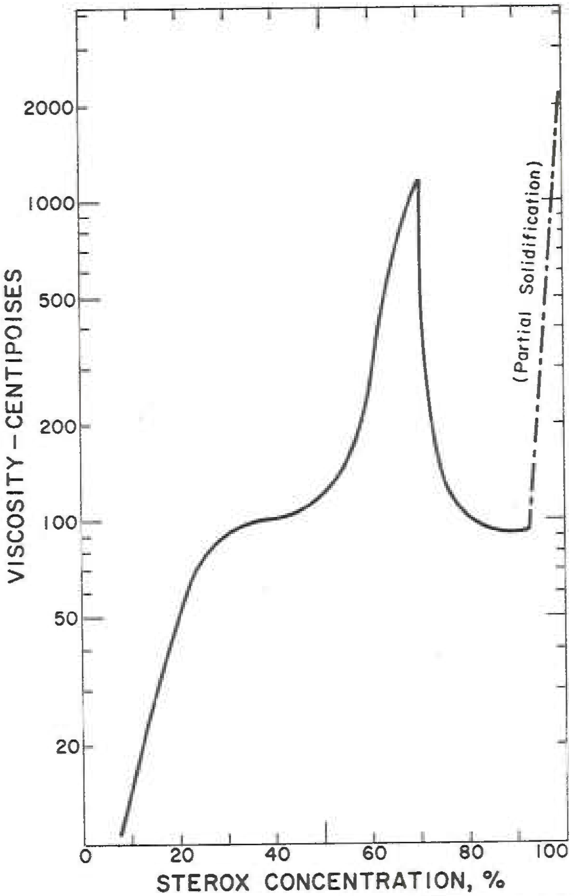

Fig. 4.37. Viscosity of aqueous solutions of STEROX AJ-100 sample at 25°C (*148*).

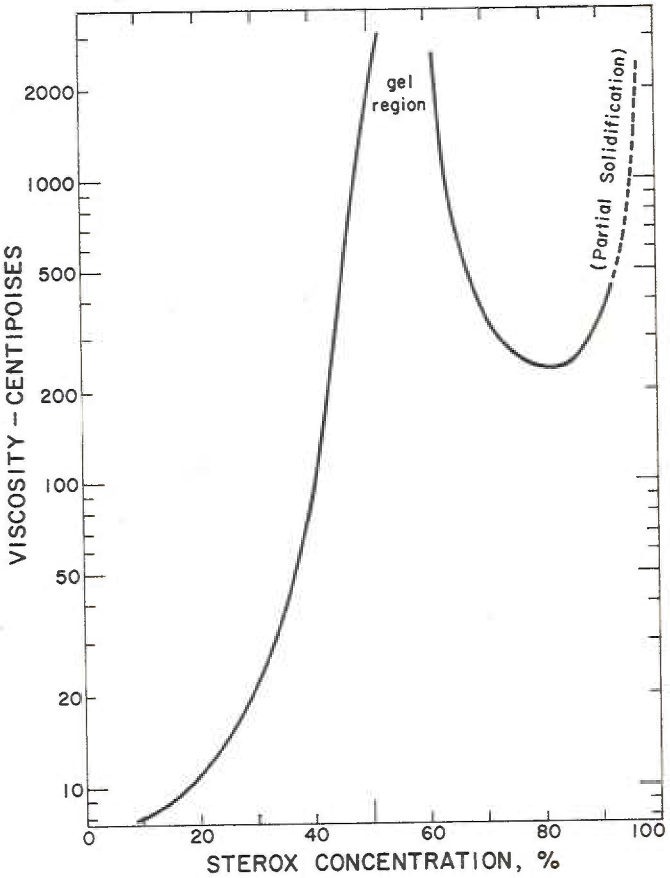

Fig. 4.38. Viscosity of aqueous solutions of STEROX AP-100 sample at 25°C (*149*).

TABLE 4.7

Detersive Efficiency (*150*)

		Detergency, per cent soil removal			
		U.S. Testing Co. fabric		F. D. Snell fabric	
Nonionic surfactant	Cloud point, °C	50 ppm	150 ppm	50 ppm	150 ppm
TERGITOL 15-S-9[a]	64	28	27	21	20
Ziegler alcohol-ethylene oxide condensates[b]	64	27	27	22	23

Formulation	Parts by weight
Nonionic surfactant	12.0
Sodium tripolyphosphate	40.0
Sodium metasilicate	10.0
Sodium carboxymethylcellulose	1.0
Sodium sulfate	37.0

Terg-o-tometer conditions	
Detergent concentration, %	0.2
Wash temperature, °F	120 (49°C)
Wash cycle, min	15
Agitation, rpm	100
Water hardness, ppm as $CaCO_3$	50, 150

[a] Trademark product of Union Carbide Corp.

[b] Ziegler Alcohol Composition: C_{14}, C_{16}, and C_{18} in the ratio of 40:40:20.

b. Wetting

Tables 4.8 and 4.9 contain data on the wetting properties of each of the three different types of alcohol-ethylene oxide adducts.

TABLE 4.8

Draves Clarkson Wetting Time[a] (*148,149*)

	Wetting time, sec	
Concentration, %	STEROX AJ	STEROX AP
0.5	Instantaneous	4.3
0.25	3.0	7.5
0.125	7.9	13.4
0.0625	17.9	36.6
0.031	96	144
0.015	>180	>180

[a] 0-ppm H_2O hardness; 25°C.

TABLE 4.9

Wetting Properties (*150*)

Nonionic surfactant	Cloud point, °C	Wetting time,[a] sec. 0.2%	0.1%	0.05%
TERGITOL 15-S-9	64	3.6	12.3	27.8
Ziegler alcohol-ethylene oxide adducts[b]	64	60.4	98.9	202.6

[a] Measured at 25°C by the Draves-Clarkson method at surfactant concentrations.

[b] Ziegler alcohol is a mixture of C_{14}, C_{16}, and C_{18} in the ratio of 40:40:20.

c. Foam

Tables 4.10 and 4.11 give Ross-Miles lather values for the three different types of alcohol-ethylene oxide adducts.

TABLE 4.10

Foam Height in the Ross-Miles Tests[a] (*148,149*)

H_2O hardness	Foam height, cm STEROX AJ-100	STEROX AP-100
50-ppm		
at once	9.7	15.6
after 5 min	7.7	13.9
300-ppm		
at once	10.6	15.6
after 5 min	6.0	10.0

[a] 0.1% concentration; 25°C.

TABLE 4.11

Ross-Miles Foam Test[a] (*150*)

Nonionic surfactant	Cloud point, °C	Foam height, mm Initial	5 min
TERGITOL 15-S-9	64	165.0	25.0
Ziegler alcohol-ethylene oxide adducts[b]	64	121.0	10.7

[a] Test run at 120°F with 0.2% of the nonionic surfactant.

[b] Ziegler alcohol is a mixture of C_{14}, C_{16}, and C_{18} in the ratio of: 40:40:20.

d. Surface and Interfacial Tension

Tables 4.12 and 4.13 contain data on the surface tension and interfacial tension of the three different types of nonionic surfactants derived from a hydrophobic alcohol.

TABLE 4.12

Surface and Interfacial Tension (*148,149*)

Concentration, %	Temp., °C	STEROX AJ-100	STEROX AP-100
	Surface tension, dynes/cm		
1.0	25	29.8	25.2
0.25	25	29.8	36.0
0.0625	25	29.9	26.2
1.0	50	28.7	
0.25	50	28.8	
0.0625	50	29.1	
	Interfacial tension, NUJOL, dynes/cm		
1.0	25	2.1	6.1
0.25	25	2.7	6.7
0.0625	25	3.5	7.0
1.0	50	1.7	
0.25	50	1.2	
0.0625	50	2.5	

TABLE 4.13

Surface Tension[a] (*150*)

Nonionic surfactant	Cloud point, °C	Concentration, %	
		0.1	0.005
TERGITOL 15-S-9	64	29.4	30.3
Ziegler alcohol-ethylene oxide adducts[b]	64	31.6	33.1

[a] Surfactant solutions were prepared with distilled water and surface tension (dynes/cm) was measured at 25°C by the du Nuoy ring method using an Instron tensile tester.

[b] Ziegler alcohol is a mixture of C_{14}, C_{16}, and C_{18} in the ratio of 40:40:20.

4.5. APPLICATIONS

The uses of nonionic surfactants based on polyoxyethylene alcohols are so many and so varied that it is impossible to discuss each one in detail. Thus the over-all use of these products can only be discussed in general terms. In addition there are hundreds of polyoxyethylene alcohols produced commercially in the world. Some of these products are designed for a specific application, whereas others have a variety of applications.

A. Household Surfactants

The largest outlet for the polyoxyethylene alcohols in the future will be in the formulation of cleaners for household and industrial use. They can be compounded as liquids, powders, pastes, or bars depending upon the specific application. A typical controlled-sudsing laundry-detergent formulation for the household market follows (*148,149*):

STEROX AJ	5–10%
Water (plus dye if desired)	3–5
Sodium tripolyphosphate	20–30
Sodium sulfate	20–30
Soda ash	20–30
Sodium silicate ($Na_2O:SiO_2 = 1:2$)	20–30
Sodium carboxymethylcellulose	1–2

A typical formulation for automatic-dishwashing-machine detergent is as follows (*148,149*):

STEROX AJ	0.5–1.0%
Tetrasodium pyrophosphate	20–30
Sodium tripolyphosphate	20–30
Soda ash	20–30
Sodium metasilicate	30–40
PLURONIC* L-60	0.5–1.0

* Trademark of Wyandotte Chemicals Corp.

The following formulation may be used for hand dishwashing (*148,149*):

STEROX AJ or AP	3–5%
SANTOMERSE* #1	30–45
Tetrapotassium phosphate	10–15
Isopropanol	15–25
Water and perfume	15–25

* Trademark of Monsanto Co.

The washing of wool goods in the home usually requires some special treatment. A cold-water wool detergent formulation which has been used for this purpose is (*148,149*):

STEROX AJ	15.0–20.0%
Tetrapotassium phosphate	5.0–10.0
Propylene glycol	25.0–35.0
Fluorescent brighteners	0.1–0.2
Dye coloring	0.01–0.03
Water	35.0–55.0

The following solid hard-surface cleaner (dry powder) formulation is a heavy-duty type for use in cleaning floors, walls, or painted surfaces (*148,149*):

STEROX AJ or AP	0.5–1.0%
Trisodium phosphate	30–40
Sodium tripolyphosphate	20–30
SNOW FLAKE* crystals	40–50

* Trademark of Allied Chemicals Corp.

A typical heavy-duty floor-cleaner and wax-stripper (liquid) formulation for cleaning floors is as follows:

STEROX AJ or AP	5–10
Oleic acid	10–15
Triethanolamine	5–10
Sodium carbamate	10–15
VERSENE*	1–2
Water	50–60

* Trademark of Dow Chemical Co.

The use of a waterless hand cleaner has been practiced in industry for a number of years. An example of a typical formulation is (*148,149*):

STEROX AJ	4.0–6.0%	4.0–6.0%
Mineral oil	40.0–41.0	
Kerosene		40.0–41.0
Oleic acid	12.0–13.0	12.0–13.0
Triethanolamine	3.0–4.0	6.0–8.0
Monethanolamine	1.0–1.5	
SANTOMERSE* 85	2.0–3.0	2.0–3.0
Propylene glycol	45.0–55.0	45.0–55.0

* Trademark of Monsanto Co.

B. Industrial Surfactants

1. Textile

a. Scouring

In the textile-scouring operations for both natural and synthetic fibers, nonionics based on alcohols have played a very important role. Typical examples in this area are STEROX AJ and TERGITOL 15-S-9. The process conditions for scouring are so varied that no one product is used exclusively.

Wool-scouring, cotton Kier boiling, boiling-off of viscose, and soaping-off are examples of some of the types of scouring operations. The polyoxyethylene alcohols are normally used in the 0.1 to 1.0 per cent concentration range plus some polyphosphates, silicates, or other alkali. By use of the nonionics, the scouring time is reduced and soap "curds" are eliminated (*148,149,152*).

Also, since nonionics are not substantitive to fibers, balling as a result of detergent residues is eliminated in the cording operation.

b. Lubricating

Since the scouring operation removes the fats present in the initial material, materials have to be added back which will serve as lubricants (*153*), softeners, and antistatics (*154–156*) for the cording, spinning, and weaving operation. Mineral oil and/or vegetable oil are normally used as lubricants. However, in order that these oils be uniformly distributed, emulsifiers such as STEROX AJ are added to the oils.

c. Dyeing and Finishing

The largest surfactant-consuming step in cotton processing is the dyeing and finishing step. Polyoxyethylene alcohols play an important role in this process, owing to their actions as penetrants, wetting agents, and dyeing assistants (*157–173*). The mode of action of dyeing assistance seems to involve the agglomeration of dyestuff molecules into micelles, and polyoxyethylene alcohols such as STEROX AJ serve well in this capacity.

2. Agricultural

Nonionics are excellent emulsifiers for agricultural sprays because they are unaffected by hard water and by pH changes. The general types of agricultural sprays are the "ready-to-emulsify" hydrocarbon solutions of various insecticides and plant toxicants such as DDT, PARATHION, CHLORDANE, TOXAPHENE, 2,4-D, and 2,4,5-T esters (*174-176*). Sprays of this type are sold as emulsifiable concentrates and are usually diluted with water at the time of application. The hydrocarbon is utilized to dilute the toxicant to safe strength or to keep the material in liquid form. Polyoxyethylene alcohols are very useful in this application. Examples of typical formulations are:

85% CHLORDANE Emulsifiable Concentrate

CHLORDANE	80–90%
STEROX AJ	10–20

65% TOXAPHENE Emulsifiable Concentrate

TOXAPHENE	60–70%
Kerosene	20–30
ARQUAD* 2C	4–6
STEROX AJ	4–6

* Trademark of Armour Industrial Chemical Co.

2,4-D Herbicide Emulsion

2,4-D acid	40–45%
STEROX AJ	0.75–1.50
Methanol	10.0–12.0
Dimethylamine	8.0–10.0
Water	34.0–36.0

Tests have been made showing the beneficial effects from the use of surfactants, including specifically STEROX AJ, in the manufacture of superphosphate for fertilizer use (*177*). Addition of STEROX AJ to the reaction mixture increases the rate and degree of conversion of the phosphate to the available form. The surfactant is added to the extent of 0.01 to 0.04 per cent concentration in the finished product (0.2 to 0.8 pound STEROX AJ per ton of superphosphate).

3. Paper

Polyoxyethylene alcohols find a number of uses in the paper industry (*178–180*). Rewetting agents such as STEROX AJ are used to improve the absorbency of wet-strength paper, i.e., paper towels. STEROX AJ is also used for the rapid penetration of treating solutions into impregnated paper or box board. Also polyoxyethylene alcohols are used in pulping of old paper, as well as in the deinking of old newsprint.

4. Rubber

Polyoxyethylene alcohols are excellent stabilizers for rubber latex during the compound operations (*181,182*).

5. Leather

Normally, leather goes through four basic processing operations—degreasing, tanning, fat-liquoring, and finishing. In each operation the use of a surfactant, particularly the polyoxyethylene alcohols, is helpful (*183*).

6. Paint

The use of wetting agents and emulsifiers in the emulsion polymerization of base latices is well-known (*184*). The choice of a particular surfactant depends on the particular monomer being reacted and the properties desired in the final emulsion. Polyoxyethylene alcohols as well as other nonionics are superior emulsifiers because of their tolerance for hard water.

In paint-formulating operations, stabilized latex emulsions are sometimes subject to coagulation with severe agitation or milling. The use of polyoxyethylene alcohols (such as BRIJ* 30 and BRIJ* 35) overcomes this problem.

7. Plastics

Polyoxyethylene alcohols have been reported to be of use in this industry (*185–187*).

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* Trademark of Atlas Chemical Industries, Inc.

REFERENCES

1. L. Bouveault and G. Blanc, *Bull. Soc. Chem.*, **29**, 787 (1903).
2. L. Bouveault and G. Blanc, *Compt. Rend.*, **136**, 1679 (1903).
3. *Ibid.*, **137**, 60 (1903).
4. *Ibid.*, **137**, 328 (1903).
5. H. Adkins and R. Conner, *J. Am. Chem. Soc.*, **53**, 1091 (1931).
6. H. Adkins and K. Folkers, *J. Am. Chem. Soc.*, **53**, 1095 (1931).
7. H. Adkins and J. Sauer, *J. Am. Chem. Soc.*, **59**, 1 (1937).
8. H. R. Arnold and W. A. Lazier (to E. I. du Pont de Nemours & Co.), U.S. 2,116,552 (1938).
9. E. W. Eckey and J. E. Taylor (to Proctor & Gamble Co.), U.S. 2,413,612 (1946).
10. S. J. Green, U.S. 2,080,419 (1937).
11. S. J. Iwai, *Nippon Oil Technol. Soc.*, **2** (6), 19 (1949); *C.A.* **44**, 5618c (1950).
12. W. B. Johnston (to American Cyanamid Co.), U.S. 2,347,562 (1944).
13. S. Komori, *Kogyo Kagaku Zasshi*, **41**, 219 (1938); *C.A.* **33**, 8564 (1939).
14. *Ibid.*, **43**, 34 (1940); *C.A.*, **34**, 3673 (1940).
15. *Ibid.*, **43**, 122 (1940); *C.A.*, **34**, 5411 (1940).
16. *Ibid.*, **43**, 337 (1940); *C.A.*, **35**, 1758 (1941).
17. *Ibid.*, **43**, 428 (1940); *C.A.*, **35**, 4345 (1941).
18. *Ibid.*, **44**, 740 (1941); *C.A.*, **42**, 2228 (1948).
19. *Ibid.*, **45**, 141 (1942); *C.A.*, **43**, 5363 (1949).
20. S. Komori, Y. Shigeno, and I. Yoneda, *C.A.*, **47**, 11762a (1953).
21. W. A. Lazier (to E. I. du Pont de Nemours), U.S. 1,839,974 (1932).
22. *Ibid.*, 2,079,414 (1937).
23. *Ibid.*, 2,094,127 (1937).
24. *Ibid.*, 2,109,844 (1938).
25. *Ibid.*, 2,114,717 (1938).
26. A. S. Richardson and J. E. Taylor (to Proctor & Gamble Co.), U.S. 2,340,343 (1944).
27. *Ibid.*, 2,340,344 (1944).
28. *Ibid.*, 2,340,687 (1944).
29. *Ibid.*, 2,340,690 (1944).
30. *Ibid.*, 2,340,691 (1944).
31. *Ibid.*, 2,375,495 (1945).
32. W. Rittmeister (to American Hyalsol Corp.), U.S. 2,374,379 (1945).
33. Rohm & Haas Co., French 802,542 (1936).
34. O. Schmidt and K. Huttner (to I.G. Farbenindustrie), U.S. 2,009,948 (1935).
35. Y. Sinozaki and S. Sumi, *Nippon Nogei Kagabu Kaishi*, **14**, 1113 (1938); *C.A.*, **32**, 8044 (1938).
36. *Ibid.*, **15**, 531 (1939); *C.A.*, **34**, 2791 (1940).
37. *Ibid.*, **16**, 23 (1940); *C.A.*, **34**, 3673 (1940).
38. J. Takashashi, *Nippon Oil Technol. Soc.*, **2** (5), 19 (1949); *C.A.*, **44**, 5618 (1950).
39. G. A. Weber and C. H. Hamblet (to E. I. du Pont de Nemours & Co.), British 582,699 (1946).
40. A. Guyer, A. Bieler, and K. Jaberg, *Helv. Chim. Acta.*, **30**, 39 (1947).
41. *De Nora High Pressure Hydrogenation Process*, Lummus Co., 385 Madison Ave., New York 17, N.Y.
42. E. F. Hill, G. R. Wilson, and E. C. Steinle, *Ind. Eng. Chem.*, **46** (9), 1917 (1954).
43. V. L. Hansley, *Ind. Eng. Chem.*, **39**, 55 (1947).
44. M. L. Kastens and H. Peddicord, *Ind. Eng. Chem.*, **41**, 438 (1949).
45. R. E. Kirk and D. F. Othmer, eds., *Encyclopedia of Chemical Technology*, Vol. 8, 1st ed., Wiley-Interscience, New York, 1952, p. 778; A. Landgraf and O. Roelen, German 931,405 (1955).
46. M. Orchin, L. Kirch, and I. Goldfarb, *J. Am. Chem. Soc.*, **78**, 5450 (1956); D. S. Breslow and R. F. Heck, *Chem. & Ind.*, **17**, 467 (1960).

47. I. Wender, S. Metun, S. Ergun, H. W. Sternberg, and H. Greenfield, *J. Am. Chem. Soc.*, **78**, 5401 (1956).
48. I. Wender, H. W. Sternberg, and M. J. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).
49. I. Wender, H. W. Sternberg, and M. J. Orchin, in *Catalysis*, Vol. V (P. E. Emmett, ed.), Reinhold, New York, 1957, Chap. 2.
50. L. F. Hatch, *Higher Oxo Alcohols*, Wiley, New York, 1957.
51. R. E. Kirk and D. F. Othmer, eds., *Encyclopedia of Chemical Technology*, Second Supplement Volume, Wiley-Interscience, New York, 1960, p. 548.
52. *Chem. Week*, p. 19 (August 15, 1964).
53. D. Justice and V. Lamberti, *Chem. Eng. Progr.* **60** (12), 35 (1964).
54. Continental Oil Co., *Tech. Bull.* AL-11 (1963).
55. K. Ziegler, British 763,828 (1956).
56. *Ibid.*, British 713,081 (1954).
57. *Ibid.*, British 777,701 (1957).
58. *Ibid.*, British 804,335 (1958).
59. *Ibid.*, U.S. 2,892,858 (1959).
60. K. Ziegler and H. Gellert, U.S. 2,699,457 (1955).
61. *Ibid.*, U.S. 2,826,598 (1958).
62. K. Zosel (to Studiengesellschaft Kohle m.b.H., Germany), U.S. 2,930,808 (1960).
63. M. T. Atwood, *J. Am. Oil Chemists' Soc.*, **40** (2), 64 (1963).
64. *Chem. Eng. News*, 31 (June 8, 1964).
65. D. K. Barnes (to Pan American Petroleum Corp.), U.S. 2,819,319 (1958).
66. I. E. Levine and E. Clippinger (to California Research Corp.), U.S. 3,018,308 (1962).
67. M. S. Kharasch and W. M. Potts, *J. Org. Chem.*, **2**, 195 (1937).
68. E. Clippinger, *I. & E. C. Product Research and Development*, **3**, (1) 3 (1964).
69. F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).
70. W. J. Hickinbottom *Reactions of Organic Compounds, 2nd ed.*, Longmans, Green, London, 1948, p. 23.
71. P. J. Garner and H. N. Short (to Shell Development Co.), U.S. 2,587,990 (1952).
72. L. C. Rubin (to M. W. Kellogg Co.), U.S. 2,573,730 (1951).
73. K. L. Butcher and G. M. Nickson, *J. Appl. Chem.* (*London*), **10**, 65 (1960).
74. P. L. Kooijman, *Proc. Intern. Congr. Pure Appl. Chem., 11th, London*, Vol. I, 499 (1950).
75. A. N. Bashkirov and V. V. Kamzolkin, *World Petrol. Congr. Proc., 5th, N.Y., 1959*, **4**, 175 (1960); *CA*, **57**, 13597*a* (1962).
76. French 1,166,679 (1958) (to Société anon d'innovations chimique Sinnova on Sidac); *CA*, **55**, 378 (1961).
77. J. J. Astle, *The Chemistry of Petrochemicals*, Reinhold, New York, 1956, p. 67.
78. R. E. Engelbrecht, *J. Org. Chem.*, **29**, 24517 (1964).
79. J. M. Corkill, J. F. Goodman, and R. H. Ottewill, *Trans. Faraday Soc.*, **57**, 1627 (1961).
80. F. C. Cooper and M. W. Patridge, *J. Chem. Soc.*, **1950**, 459.
81. B. A. Mulley, *J. Chem. Soc.*, **1958**, 423, 2065.
82. B. A. Mulley, *Proc. Intern. Congr. Surface Activity, 3rd, Cologne*, **A1**, 31 (1960).
83. A. F. Sirianni and B. A. Gingras, *Can. J. Chem.*, **39**, 331 (1961).
84. D. A. Shirley, J. R. Zietz, Jr., and W. H. Reedy, *J. Org. Chem.*, **18**, 378 (1953).
85. D. A. Shirley and W. H. Reedy, *J. Am. Chem. Soc.*, **73**, 4886 (1951).
86. J. V. Karabinos, G. E. Bartels, and G. E. Kapella, *J. Am. Oil Chemists' Soc.*, **31**, 419 (1954).
87. A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, **34**, 39 (1957).
88. H. F. Drew and J. R. Schaeffer, *Ind. Eng. Chem.*, **50**, 1253 (1958).
89. I.G. Farbenindustrie, British 271,169 (1926).
90. C. Schoeller and M. Wittwer (to I.G. Farbenindustrie), U.S. 1,970,578 (1934).
91. G. J. Stockburger and J. D. Brandner, *J. Am. Oil Chemists' Soc.*, **40**, 590 (1963).
92. W. B. Satkowski and C. G. Hsu, *Ind. Eng. Chem.*, **49**, 1875 (1957).
93. D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **105**, 2117 (1914).
94. L. Schechter and J. Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).

95. E. H. Madsen, *J. Chem. Soc.*, **103**, 966 (1913).
96. T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **44**, 684 (1922).
97. A. T. Ballun, J. N. Schumacher, G. E. Kapella, and J. V. Karabinos, *J. Am. Oil Chemists' Soc.*, **31**, 20 (1954).
98. M. Engel, *Compt. Rend.*, **103**, 156 (1886); H. Lescoeur, *Compt. Rend.*, **121**, 692 (1895); D. William and R. W. Bost, *J. Chem. Phys.*, **4**, 251 (1936).
99. C. A. Carter (to Union Carbide and Carbon Corp.), U.S. 2,870,220 (1959).
100. J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).
101. A. N. Wrigley, A. J. Stirton, and E. Howard, Jr., *J. Org. Chem.*, **25**, 439 (1960).
102. B. Weibull and B. Nycander, *Acta Chem. Scand.*, **8**, 847 (1954).
103. M. E. Puthoff and J. H. Benedict, *Anal. Chem.*, **33**, 1884 (1961).
104. J. V. Karabinos and E. J. Quinn, *J. Am. Oil Chemists' Soc.*, **33**, 223 (1956).
105. M. J. Schick, *J. Am. Oil Chemists' Soc.*, **40**, 680 (1963).
106. G. Tischbirek, *Proc. Intern. Congr. Surface Activity, 3rd, Cologne*, **A1**, 126 (1960).
107. R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
108. P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).
109. Dow Chemical Co., *Tech. Bull.* 125-273-60, "Alkylene Oxides," Midland, Mich., 1960.
110. Union Carbide Chemicals Co., *Tech. Bull.*, "Alkylene Oxides," New York, 1961.
111. L. G. Hess and V. V. Tilton, *Ind. Eng. Chem.*, **42**, 1251 (1950).
112. Mfg. Chemists Assoc. Chem. Safety Data Sheet SD-38, "Properties and Essential Information for Safe Handling and Use of Ethylene Oxide," 1951.
113. J. D. Malkemus, *J. Am. Oil Chemists' Soc.*, **33**, 571 (1956).
114. W. Baird, P.B. Rept. 28754 (BIOS Final Rept. No. 421, Item No. 22 (Sept. 1945).
115. I. R. Hoyt, P.B. Rept. 3868 (Sept., 1945).
116. R. E. Richardson, J. G. Kern, R. L. Murray, and R. W. Sudhoff, P.B. Rept. 6684 (May, 1945).
117. C. B. Brown, P.B. Rept. A63822 (BIOS Final Rept. 418, Item 22) (Feb., 1946).
118. J. D. Brandner, W. H. Lockwood, R. H. Nagel, and K. L. Russell, P.B. Rept. 81819, FIAT Final Rept. No. 1141 (1947).
119. E. J. Mills and D. G. Leis, U.S. 2,988,572 (1961).
120. R. W. Wilson (to Monsanto Co.), U.S. 2,586,767 (1952).
121. W. P. Krause (to Jefferson Chemical Co.), U.S. 2,983,763 (1961).
122. W. D. Beauchamp, R. E. Booth, and E. R. Degginger (to Allied Chemical Corp.), U.S. 3,016,404 (1962).
123. P. M. T. Matell, Canadian 656,392 (1963).
124. E. M. Stolz (to Olin Mathieson Chemical Corp.), U.S. 2,778,854 (1957).
125. J. D. Brandner and R. M. Geopp, P.B. Rept. 85159, FIAT Rept. No. 1311 (1947).
126. D. E. Gushee and O. L. Scherr, *Ind. Eng. Chem.*, **51**,798 (1959).
127. Jefferson Chemical Co., Inc., *Tech. Bull.* JO-044, "Propylene Oxide," Houston, Tex., 1960.
128. P. P. McClellan, *Ind. Eng. Chem.*, **42**, 2402 (1950).
129. F. N. Hill, F. E. Bailey, and J. T. Fitzpatrick, *Ind. Eng. Chem.*, **50**, 5 (1958).
130. F. E. Bailey, G. M. Powell, and K. L. Smith, *Ind. Eng. Chem.*, **50**, 8 (1958).
131. R. A. Miller and C. C. Price, *J. Polymer Sci.*, **34**, 161 (1959).
132. G. O. Curme and F. Johnston, *Glycols*, Reinhold, New York,1952, Chap. 11.
133. Oxirane, Ltd., British 757,309 (1956)
134. *Ibid.*, British 736,991 (1955).
135. J. C. Moseley, G. Ellis, E. J. Hayward, and A. C. Houston (to Shell Oil Co.), U.S. 3,030,426 (1962).
136. Monsanto Co., unpublished data, 1958–1962.
137. J. C. Harris, *Detergency Evaluation and Testing*, Wiley-Interscience, New York, 1954.
138. J. T. Patton (to Wyandotte Chemicals Corp.), Canadian 578,790 (1959).
139. A. B. Steele, Jr., E. J. Mills, and D. G. Leis (to Union Carbide and Carbon Corp.), Canadian 578,790 (1959).
140. M. E. Pruitt and W. A. Rogers, Jr., (to Dow Chemical Co.), Canadian 540,359 (1957).
141. *Ibid.*, Canadian 577,315 (1959).

142. D. R. Jackson and L. G. Lundsted (to Wyandotte Chemicals Corp.), Canadian 540,359 (1957).
143. *Ibid.*, U.S. 3,036,130 (1962).
144. J. W. McCutcheon, *Detergent and Emulsifier* (*1964 Annual*), J. W. McCutcheon Inc., New Jersey.
145. P. J. Sisler, *Encyclopedia of Surface Active Agents* (English translation), Chemical Publ. Co., New York, 1952.
146. N. Schoenfeldt, *Oberflaechenaktive Anlagerungs-produkte des Aethyleaoxyds*, Wissenschatliche Verlagsgesellschaft mbH, Stuttgart, 1959.
147. R. D. Fine, *J. Am. Oil Chemists' Soc.*, **35**, 542 (1958).
148. STEROX AJ, *Tech. Bull.* I-147, Monsanto Co., St. Louis, Mo., 1958.
149. STEROX AP, *Tech. Bull.* I-201, Monsanto Co., St. Louis, Mo., 1962.
150. J. H. McFarland and P. R. Kinkel, *J. Am. Oil Chemists' Soc.*, **41**, 742 (1964).
151. T. P. Matson, *Soap Chem. Specialties*, **39** (11), 52 (1963).
152. Farbenfabriken Bayer, British 690,355 (1953); *CA*, **48**, 6463*g* (1953).
153. N. I. Chernozhukov and A. I. L'vova, *Tr. Groznensk Neft. Inst., Sb.*, **23**, 225 (1960); *C.A.* **35**, 15899d (1961).
154. Montecatini Soc. Generale Per L'Industria Mineraria E Chimica, British 804,964 (1958).
155. Monsanto Co., British 920,621 (1963).
156. Montecatini Soc. Generale Per L'Industria Mineraria E Chimica, Belgian 628,978 (1963).
157. W. H. Hindle (to Monsanto Co.), U.S. 3,096,139 (1963).
158. C. Mazzon, L. Mazzon, and A. Mazzon, Italian 623,239 (1961).
159. Farbwerke Hoechst A.G., German 1,021,826 (1958).
160. W. Carr, *Compt. Rend. Congr. Intern. Chim. Ind., 31st, Liége, 1958*; *C.A.*, **54**, 3960b (1960).
161. Badische Anilin & Soda Fabrik A.G. Ludwigshafen/Rhein, German 1,006,389 (1957).
162. Imperial Chemical Industries Ltd., British 869,150 (1961).
163. Farbwerke Hoechst A.G., German 1,060,350 (1959).
164. Societe Rhodiaceta, French 1,016,438 (1952).
165. Farbwerke Hoechst A.G., German 933,271 (1955).
166. Compagnie Francaise des Matieres Colorantes, French 1,096,491 (1955).
167. W. Ender, German 896,938 (1953).
168. Farbenfabriken Bayer A.G., German 1,132,092 (1962).
169. Z. Bayer, T. Robinson, and J. Tomanek, Czech. 99,905 (1961).
170. Farbenfabriken Bayer A.G., Belgian 615,207 (1962).
171. Kurashik Rayon Co. Ltd., Japanese 19,213 (1961).
172. J. Nusslein, C. Kuch, and H. Bartl (to Farbwerke Hoechst A.G. Vorm.), U.S. 2,901,311 (1959).
173. H. Werdenberg (to Ciba Co.), U.S. 3,068,058 (1962).
174. R. L. Sundberg and J. M. Cross (to General Aniline & Film Corp.), U.S. 2,965,678 (1960)
175. J. C. Wiedow (to Monsanto Co.), U.S. 2,893,913 (1959).
176. L. L. Jansen, *J. Agr. Food Chem.* **12B**, 223 (1964).
177. P. G. Arvan, R. P. Langguth, and R. R. Eckstein, *J. Agr. Food Chem.*, **3**, 131 (1955).
178. C. W. Schroeder (to Shell Development Co.), U.S. 2,913,356 (1959).
179. K. J. Lissant (to Petrolite Corp.), U.S. 3,069.306 (1962).
180. *Ibid.*, U.S. 3,069,308 (1962).
181. Food Machinery and Chemical Corp., German 1,080,025 (1958).
182. M. R. Buffington, U.S. 2,442,341 (1948).
183. L. H. Wilson (to American Cyanamid Co.), U.S. 2,769,712 (1956).
184. British Titan Products Co. Ltd., British 944,292 (1963).
185. E. C. Suhrie (to Koppers Co.), U.S. 2,921,930 (1960).
186. Siemens-Schuckertwerke GmbH, German 1,092,056 (1960).
187. M. A. Manganelli (to Monsanto Co.), U.S. 2,772,257 (1956).
188. H. Lemke, *Hydrocarbon Process. Petrol. Refiner*, **45(2)**, 148 (1966).
189. R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).
190. L. Marko, G. Bor, G. Almasy, and P. Szabo, *Brennstoff-Chem.*, **44**, 184 (1959).
191. L. Kirch and M. Orchin, *J. Am. Chem. Soc.* **80**, 4428 (1958); **81**, 3597 (1959).

CHAPTER 5

POLYOXYETHYLENE ESTERS OF FATTY ACIDS

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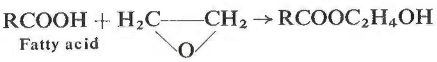
5.1. INTRODUCTION

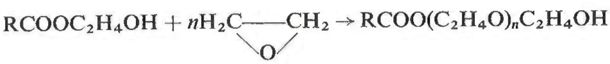
The nonionic surfactants discussed in Chapters 3 and 4 were based on either alkylphenol or alcohol hydrophobic groups. A third important hydrophobic base for nonionic surfactants are fatty acids, particularly those in the C_{12} to C_{18} range. These polyoxyethylene esters of fatty acids are covered in this chapter.

Nonionic surfactants of this type are made by reacting a fatty acid with ethylene oxide in a manner similar to that used to prepare the polyoxyethylene alkylphenols (Chapter 3) or alcohols (Chapter 4). They can also be prepared by esterifying a previously prepared polyethylene glycol with a fatty acid. Both methods of preparation are discussed.

The basic chemical reactions for the preparation of the straight-chain fatty acid esters of polyethylene glycol are



$$\underset{\text{Fatty acid}}{\mathrm{RCOOH}} + \underset{\diagdown \mathrm{O} \diagup}{\mathrm{H_2C{-}{-}CH_2}} \rightarrow \mathrm{RCOOC_2H_4OH} \qquad (5.1)$$



$$\mathrm{RCOOC_2H_4OH} + n\underset{\diagdown \mathrm{O} \diagup}{\mathrm{H_2C{-}{-}CH_2}} \rightarrow \mathrm{RCOO(C_2H_4O)_{\mathit{n}}C_2H_4OH} \qquad (5.2)$$

From Eq. (5.1) it is evident that the first step in the oxyethylation process is the addition of 1 mole of ethylene oxide to give the alcohol ester of the fatty acid. Further addition of ethylene oxide gives the polyoxyethylene esters of the fatty acid. A discussion of the kinetics of this reaction has been given in Chapter 2 and is amplified in this chapter. The various sources of hydrophobic intermediates are reviewed in Section 5.2. The synthesis of the hydrophilic intermediate, i.e., ethylene oxide, has been described in Chapter 3. Discussions of the preparation, properties, and applications of the polyoxyethylene esters of fatty acids are given in Sections 5.3 to 5.5. The commercial importance of this type of nonionic surfactant may be assessed from examination of Table 5.9.

5.2. SOURCES OF HYDROPHOBIC INTERMEDIATES

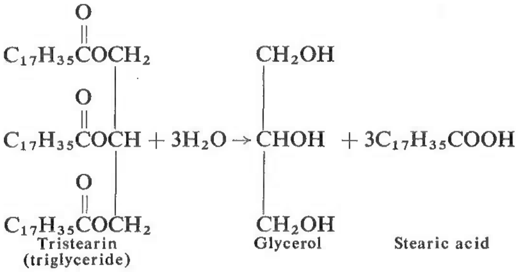
A. Natural Sources

Fatty acids are an important group of organic acids which occur in nature, usually in combination with glycerol in the form of the glycerol ester or triglyceride. These naturally occurring fats and oils offer one of the largest potential sources of raw materials for the preparation of chemical synthetics, which includes the manufacture of nonionic surfactants.

The higher members of the series of fatty acids (lauric, myristic, palmitic, stearic, oleic, linoleic, etc.) in chemical combination with glycerol form the main constituents of the animal and vegetable fats and oils. The lower members (caproic, caprylic, capric) are not widely distributed in nature and form a minor constituent in only a few natural oils such as coconut, babassu, and palm kernel.

1. Hydrolysis (Fat-Splitting)

The starting point for most fatty acid manufacture is hydrolysis or fat splitting (*1–8*). The over-all reaction for this manufacturing procedure is given in (5.3).



$$\begin{array}{lcll} C_{17}H_{35}\overset{\displaystyle O}{\overset{\|}{C}}OCH_2 & & CH_2OH & \\ C_{17}H_{35}\overset{\displaystyle O}{\overset{\|}{C}}OCH + 3H_2O & \rightarrow & CHOH & + 3C_{17}H_{35}COOH \\ C_{17}H_{35}\overset{\displaystyle O}{\overset{\|}{C}}OCH_2 & & CH_2OH & \\ \text{Tristearin (triglyceride)} & & \text{Glycerol} & \text{Stearic acid} \end{array} \tag{5.3}$$

This process of reacting the fat with water to form glycerol and fatty acid usually requires three hydrolysis steps to obtain free acid and free glycerol. It is believed that these are homogeneous reactions taking place mainly in the fat phase, as the solubility of water in a fat is greater than the solubility of a fat in water (*9,10*).

In reaction (5.3) it is only necessary to mix fat with water to cause some hydrolysis, but the reaction is very slow. When sulfuric acid is added to a fat, the sulfonated product formed increases the solubility of water in fat, and hydrolysis takes place at a faster rate. Solubility is further increased by the use of an alkaline catalyst (*11*). Also, splitting is accelerated by increasing the temperature, largely because of the increased solubility of water in the fat phase (*12*).

a. Twitchell Process

A major development in hydrolysis technique was made by Twitchell (*13*), who developed the sulfonic acid catalyst bearing his name. The first Twitchell reagents were made by the condensation and ring sulfonation of an aromatic hydrocarbon with oleic acid. The sulfuric acid used with the Twitchell reagent depresses the solubility of the reagent in the aqueous phase and increases its solubility in the fat phase, where acid-catalyzed hydrolysis occurs. From a study of the distribution of the reagent between oil and water, it was found that the degree of hydrolysis depended upon the relative amount of the reagent in the oil phase (*14*). Present-day fat-splitting catalysts also include alkylbenzene sulfonates and petroleum sulfonates (*14*). The use of phosphoric acid in place of sulfuric acid is mentioned in the literature (*15*).

The Twitchell process is no longer widely used in the U.S., but is still used commercially throughout the world. The advantages of the Twitchell process are its low initial capital cost and simplicity of installation and operation. However, this process does require considerable time and high steam consumption.

b. High-Pressure Splitting; Batch Operation

The autoclave method of fat splitting is actually the oldest method practiced on a commercial scale. It is used for splitting high-grade stock to produce light-colored fatty acids which do not require distillation. In addition, the autoclave process is much more rapid than the Twitchell process.

A catalyst is required for the autoclave process. These catalysts are usually the zinc, magnesium, and calcium oxides, of which zinc oxide (*9,10,16*) is the most active. About 2 to 4 per cent catalyst is used, based on the weight of the fat, and often a fraction of 1 per cent of zinc dust is added to improve the color of the fatty acid.

c. Continuous Splitting

Since the issuance of the first patents on continuous hydrolysis of fat (*17,18*), several companies have designed and built successful continuous hydrolyzers which are now rapidly replacing the older processes. The countercurrent high-pressure process is the most efficient of the current methods of fat hydrolysis. The high temperatures and pressures used permit short reaction time, and full countercurrent oil and water flow produces high degrees of splitting. A number of developments (*19–30*) led to the high efficiency of this process today.

d. Methyl Ester Process

The trans-esterification of fats with anhydrous methanol (*31*) in the presence of alkaline catalyst has the disadvantage of a multistage process; consequently it is a high-cost operation because of the enormous quantities of chemicals required for the process.

e. Purification of Fatty Acid for Use

The above types of processing only enable one to obtain the fatty acid from its natural source. Thus, the output of any fat-splitting process must be treated further to obtain the type of fatty acid required to prepare a surfactant.

Distillation under vacuum, either batch or continuous, is widely employed for purification. This normally removes any residual fatty glycerides and also improves the color and odor of the resulting fatty acid. Fractional distillation serves to separate materials of different boiling points that do not form constant boiling mixtures. There are a number of references on the distillation of fatty acids, some of which (*32–39*) are given below.

The separation of tallow fatty acids into solid (saturated) and liquid (unsaturated) components cannot be accomplished by distillation because the major components have the same chain length and are not significantly different in boiling point. Two major separation processes are used commercially: the " pressing method " and solvent crystallization.

In the pressing method, the mixed acids are cooled to about 40°F, and partial solidification takes place. A pressing of the cakes formed then removes the entrapped liquids. By two or three subsequent melting-cooling-pressing cycles, followed by a bleaching operation, a commercial stearic acid of high purity is obtained.

Of the many solvent-crystallization separation methods reported in the literature (*40–42*), the Emersol process (*43,44*) has achieved most commercial acceptance. This process involves the controlled crystallization of fatty acids from a polar solvent to achieve a separation of solid fatty acids from liquid fatty acids.

2. Tall Oil

In the sulfate or Kraft paper process, chips of pine wood are digested under heat and pressure with a solution of sodium hydroxide and sodium sulfide to free the cellulose of other wood constituents. The highly alkaline solution forms sodium soaps of the lignin and rosin and of the fatty acids originally present as esters. These are washed out of the wood pulp as a dark solution, known as black liquor, which is concentrated in multiple-effect evaporators. When the partially concentrated solution is cooled and allowed to settle, fatty acid and rosin soaps separate as a brown, curdy mass called black-liquor soap, which is skimmed off for processing into tall oil (*45,46*).

The black-liquor soap is boiled with sulfuric acid to convert the sodium soaps into free rosin and fatty acids. The reaction mixture is allowed to settle, and the clear, brown tall oil separates from the sodium sulfate solution formed during the acidification, and from lignin and other impurities. The sodium sulfate is returned to the alkali-recovery liquors of the paper mill. The tall oil is then washed with hot water to remove the acid and allowed to settle in storage tanks to reduce the water content of the material. This material is now what is known to the trade as crude tall oil.

There are two processes by which the crude tall oil can be further purified. One process is the simple distillation of the crude tall oil to give a tall oil which is lower in color than it was originally. However, if one uses fractional distillation, a tall oil which has only 0 to 5 per cent rosin acids can readily be obtained.

The other purification process for crude tall oil is the acid-refining technique. By this process the crude tall oil is further treated with small amounts of sulfuric acid in the presence of a solvent. The color bodies present react with the sulfuric acid to give a dark oil which can be separated from the main body by decantation and/or centrifugation. Time, temperature, and concentration of sulfuric acid are very critical in this step. Any free acidity remaining after separation of the color oils is removed by passing the material through an alkaline bed or by the addition of Fullers earth, which is subsequently removed by filtration. The last step in the process is the removal of the inert solvent under very mild distillation conditions to prevent discoloration. Acid refined tall oil has about 36 to 46 per cent rosin acids.

Polyoxyethylene esters of fatty acids have been prepared from crude tall oil but are too dark in color for most practical purposes (*47*). Tall oil, purified either by distillation or by acid refining, has been used quite extensively for the preparation of nonionic surfactants, since it is a very cheap source of unsaturated fatty acids.

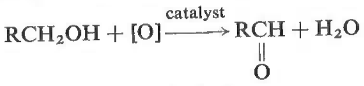
B. Chemical Synthesis of Fatty Acids

There are a number of chemical synthesis routes for the preparation of fatty acids. Some of the methods of preparation involve a change in the length of the carbon chain, whereas others do not involve any changes in carbon chain length. The first reactions to be discussed are in the latter group.

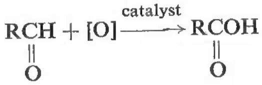
1. Oxidation of ROH and RCHO

The oxidation of ROH and RCHO depends to a considerable extent on the availability of pure alcohols and pure aldehydes. Thus many of the commercially available alcohols produced from hydrocarbons (Chapter 4) are mixtures of isomers, and most of the long-chain alcohols obtained by saponification of natural waxes are difficult to separate into pure species.

Oxidation of an alcohol or aldehyde to an acid is usually done with air in the presence of a catalyst [(5.4) and (5.5)]. Catalysts (*48–53*) for the mild oxidation



$$\mathrm{RCH_2OH} + [\mathrm{O}] \xrightarrow{\text{catalyst}} \mathrm{R}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + \mathrm{H_2O} \tag{5.4}$$

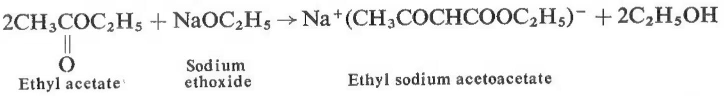


$$\mathrm{R}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} + [\mathrm{O}] \xrightarrow{\text{catalyst}} \mathrm{R}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OH} \tag{5.5}$$

of alcohols to aldehydes are usually potassium permanganate, sulfuric acid, and chromium oxide. Although these same catalysts can be used for the oxidation of the aldehyde to the acid, silver oxide (*54–58*) has become the preferred catalyst for reaction (5.5). An excellent review on the mechanism of the oxidation of alcohols with chromic acid is given by Westheimer (*59*).

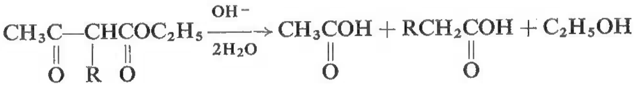
2. Acetoacetic Ester Synthesis

The synthesis of acetoacetic ester has been found to be very useful in the synthesis of the intermediate and higher aliphatic acids. One of the important chemicals in this over-all synthesis is ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$. This can be readily prepared in the form of the sodium derivative by the condensing action of sodium on dry ethyl acetate or by using sodium ethoxide rather than sodium itself. Equation (5.6) illustrates the preparation of the acetoacetic ester (*60–62*). Then the sodium derivative of the acetoacetic ester on treatment with an alkyl halide (RX) gives ethyl α-monoalkyl acetoacetates (5.7) (*65–67*). The ethyl monoalkyl acetoacetate under basic conditions can then be hydrolyzed to the acid, as illustrated in (5.8).



$$\underset{\text{Ethyl acetate}}{2CH_3\underset{\underset{O}{\|}}{C}OC_2H_5} + \underset{\substack{\text{Sodium}\\\text{ethoxide}}}{NaOC_2H_5} \rightarrow \underset{\text{Ethyl sodium acetoacetate}}{Na^+(CH_3COCHCOOC_2H_5)^-} + 2C_2H_5OH \quad (5.6)$$

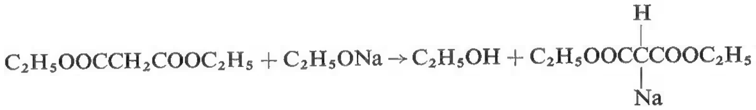
$$Na^+(CH_3COCHCOOC_2H_5)^- + RX \rightarrow NaX + \underset{\text{Ethyl alkyl acetoacetate}}{CH_3COCH(R)COOC_2H_5} \quad (5.7)$$



$$CH_3\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{C}H\underset{\underset{O}{\|}}{C}OC_2H_5 \xrightarrow[2H_2O]{OH^-} CH_3\underset{\underset{O}{\|}}{C}OH + RCH_2\underset{\underset{O}{\|}}{C}OH + C_2H_5OH \quad (5.8)$$

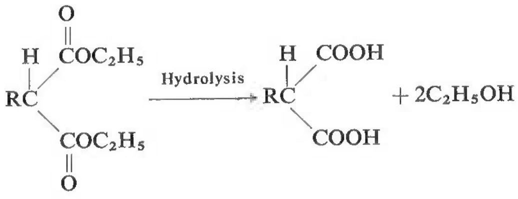
3. Malonic Ester Synthesis

The classical method of malonic ester synthesis for increasing the chain length of the lower members of an aliphatic series has been used to prepare a variety of long chain acids. Equations (5.9) to (5.12) represent this synthesis.

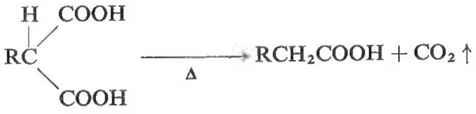


$$C_2H_5OOCCH_2COOC_2H_5 + C_2H_5ONa \rightarrow C_2H_5OH + C_2H_5OOC\overset{\overset{H}{|}}{\underset{\underset{Na}{|}}{C}}COOC_2H_5 \quad (5.9)$$

$$RX + C_2H_5OOCCHNaCOOC_2H_5 \rightarrow NaX + RCH(COOC_2H_5)_2 \quad (5.10)$$



(5.11)



(5.12)

There are a number of pertinent references on this route of synthesis of which several are of general interest (*63–70*).

4. Nitrile Synthesis

One of the earliest syntheses was based on increasing the chain length by way of nitriles (*71,72*). Later, others (*73*) applied this method of preparation to obtain fatty acids in the carbon chain length range of C_{17} to C_{26}. The preparation of *n*-nonadecanoic acid from stearic acid is illustrated in (5.13) to (5.16).

$$C_{17}H_{35}COOC_2H_5 + H_2 \rightarrow C_{17}H_{35}CH_2OH \tag{5.13}$$

$$C_{17}H_{35}CH_2OH + HI \rightarrow C_{17}H_{35}CH_2I \tag{5.14}$$

$$C_{17}H_{35}CH_2I + HCN \rightarrow C_{17}H_{35}CH_2CN \tag{5.15}$$

$$C_{17}H_{35}CH_2CN + HOH \rightarrow C_{17}H_{35}CH_2COOH \tag{5.16}$$

5. Grignard Synthesis

The application of the Grignard (*74*) carbonation reaction is one of the most frequently used reactions in the field of fatty acid synthesis. Both saturated and unsaturated fatty acids have been prepared by this route (*75–82*). Equations (5.17) and (5.18) represent this method of synthesis.

$$\underset{\substack{\text{Grignard}\\ \text{reagent}}}{RMgX} + CO_2 \rightarrow RCOOMgX \tag{5.17}$$

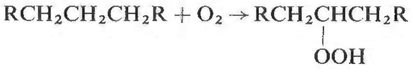
$$RCOOMgX + HOH \rightarrow RCOOH + Mg(OH)X \tag{5.18}$$

6. Synthesis from Hydrocarbons

a. Oxidation of Paraffins

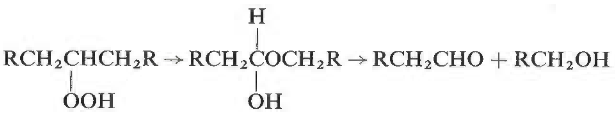
The air oxidation of paraffins in the presence of a permanganate catalyst was operated on a commercial scale in Germany, starting in 1939, as a result of a concentrated effort on Fischer-Tropsch processes. This development is covered by a number of patents (*83–91*) and publications (*92–101*).

The oxidation step is relatively simple and consists essentially of contacting air and paraffin in the presence of a suitable catalyst, generally $KMnO_4$ or a manganese soap. It is believed that the oxygen (O) adds at various positions along the carbon chain to form hydroperoxides (5.19). These hydroperoxides are



$$RCH_2CH_2CH_2R + O_2 \rightarrow RCH_2\underset{\substack{|\\ OOH}}{C}HCH_2R \tag{5.19}$$

unstable and are converted successively to alcohols, aldehydes, and acids, presumably according to the equations



$$RCH_2\underset{\substack{|\\ OOH}}{C}HCH_2R \rightarrow RCH_2\overset{\substack{H\\ |}}{\underset{\substack{|\\ OH}}{C}}OCH_2R \rightarrow RCH_2CHO + RCH_2OH \tag{5.20}$$

$$2RCH_2CHO + O_2 \rightarrow 2RCH_2COOH \tag{5.21}$$

Other reactions also occur in this process so that the final product actually consists of a complex mixture of unreacted paraffins, aldehydes, alcohols, fatty acids, ketones, hydroxy acids, esters, and aldols. By recycling the paraffins, approximately 80 per cent of the original paraffin is ultimately recovered as the fatty acid.

b. Oxonation of Olefins

The basic process for this synthesis is the oxo process (Chapter 4) in which the olefins are converted to aldehydes. The aldehyde is then converted to the corresponding acid by oxidation (5.22).

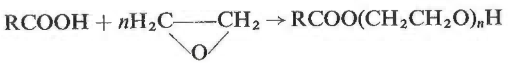
$$RCH_2CHO + \tfrac{1}{2}O_2 \rightarrow RCH_2COOH \qquad (5.22)$$

5.3. PREPARATION OF POLYOXYETHYLENE ESTERS OF FATTY ACIDS

The known methods for the preparation of polyoxyethylene esters of fatty acids are (*102*): (a) esterification of fatty acids with ethylene oxide, (b) esterification of fatty acids with polyethylene glycol, (c) reaction of fatty acid anhydride with polyethylene glycol, (d) reaction of fatty acid chloride with polyethylene glycol, (e) reaction of metal salt of fatty acid with polyethylene glycol, and (f) ester interchange of fatty acid ester with polyethylene glycol. Of these methods, only (a) and (b) are of commercial interest because of the availability and low cost of raw materials and the simplicity in processing.

A. Esterification of Fatty Acids with Ethylene Oxide

The reaction of fatty acid with ethylene oxide in the presence of an alkaline catalyst is used industrially for the manufacture of polyoxyethylene esters of fatty acids. As mentioned in Chapter 2, the alkali-catalyzed oxyethylation of fatty acids is accompanied by a transesterification (ester interchange) reaction [Eq. (5.24)] (*103–106*). Consequently, the product is a mixture of polyethylene glycol monoester, polyethylene glycol diester, and polyethylene glycol similar to that resulting from direct esterification of polyethylene glycol with fatty acid.



$$RCOOH + nH_2C\underset{O}{\text{——}}CH_2 \rightarrow RCOO(CH_2CH_2O)_nH \qquad (5.23)$$

$$2RCOO(CH_2CH_2O)_nH \rightleftharpoons RCOO(CH_2CH_2O)_nOCR + HO(CH_2CH_2O)_nH \qquad (5.24)$$

The occurrence of the transesterification reaction (5.24) is evidenced by the following findings: (a) the ethylene oxide does not react with ethylene glycol dilaurate using an alkali catalyst but reacts with ethylene glycol monolaurate to form diesters and ethylene glycol in a similar experiment (*105*), and (b) the ethylene oxide reacts with an equimolar mixture of ethylene glycol dilaurate and ethylene glycol, forming a mixture of ethylene glycol, ethylene glycol monolaurate, and ethylene glycol dilaurate (*104*).

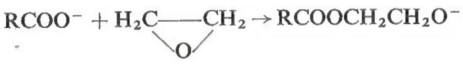
This transesterification is rapid since the average polyoxyethylene chain length of all three components of the equilibrium mixture—free polyethylene glycol, monoester, and diester—are essentially the same (*103,104,106,107*). The composition of these three components has been shown to be close to the theoretical molar proportions of 1:2:1 (*104–107*) and the equilibrium constant has been found to be close to 4 (*104*), where the equilibrium constant is expressed as

$$K = [\text{monoester}]^2/[\text{diester}][\text{polyethylene glycol}]$$

The base-catalyzed reaction of ethylene oxide with fatty acids can be divided into two stages. The initial stage consists of a slow reaction of fatty acids with ethylene oxide to form principally ethylene glycol monoester, and the formation of diester and glycol by transesterification is much slower. In the second stage, after the addition of approximately 1 mole of ethylene oxide, the reaction rate is increased and the transesterification equilibrium is rapidly established. Therefore, after the initial stage the molar proportion of the monoester, diester, and polyethylene glycol approaches a constant with increasing moles of ethylene oxide reacted (*104,105*).

As discussed in Chapter 2, the mechanism of the base-catalyzed oxyethylation of fatty acids involves the following sequence of reactions for the initial stage (*108,109*):

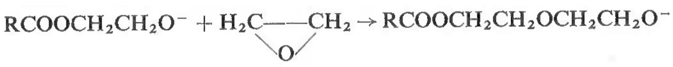
$$\text{RCOOH} + \text{base} \rightarrow \text{RCOO}^- \tag{5.25}$$



$$\text{RCOO}^- + H_2C\underset{O}{—}CH_2 \rightarrow \text{RCOOCH}_2\text{CH}_2\text{O}^- \tag{5.26}$$

$$\text{RCOOCH}_2\text{CH}_2\text{O}^- + \text{RCOOH} \rightarrow \text{RCOOCH}_2\text{CH}_2\text{OH} + \text{RCOO}^- \tag{5.27}$$

The basicity of the alcoholate ion, which is much higher than the carboxylate ion, results in an over-all selective reaction of ethylene oxide with fatty acid until the latter is completely oxyethylated; then the rapid and random reaction of alcoholate ion with ethylene oxide is started (5.28).



$$\text{RCOOCH}_2\text{CH}_2\text{O}^- + H_2C\underset{O}{—}CH_2 \rightarrow \text{RCOOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}^- \tag{5.28}$$

In agreement with the base-catalyzed oxyethylation mechanism, the difference in reaction rate of the carboxylate ion and alcoholate ion with ethylene oxide is attributed to the difference in basicity of the anions. Figure 2.3 illustrates the difference in oxyethylation rates of stearic acid at the two stages (*108*). The inflection point indicates the complete consumption of free fatty acid by reaction.

Analogous to oxyethylation of alcohols and phenols, the alkaline catalysts used for oxyethylation of fatty acids are alkali hydroxides, alkali alcoholates, and alkali metals (*104,110*). In addition, alkali carbonates as well as the alkali salts of low-molecular-weight carboxylic acids are also reported as catalysts for oxyethylation of fatty acids (*108,111–113*).

The use of ammonium halides and their derivatives as catalysts for oxyethylation of fatty acids to improve the yield of monoester is described in the patent literature (*114*).

As governed by the laws of mass action and kinetics, the pressure of ethylene oxide and the temperature of oxyethylation affect the reaction rate of ethylene oxide and fatty acid. The effects are similar to those for oxyethylation of alcohols and phenols (Chapters 3 and 4).

B. Production of Polyoxyethylene Esters of Fatty Acids

The descriptions in Section 4.3,B for the production of polyoxyethylene alcohol are, in general, adaptable to the production of polyoxyethylene fatty acids.

After oxyethylation, the deodorization and decolorization steps are usually incorporated to improve the odor and color characteristics of the product. As mentioned in Section 5.2, tall oil, which consists of a mixture of rosin acids and fatty acids, is a source of low-cost hydrophobe for the preparation of nonionic surfactants. Several processes for the manufacture of tall oil-ethylene oxide adducts are reported in patent literature (*115,116*). Also reported is the method for decolorizing the tall oil-ethylene oxide adducts by use of ozone or hydrogen peroxide (*117*). Production of nonionic detergents by reacting fatty acids or fatty acid-paraffin mixture obtained from paraffin oxidation with ethylene oxide was described by Griesinger et al. (*101,118*).

The important control analysis for the oxyethylation of fatty acids involves the determination of saponification and hydroxyl values. Methods for the direct and indirect determination of the content of polyethylene glycol, monoester, and diester of a wide range of oxyethylated fatty acids have been published (*106,107, 119,120*).

C. Esterification of Fatty Acids with Polyethylene Glycol

The polyoxyethylene esters of fatty acids may also be manufactured by esterifying fatty acids with polyethylene glycol, which is commercially available in various molecular-weight ranges.

The reaction of fatty acids with polyethylene glycol to form esters and water is reversible [(5.29) and (5.30)]. Because the polyethylene glycol has two hydroxy

$$\mathrm{RCOOH + HO(CH_2CH_2O)_nH \rightleftharpoons RCOO(CH_2CH_2O)_nH + H_2O} \qquad (5.29)$$

$$\mathrm{2RCOOH + HO(CH_2CH_2O)_nH \rightleftharpoons RCOO(CH_2CH_2O)_nOCR + 2H_2O} \qquad (5.30)$$

groups available to react with the carboxylic acid, fatty acid diester is also formed, as in (5.30). The relative contents of monoester and diester in the equilibrium mixture depend upon the ratio of the reactants. An equal molar ratio of fatty acid and polyethylene glycol results in a mixture which is predominant in monoester and is similar to that resulting from base-catalyzed reaction of ethylene oxide and fatty acids (*119*).

A higher molar ratio of fatty acid to polyethylene glycol favors the greater concentration of diester in the mixture. In the preparation of monoesters, an excess of polyethylene glycol is usually used to react with fatty acid to assure its high conversion (*102,121*).

As illustrated in (5.29) and (5.30), the esterification of polyethylene glycol with fatty acids is reversible, and consequently the reaction is never complete. In most commercial operations, as the reaction approaches complete conversion, the equilibrium is shifted by removing one of the products formed, such as water. If the water is eliminated as fast as it is formed, there can be no reverse reaction, which is the hydrolysis of ester to fatty acid and polyethylene glycol. The water of esterification is often removed by one or several of the following methods: (a) formation of azeotropes with water-immiscible solvents such as benzene, toluene, xylene, carbon tetrachloride, or hexane (*121–124*); (b) formation of azeotropes with water-miscible solvents and subsequent treatment of the azeotropes with drying agent such as calcium chloride and calcium carbide (*125*); (c) esterification under vacuum; and (d) employment of inert gases such as nitrogen or carbon dioxide to carry off moisture and to promote agitation of the reaction mixture (*126,127*).

The esterification of polyethylene glycol with fatty acids is usually carried out at 100 to 250°C with or without a catalyst. As analogous to other esterifications, the rate of esterification increases with the increase in reaction temperature. However, the selection of reaction temperature is dependent on the boiling point and thermal stability of the components of the reaction mixture.

Although the esterification of fatty acids with polyethylene glycol may occur in the absence of a catalyst, this generally requires high temperature and long reaction time (*126,128,129*). To reduce the reaction time, many catalysts have been reported to increase the reaction rate of esterification. Sulfuric acid is most commonly used in the plant operations (*122,123,130,131*). Organic sulfonic acids of benzene, *o*-toluene, naphthalene, which have the effectiveness of sulfuric acid but do not have its carbonizing action, are widely used as catalysts (*108,121, 132,133*). Cation-exchange resins of polystyrene-sulfonic acid type have been used effectively as catalysts to give improved yields of monoesters (*121,133*). In addition to better color products, the use of a cation-exchange resin as catalyst has other advantages over the conventional acid catalysts. It can be readily separated from the reaction mixture; therefore, no neutralization of the product is necessary. Also, it can be reused without regeneration; therefore, continuous process of fixed-bed operation is feasible. Hydrogen chloride is generally limited in its use as catalyst for laboratory preparation of esters, because of its corrosiveness and process requirements (*102,131*). The use of powdered metals, such as zinc, tin, or iron, and their salts, which shorten the reaction time and result in light-color product has been reported (*131,134,135*).

Esterification is usually followed by decolorization and deodorization treatments of the product. The product is protected by inert atmospheres against air oxidation, which results in degradation products causing odor and color formation.

The esterification of fatty acids with polyethylene glycol is controlled by analyzing hydroxyl and saponification values of the reaction mixture.

Both continuous and batch processes are used commercially for the esterification of polyethylene glycol with fatty acids. However, the batch process based on a combination of reactor and distilling column is more extensively used.

5.4. PROPERTIES OF POLYOXYETHYLENE ESTERS OF FATTY ACIDS

A. Physical Properties

1. Solubility

The polyoxyethylene esters of fatty acids range in solubility from complete oil solubility to complete water solubility. This characteristic, as with other nonionic surfactants, is dependent upon the number of moles of ethylene oxide added to a specific fatty acid. Generally the addition of 1 to 8 moles of ethylene oxides gives a product which is completely oil soluble and also completely soluble in hydrocarbons. When the mole ratio of ethylene oxide is increased to about 12 to 15 oxyethylene groups, water dispersibility and visual water solubility begin (*136*,*137*).

Table 5.1 contains the solubility data of STEROX CD (trademark of Monsanto Co.) in a number of common organic solvents. From the data it is evident that the polyoxyethylene esters of fatty acids are readily soluble in polar solvents but only slightly soluble in nonpolar solvents.

TABLE 5.1

Solubility of STEROX CD in Organic Solvents[a]

Solvent	Solubility
Carbon tetrachloride	3
Acetone	>100
95% ethanol	>100
Trichlorethylene	>100
Toluene	4
n-Hexane	0.5
Diethyl ether	8
Ethyl acetate	>100
Mineral oil	0.8
Kerosene	0.1
VARSOL[b] No. 1 (Stoddard solvent)	0.1
VARSOL No. 2 (Stoddard solvent)	0.2

[a] Volume/100 volumes solvent at 25°C.
[b] Trademark of Enjay Chemical Co.

Table 5.2 gives the solubility data on STEROX CD and RENEX* 20 (*138*), typical nonionic surfactants based on fatty acids, in a number of salt solutions and in NaOH solutions. As shown in this table, both typical nonionic surfactants exhibit a low solubility in salt solutions.

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* Trademark of Atlas Chemical Industries.

TABLE 5.2

Solubility in Salt and NaOH Solutions

Reagent	Concentration, %	Temp., °C	Volume % STEROX CD	Volume % RENEX 20
Na_2CO_3	5	25	0.2	0.2
	5	60	0.2	0.2
	10	25	<0.2	<0.2
	10	60	0.2	<0.2
NaCl	5	25	1.2	1.0
	5	60	0.2	0.2
	10	25	<0.4	0.2
	10	60	0.4	0.2
Na_2SO_4	5	25	1.5	0.4
	5	60	0.2	0.2
	10	25	<0.2	<0.4
	10	60	0.2	<0.4
$Na_3PO_4 \cdot 12H_2O$	5	25	1.5	1.0
	5	60	0.2	0.4
	10	25	<0.2	<0.4
	10	60	0.2	<0.4
NaOH	5	25	0.2	0.2
	5	60	0.2	0.2
NaOH	10	25	<0.8	<0.2
	10	60	0.8	<0.2
$Na_2SiO_3 \cdot 5H_2O$	5	25	1.5	1.0
	5	60	0.2	0.4
	10	25	<1.2	<0.4
	10	60	1.2	<0.4

Table 5.3 contains cloud-point data on RENEX 20 (*138*) over a concentration range of 0.1 to 5.0 per cent. It is evident that the concentration has very little effect on the cloud point of an aqueous solution.

TABLE 5.3

Cloud Point for RENEX 20

Concentration, %	Cloud point, °C
5	68.5
1	68.5
0.5	68.5
0.1	67.0

2. Specific Gravity

As the number of moles of ethylene oxide added to a given fatty acid increases, the specific gravity of the polyoxyethylene esters of fatty acids increases. Also, for a given ethylene oxide content, the specific gravity of the compound will vary with changes in the source of the fatty acid used for oxyethylation—the higher the initial viscosity of the hydrophobe the higher the specific gravity of the ethylene oxide adduct. In addition, as the temperature of a specific polyoxyethylene ester of fatty acids is increased, the specific gravity of the material is decreased (*137*). This effect is illustrated in Table 5.4.

TABLE 5.4

Specific Gravity versus Temperature
of STEROX CD

Temperature, °C	Specific gravity[a]
25	1.065
40	1.052
60	1.035
80	1.022

[a] 60°F/60°F.

3. Viscosity

In general, the viscosity of polyoxyethylene esters of fatty acids increases with increasing number of oxyethylene units. The viscosity decreases as the temperature of polyoxyethylene esters of fatty acids is increased (*137*). Table 5.5 illustrates this point.

TABLE 5.5

Viscosity versus Temperature
for STEROX CD

Temperature, °C	Viscosity, centipoises
25	380
40	200
60	80
80	40

The viscosity plots (Figure 5.1) of aqueous STEROX CD solutions are noteworthy. In line with most other nonionic surfactants, a very viscous solution is formed at concentrations between 25 and 80 per cent of the anhydrous surfactant. In the range of 35 to 75 per cent a gel is formed which is so viscous it will not pour from a container at room temperature (*136*,*137*).

B. Chemical Properties

Chemically, the polyoxyethylene esters of fatty acids may be represented by the formula $RCOO(C_2H_4O)_nC_2H_4OH$. It thus has two functional groups

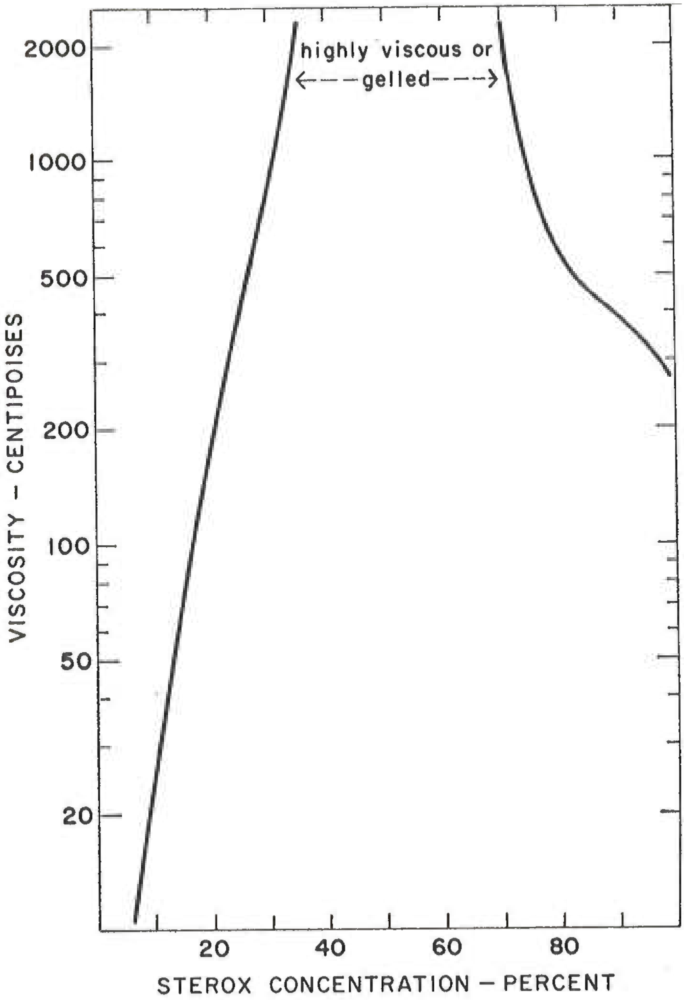

Fig. 5.1. Viscosities of aqueous STEROX CD solutions (*136*).

capable of chemical reaction: the carboxylic ester linkage and the terminal hydroxyl group.

The hydroxyl group present in these nonionics is capable of undergoing such chemical reactions as esterification, sulfation, and chloromethylation under reaction conditions which do not lead to cleavage of the ester linkage (*47*). The ester linkage is susceptible to hydrolysis in strongly acid or alkaline solutions. Under alkaline conditions for hydrolysis, the polyoxyethylene esters of fatty acid are saponified to the fatty acid soap and polyethylene glycol. In the presence of heavy metal cations (i.e., in hard water) the resultant soaps could tend to precipitate and, therefore, affect the use and applications of this type of nonionic surfactant. However, it has been shown that the polyoxyethylene esters derived from tall oil are markedly stable (*47*), owing to the resistance of rosin acid esters to hydrolysis under very strongly alkaline or acid conditions and high temperatures.

C. Surface Properties

1. Chemical Structure versus Functional Properties

Wrigley et al. (*108*) have investigated the surface properties such as detergency, wetting, foaming, surface tension, and interfacial tension of the ethylene oxide adducts derived from the following fatty acids: lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, hydroxystearic acid, 9,10-dihydroxystearic acid, phenylstearic acid, and *o*-xylylstearic acid.

a. Detergency

The data (*108*) for the detersive properties of oxyethylated fatty acids at an average of 10 and 20 moles of ethylene oxide per mole of acid are listed in Table 5.6. Detergency was expressed as the increase in reflectance after washing

TABLE 5.6

Detergency[a] of Oxyethylated Fatty Acids (*108*)

	Moles of ethylene oxide per mole of acid	
Nonionic surfactant derived from	10	20
Lauric acid	35.6	36.9
Palmitic acid		36.8
Stearic acid	36.6	36.9
Oleic acid	37.8	36.4
Hydroxystearic acid		38.2
Dihydroxystearic acid		38.3
Phenylstearic acid		37.8
Xylylstearic acid		38.6

Formulation	Parts by weight
Nonionic surfactant	20.0
$Na_4P_2O_7$	20.0
$Na_5P_3O_{10}$	20.0
Na_2CO_3	39.0
Sodium carboxymethylcellulose	1.0

Terg-O-Tometer Conditions[b]	
Formulated nonionic detergent concentration, %	0.25
Wash temperature, °F	120
Wash cycle, min	20
Agitation, cpm	110

[a] 10 replicates; 95% confidence limits ±1.0.

[b] Fabric: A.C.H. No. 114 standard soiled cotton.

10 replicate swatches in the Terg-O-Tometer at 0.25 per cent concentration of built nonionic surfactant solution and 300-ppm water hardness. The data in Table 5.6 show that the maximum detergency of oxyethylated fatty acids on built basis is not significantly affected by the C_{12} to C_{18} chain length of the fatty acid. In the range studied, the ethylene oxide content does not affect the detergency of the oxyethylated fatty acids markedly. Once the maximum detergency is reached, it levels off at the maximum value with further addition of ethylene oxide. However, in case of the oxyethylated lauric acid higher ethylene oxide content results in better detergency, and for oxyethylated oleic acid, lower ethylene oxide content results in better detergency.

The data in Table 5.6 also indicate that the introduction of the aryl or hydroxyl group to the fatty acid improves the detergency of the oxyethylated fatty acids.

As discussed in Section 5.2, tall oil, which is a mixture of rosin and fatty acids, is an important hydrophobe for the preparation of nonionic surfactants. The effect of composition of tall oil, as well as the ethylene oxide content, upon detergency of the oxyethylated tall oil was studied (*139*).

Detergency values of formulated polyoxyethylene esters (14 moles ethylene oxide per mole of tall oil) based on tall oil of various compositions ranging from pure abietic acid to pure oleic acid are listed in Table 5.7. The results

TABLE 5.7

Detergencies of Various Oxyethylated Tall Oils[a]

Nonionic detergent mix[b]		Soil removal, %	
Rosin acid	Fatty acid	Hard water	Soft water
0	100[c]	112	109
10	90	99	112
30	70	119	116
45	55	120	144
55	45	124	129
90	10	110	122
100[d]	0	132	127

Formulation	Weight %
Nonionic detergent	20
Tetrasodium pyrophosphate	20
Sodium tripolyphosphate	20
Soda ash	39
Carboxymethylcellulose	1

[a] Test method: procedure described by Vaughn and Suter (*140*). Concentration is 0.25% formulated nonionic detergent.

[b] Commercially available.

[c] Oleic acid.

[d] Abietic acid.

indicate that oxyethylated tall oils containing a larger proportion of rosin acid have slightly improved detergency. However, a difference in composition does not appear to be a significant factor.

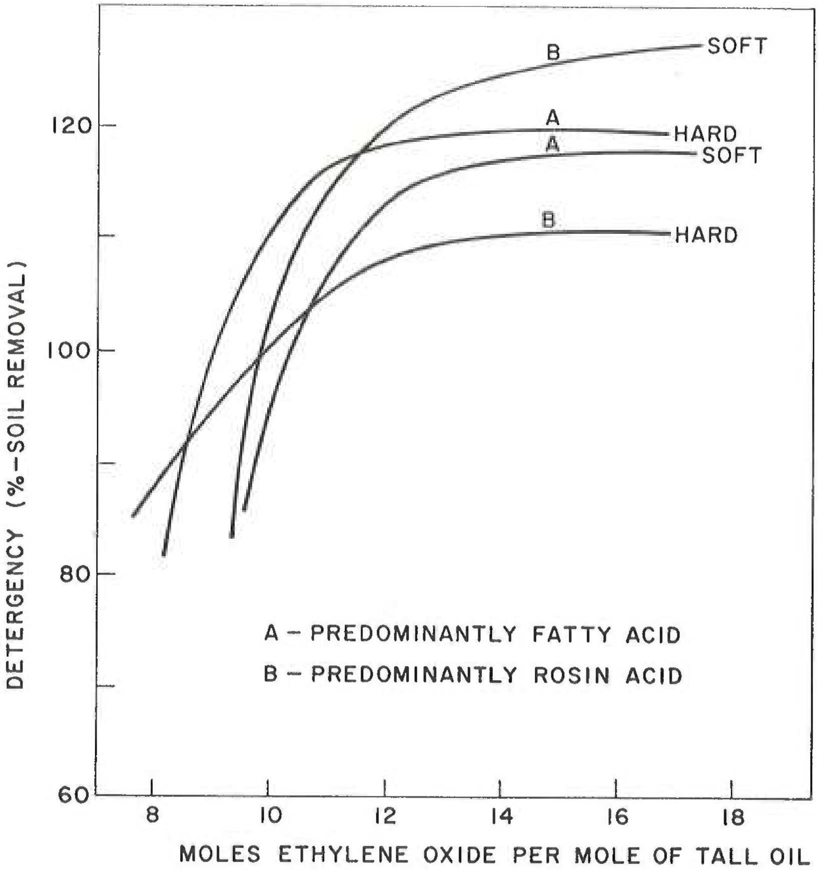

Fig. 5.2. Variation in detergency in hard and soft water with ethylene oxide content (*139*).

Figure 5.2 shows detergency (as per cent soil removal) versus ethylene oxide content curves for polyoxyethylene esters derived from tall oil A and B, which had a rosin acid to fatty acid ratio of 30 : 70 and 90 : 10, respectively. From Figure 5.2, it is apparent that the detergency increases with increasing ethylene oxide content but levels off at a maximum value. The minimum ethylene oxide content for optimum detergency is approximately 13 to 15 moles of ethylene oxide per mole of tall oil.

It would appear that water hardness has less effect on detergency of the nonionic surfactant derived predominantly from the fatty acids.

The effects of various substituents introduced to the hydrophobic or hydrophilic portion of the polyoxyethylene esters of tall oil upon detergency were also investigated (*141*).

b. Wetting Properties

The wetting properties of 0.1 per cent concentration of oxyethylated fatty acids in 300-ppm hard water were measured at 25°C by the method developed by Shapiro (*142*) using standard binding tape, a 1-g hook, and a 40-g anchor. The wetting times at 10 and 20 moles ethylene oxide per mole of acid are listed in Table 5.8.

TABLE 5.8

Wetting Properties

	Wetting time, sec	
	Moles EO per mole acid	
Nonionic surfactant derived from	10	20
Lauric acid	30	38
Myristic acid	38	60
Palmitic acid	160	85
Stearic acid	380	125
Oleic acid	100	76
Dihydroxystearic acid	53	56
Phenylstearic acid	530	200

As shown by curves of wetting times versus ethylene oxide content in Figure 5.3 for a given fatty acid, there is generally an ethylene oxide content which results in an adduct of minimum wetting times. Also, the wetting times of the oxyethylated fatty acids are increased with the increasing molecular weight of the fatty acids. The presence of double bond or of hydroxyl group on the fatty acid hydrophobe improved the wetting properties of the oxyethylated fatty acids.

c. Foaming Properties

The foam values of the oxyethylated fatty acids were measured by the Ross-Miles foam test (*143*) at 60°C with a 0.25 per cent nonionic surfactant solution in 300-ppm hard water. The initial foam value of these oxyethylated fatty acids was in the range of 20 to 50 mm at an ethylene oxide content of 15 moles per mole of acid and in the range of 50 to 80 mm at an ethylene oxide content of 30 moles per mole of acid. Foam stability was poor in all cases.

d. Surface and Interfacial Tension

Surface- and interfacial-tension measurements of 0.1 per cent solutions of these oxyethylated fatty acids in distilled water were made at 28°C by the DuNouy tensiometer method (*143*). Figure 5.4 gives the range of values of surface and interfacial tension for oxyethylated C_{12}, C_{14}, C_{16}, and C_{18} saturated fatty acids as well as for the oxyethylated oleic acid.

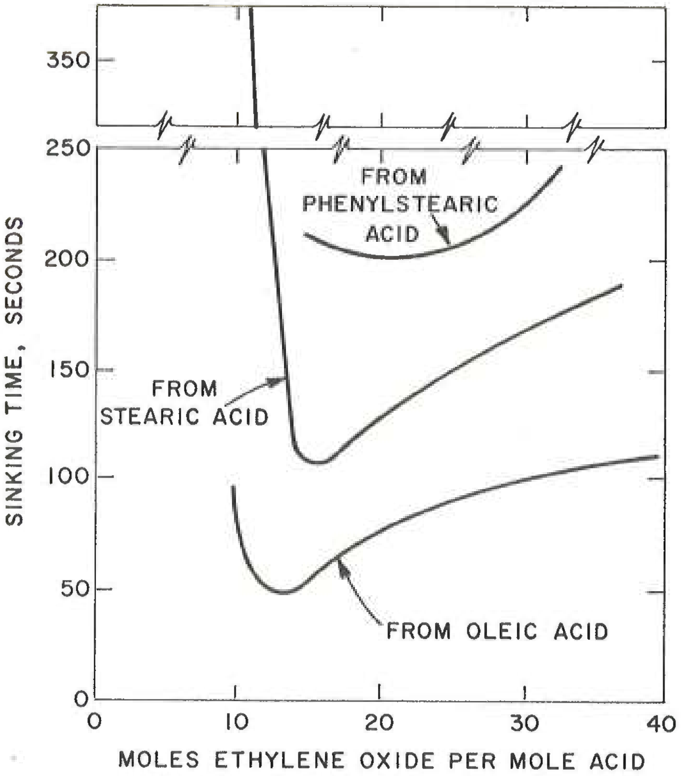

Fig. 5.3. Wetting properties of oxyethylated fatty acids, 0.1 % solutions, in 300-ppm hard water (*108*).

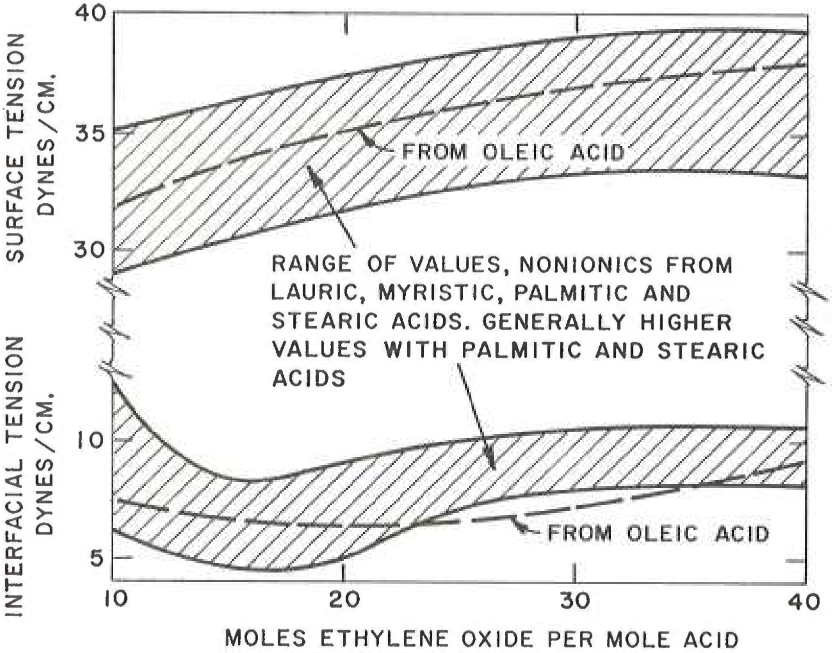

Fig. 5.4. Surface and interfacial tension of 0.1 % solutions of oxyethylated acids (*108*).

In general, with respect to the ranges shown in Figure 5.4, the surface tension and interfacial tension increase with the increasing molecular weight of the fatty acid. Also as shown by Figure 5.4, minimal interfacial tension values for oxyethylated C_{12}, C_{14}, C_{16}, and C_{18} saturated acids were obtained at the ethylene oxide content of 15 to 18 moles per mole of acid.

2. Commercial Products

A few typical commercially available nonionics derived from fatty acids and ethylene oxide are listed in Table 5.9. A more complete listing of commercial products manufactured in the U.S. and abroad is found in several pertinent references (*144–147*).

TABLE 5.9

Typical Commercial Polyoxyethylene Fatty Acids

Product[a]	Source of hydrophobe	Manufacturer
ATLAS G-2079	Palmitic acid	Atlas Chemical Industries
BASOPHOR A	Fatty acid	BASF Color & Chemicals Inc.
CARBOXANE LD	Fatty acid	Textilana Corp.
DERGON MF	Fatty acid	Arkansas Co., Inc.
EMULPHOR VN-430	Fatty acid	General Aniline & Film Corp.
EMULPHOR VT-510	Fatty acid	General Aniline & Film Corp.
EMULSYNT 900	Lauric acid	Van Dyk & Co.
ETHOFAT 242 Series	Tall oil	Armour Industrial Chemicals Co.
ETHOFAT 60 Series	Stearic acid	Armour Industrial Chemicals Co.
LIPAL 30E, 60E	Oleic acid	Drew Chemical Corp.
LIPAL 4S, 5S, 25S	Stearic acid	Drew Chemical Corp.
LIPAL 15T	Tall oil	Drew Chemical Corp.
MYRJ 45, 52, 53	Stearic acid	Atlas Chemical Industries
RENEX 20	Tall oil	Atlas Chemical Industries
SIOTOL AF, AFH	Fatty acid	Imperial Chemical Industries Ltd.
SIOTOL PG, PM	Fatty acid	Imperial Chemical Industries Ltd.
SOLE-TERGE TOE	Tall oil	Sole Chemical Corp.
STEROX CD	Tall oil	Monsanto Co.
TEOX 120	Tall oil	Olin Mathieson Chemical Corp.

[a] Trademarks of the respective manufacturers.

Surfactant data such as detergency, wetting, foaming, surface tension, and interfacial tension for a representative commercial product (STEROX CD) of the polyoxyethylene fatty acids are discussed below (*136,137*).

a. Detergency

Table 5.10 contains data on the detersive efficiency of several typical nonionic surfactants based on a fatty acid (STEROX CD, RENEX 20, and TEOX* 120) (*136,137*). Evaluation is based on the active ingredient only.

* Trademark of Olin Mathieson Chemical Corp.

TABLE 5.10

Detersive Efficiency (Active Basis)[a]

	H_2O hardness, ppm	
	50	300
STEROX CD	98	86
RENEX 20	120	116
TEOX 120	109	113

[a] 0.2% conc., 140°C, sodium lauryl sulfate = 100. Eight replicates, 95% confidence limits ±4.

Since most nonionic surfactants of the polyoxyethylene fatty acid ester type are invariably built with various inorganic salts and not used solely by themselves, the effect of builders on detersive properties can readily be seen from Table 5.11. The active ingredient was built with polyphosphates, carbonates, silicates, and sodium carboxymethylcellulose.

TABLE 5.11

Detersive Efficiency (Built Basis)[a]

	H_2O hardness, ppm	
	50	300
STEROX CD	114	116
RENEX 20	116	122
TEOX 120	114	119

[a] 0.2% conc., 140°F, sodium lauryl sulfate = 100. Eight replicates, 95% confidence limits ±4.

b. Wetting

The wetting power of surfactant solutions is of principal interest in connection with fabrics and textile processing. Some factors entering into wetting, in addition to surface tension of the solution, are the solid-liquid interfacial tension of the fabric or substrate to be wetted, the capillarity of the fabric, and interfacial tensions between solutions and various oils or foreign materials which may be contained in the fabric.

The fatty acid-based nonionics are poor wetting agents in comparison with most nonionic surfactants. Table 5.12 gives the wetting time of three typical polyoxyethylene esters of fatty acids (*136,137*).

TABLE 5.12

Draves-Clarkson Wetting Time

	Wetting time, sec		
Concentration, %	STEROX CD	RENEX 20	TEOX 120
0.5	57.8	186	79.5
0.25	180		110
0.125			180

[a] At 25°C; 0-ppm H_2O hardness.

Rewetting is a property allied to wetting but by no means parallel to it. Good wetting agents are not necessarily satisfactory as rewetting agents. A rewetting agent is a substance which may be applied to a fabric and dried on, thereby rendering the fabric readily wettable by water. STEROX CD has had wide application as a rewetting agent.

c. Foam

Foaming is a prominent but by no means exclusive characteristic of surfactants. The polyoxyethylene esters of fatty acids are well known for their low-foaming characteristics. An increase in temperature has no marked effect on the foam height of these nonionics. The presence of builders as in heavy-duty detergent formulations does not affect the low-foaming characteristics of this type of nonionic. Table 5.13 illustrates these foam properties (*136,137*).

TABLE 5.13

Ross Miles Foam Height[a]

		Foam height, cm		
H_2O hardness, ppm	Temp., °C	STEROX CD	RENEX 20	TEOX 120
50	25			
at once		3.1	4.4	3.3
after 5 min		2.4	3.5	3.2
300	25			
at once		2.8	4.7	2.9
after 5 min		2.3	3.7	2.6
50	50			
at once		3.7		
after 5 min		2.7		
300	50			
at once		2.8		
after 5 min.		2.2		

[a] 0.1% conc., 0-ppm water hardness.

d. Surface and Interfacial Tension

In Table 5.14 are presented the data on the surface and interfacial tension of a typical polyoxyethylene ester of fatty acids, STEROX CD (*136,137*).

TABLE 5.14

Surface and Interfacial Tensions of STEROX CD

Concentration, %	Temp., °C	Surface tension, dynes/cm
1.0	25	40.0
0.25	25	40.5
0.0625	25	41.2
1.0	50	35.2
0.25	50	36.8
0.0625	50	37.0
		Interfacial tension (NUJOL), dynes/cm
1.0	25	5.6
0.25	25	6.0
0.0625	25	7.4
1.0	50	2.9
0.25	50	3.4
0.0625	50	4.5

5.5. APPLICATIONS

On the basis of low foam capacity and low relative cost, the polyoxyethylene esters of fatty acids have been one of the most attractive nonionic detergent actives on the market. In combination with various types of builders, these surfactants are formulated for all types of household- and industrial-cleaning applications. Formulations included in this section will be useful as guides in incorporating this type of nonionic in products tailored for a number of detergent applications.

A. Household

1. Laundering Formulations

STEROX CD, a typical nonionic based on fatty acids, has certain properties which make it most attractive for incorporation into laundering formulations. It is an excellent detergent when used with alkaline builders and is a relatively low-cost detergent active. Its low foam permits formulations which do not interfere with the mechanical action of certain types of home-laundering machines. It is nonsubstantive and readily rinsable. The typical formulations in Table 5.15 are adapted to home laundry use and will be found useful as all-purpose household detergents (*47,136,137*).

TABLE 5.15

General-Purpose Heavy-Duty Formulations

	Formulation, %	
	1	2
STEROX CD	15	17
Sodium tripolyphosphate or tetrasodium pyrophosphate	40	45
Sodium metasilicate pentahydrate	30	17
Sodium carboxymethylcellulose	1	1
Soda ash	14	20
Fluorescent dye	as needed	
Perfume	as needed	

2. Dishwashing Formulations

STEROX CD, a typical nonionic surfactant based on fatty acid, imparts to solid formulations for mechanical dishwashers the desirable qualities of added detergency, low foam, and low dusting properties. General formulations for this purpose are given in Table 5.16 (*47,136,137*).

TABLE 5.16

Dishwashing Formulations

	Formulation, %			
	1	2	3	4[a]
STEROX CD	1	2	1	1
Sodium tripolyphosphate	40	55	65	56
Trisodium phosphate	40			
Chlorinated trisodium phosphate				15
Sodium metasilicate	19	30	34	34
Soda ash		13		

[a] For details on formulation 4 see (*108*).

The addition of STEROX CD to a powdered high-sudsing hand-dishwashing formulation increases the emulsifying power and detergency and decreases the dustiness of the product. These formulations generally embody an alkylaryl sulfonate such as SANTOMERSE (Trademark of Monsanto Co.) (*136,137*). Typical formulations are given in Table 5.17.

3. Floor and Wall Cleaner

The formulations in Table 5.18 are for heavy-duty cleaning of painted surfaces, walls, floors, etc. (*136,137*).

TABLE 5.17

	Formulation, %	
	1	2
SANTOMERSE 85	45	
SANTOMERSE Slurry		30
STEROX CD	2	2
Sodium tripolyphosphate	33	28
Sodium sesquicarbonate crystals	20	
Soda ash		40

TABLE 5.18

	Formulation, %	
	1	2
STEROX CD	10	12.5
Trisodium phosphate	25	20
Tetrasodium pyrophosphate	25	45
Soda ash	40	22.5

4. Metal Cleaning

The formulations in Table 5.19 will give satisfactory solutions for spray-type and soak-tank metal-cleaning equipment (*136,137*).

TABLE 5.19

	Formulation, %			
	1	2	3	4
STEROX CD	3	3	8	20
Trisodium phosphate	40	50		
Sodium metasilicate pentahydrate	40			
Tetrasodium pyrophosphate	10		25	40
Soda ash		40	20	40
Caustic soda	7	7		
Sodium orthosilicate			47	

An unstable type of emulsion suitable for use as a diphase cleaner in metal cleaning operations is

STEROX CD	25%
Kerosene	65
Water	10

Five parts of this concentrate mixed with 95 parts of water gives the diphase cleaning solution.

5. Rug-Cleaning Compositions

The addition of STEROX CD to rug-cleaning compositions gives a lower-dusting product and imparts emulsifying power and detergency (*136,137*). Typical formulations are given in Table 5.20.

TABLE 5.20

	Formulation, %	
	1	2
SANTOMERSE 1	65	60
STEROX CD	3	3
Soda ash	9	17
Tetrasodium pyrophosphate	10	20
Sodium metasilicate pentahydrate	13	

6. Concrete-Floor Cleaner

The following type of cleaning composition should prove suitable for cleaning and degreasing concrete floors (*136,137*):

STEROX CD	15%
Sodium metasilicate pentahydrate	60
Sodium tripolyphosphate	20
Pine oil	5

B. Industrial

1. Textile

Polyoxyethylene esters of fatty acids possess remarkably good emulsifying, lubricating, dispersing, and suspending powers, and these properties combined with their detergent and antistatic characteristics indicate their potential in a variety of textile processing applications.

a. Scouring

Nonionics are substituted for part of the soaps used in textile-scouring operations for both natural and synthetic fibers. The raw material is initially scoured to remove natural oils, fats, and waxes, as well as incidental dirt; scouring is again repeated between every textile operation to remove the agent applied in the previous step. ETHOFAT* 142/25 and STEROX CD are typical examples. The process conditions are so varied, of course, that no one product is all-purpose (*114*).

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* Trademark of Armour Industrial Chemical Co.

Wool-scouring, cotton kier boiling, boiling-off of viscose, and soaping-off are all examples of scouring operations (*136,148,149*). The nonionics are usually used in concentrations of less than 1 per cent and built with polyphosphates, silicates, or other alkalies to increase scouring activity. By their addition, scouring time is reduced, hard-water soap precipitates are eliminated, and the goods are dyed to clear bright colors. Since nonionics are nonsubstantive to fibers, little detergent is left on the material, the scouring bath is not rapidly exhausted, and balling as a result of detergent residues is not a problem during the carding process. A typical low-sudsing scouring formulation for wool is (*149*):

ETHOFAT 142/25	85–88%
Soda ash	10–12
Water	2–3

b. Lubricants and Softening Agent

Oil or waxes must be added to fibers to replace the fats lost in the scouring operations prior to carding, spinning, weaving, and other operations. These materials act as lubricants and softening agents (*150–154*).

Traditionally, mineral oil, vegetable oil, or mixtures of the two have been utilized for these purposes. Emulsifiers make it possible to distribute them evenly on the fiber from a water solution. The usual emulsifiers such as triethanolamine soaps can be replaced by nonionics of various types, primarily fatty acid esters such as STEROX CD and the ETHOFATS, and the polyoxyethylated sorbitan esters, the TWEENS (trademark of Atlas Chemical Industries). In addition to acting as emulsifiers, such products contribute extra lubricating properties to the formulation.

c. Dyeing

Good wetting, penetrating, and dispersing properties are essential for assistants to be used in dyeing, sanforizing, moth-proofing, and water-proofing (*155,156*). RENEX 20, ETHOFAT 142/25, and STEROX CD can be used in these textile-processing steps.

2. Agricultural

Surfactants are used primarily in the preparation of wettable powders and in the preparation of toxicant emulsions for insect control (*136,137,149,157*). Their relative insensitivity to hard water and use over a wide range of pH conditions make them excellent emulsifiers. They can be used either alone or in conjunction with other surface active agents. Examples of typical emulsions are:

Self-Emulsifying Spray Oil

Agricultural Sprays	97.5%
ETHOFAT 142/15	2.0
Soap	0.5

DDT-Oil Larvicide

DDT	1.0%
ETHOFAT 142/20	0.5
Kerosene	98.5

CHLORDANE-Emulsifiable Concentrate

CHLORDANE	85%
ETHOFAT 142/20	15

TOXAPHENE-Emulsifiable Concentrate

TOXAPHENE	65%
Kerosene	25
ETHOFAT 142/20	5
ARQUAD[a] 2C	5

2,4-D Herbicide Emulsion

Dimethylamine	8.75%
2,4-D Acid	42.25
STEROX CD	0.75
STEROX SK	0.75
Methanol	11.75
WATER	35.75

Trademark of Armour Industrial Chemical Co.

Wettable powders are used to form aqueous suspensions of such water-insoluble toxicants as sulfur, lead arsenate, copper compounds, and some organic pesticides. The use of STEROX CD in the formation of wettable powders from these toxicants gives a less-dusty free-flowing product which is easily dispersible in water.

3. Paper

Rewetting agents such as STEROX CD and ETHOFAT 142/15, are used to improve the absorbency of wet-strength paper used in the manufacture of paper towels (*137*,*149*).

The deinking of newsprint requires the use of a nonionic surfactant. STEROX CD and ETHOFAT 142/25 are useful in this application (*137*,*149*).

REFERENCES

1. E. S. Pattison, *Industrial Fatty Acids and Their Applications*, Reinhold, New York, 1959.
2. O. J. Ackelsberg, *J. Am. Oil Chemists' Soc.*, **35**, 635 (1958).
3. E. J. Jungermann and A. B. Herrick, *J. Am. Oil Chemists' Soc.*, **40**, 615 (1963).
4. D. Swern, *Bailey's Industrial Oil and Fat Products*, 3rd ed., Wiley-Interscience, New York, 1964.

5. K. Burrow, *Trans. Inst. Chem. Engrs.* (*London*), **31**, 250 (1953).
6. H. D. Allen, W. A. Kline, E. A. Lawrence, C. J. Arrowsmith, and C. Marvel, *Chem. Eng. Progr.*, **43**, 459 (1947).
7. *Chemistry of Fatty Acids*, Technical Bulletin, Armour & Co., 1956.
8. H. L. Barneby and A. C. Brown, *J. Am. Oil Chemists' Soc.*, **25**, 95 (1948).
9. L. Lascaray, *Ind. Eng. Chem.*, **41**, 786 (1949).
10. L. Lascaray, *J. Am. Oil Chemists' Soc.*, **29**, 362 (1952).
11. V. Mills and H. K. McClain, *Ind. Eng. Chem.*, **41**, 1982 (1949).
12. H. P. Kaufmann and M. C. Keller, *Fette Seifen Anstrichmittel*, **44**, 42, 105 (1937).
13. E. Twitchell, U.S. 601,603 (1898); *J. Am. Chem. Soc.*, **22**, 22 (1900).
14. A. J. Stirton, E. M. Hammaker, S. F. Herb, and E. T. Roe, *Oil and Soap*, **21**, 148 (1944).
15. X. Gveniot, *Bull. Mat. Grosses Inst. Colonial Marseilles*, **27**, 167 (1943).
16. J. Hetzer, *Seifen-Oele-Fette-Wachse*, **74**, 172 (1948).
17. M. H. Ittner (to Colgate-Palmolive-Peet Co.), U.S. 2,139,589; Re 22,006 (1942).
18. V. Mills (to Proctor & Gamble Co.), U.S. 2,156,863 (1939).
19. A. C. Brown (to Emery Industries), U.S. 2,486,630 (1949).
20. R. C. Daniels (to Proctor & Gamble Co.), U.S. 2,387,884 (1945).
21. W. Davey (to Colgate-Palmolive), U.S. 2,281,534 (1941).
22. W. Davey (to Colgate-Palmolive), U.S. 2,389,246 (1945).
23. M. H. Ittner (to Colgate-Palmolive), U.S. 2,435,745 (1948).
24. M. H. Ittner (to Colgate-Palmolive), U.S. 2,221,799 (1940).
25. M. H. Ittner (to Colgate-Palmolive), U.S. 2,458,170 (1949).
26. W. McCullough (to Foster Wheeler Corp.), U.S. 2,147,306 (1938).
27. V. Mills (to Procter & Gamble Co.), U.S. 2,495,071 (1950).
28. V. Mills (to Procter & Gamble Co.), U.S. 2,233,845 (1940).
29. N. G. Robisch (to Procter & Gamble Co.), U.S. 2,267,750 (1941).
30. G. P. G. Stalman (to Alien Property Custodian), U.S. 2,356,628 (1944).
31. G. B. Bradshaw and W. C. Mevly (to du Pont), U.S. 2,271,619 (1942).
32. R. H. Potts and J. E. McKee (to Armour & Co.), U.S. 2,056,096 (1936).
33. R. H. Potts and J. E. McKee (to Armour & Co.), U.S. 2,224,984 (1940).
34. R. H. Potts (to Armour & Co.), U.S. 2,322, 056 (1942).
35. R. H. Potts (to Armour & Co.), U.S. 2,674,570 (1954).
36. R. H. Potts and C. W. McBride, *Chem. Eng.*, **57**, 124 (1950).
37. R H. Potts and F. B. White, *J. Am. Oil Chemists' Soc.*, **30**, 49 (1953).
38. D. V. Stingley and H. P. Young, *Ind. Eng. Chem.*, **42**, 202 (1950).
39. W. P. Gee (to Texaco), U.S. 2,450,235 (1948).
40. C. C. Towne (to Texaco), U.S. 2,459,054 (1949).
41. L. A. Myers and V. J. Muckerheide (to Emery Industries), U.S. 2,293,676 (1942).
42. L. D. Myers and V. J. Muckerheide (to Emery Industries), U.S. 2,421,157 (1947).
43. V. J. Muckerheide (to Emery Industries), U.S. 2,514,608 (1950).
44. C. J. West, *A Bibliography of Tall Oil*, Institute of Paper Chemistry, Madison, Wisc.
45. *Tall Oil in Industry*, Bulletins, Tall Oil Division, Pulp Chemicals Association, 122 E. 42nd St., New York 17, N.Y.
46. R. J. Herrlinger, *J. Am. Oil Chemists' Soc.*, **31**, 508 (1954).
47. W. B. Satkowski and W. B. Bennet, *Soap Chem. Specialties*, **33** (7), 37 (1957).
48. T. Bruun, C. M. Hawg, and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 850 (1950).
49. C. L. Leese and R. A. Raphael, *J. Chem. Soc.*, **1950**, 2685.
50. T. Bruun, P. K. Christensen, C. M. Hawg, J. Stene, and N. A. Sörensen, *Acta Chem. Scand.*, **5**, 1244 (1951).
51. P. K. Christensen and N. Sörensen, *Acta Chem. Scand.*, **6**, 893 (1952).
52. P. C. Jocelyn and N. Polgar, *J. Chem. Soc.*, **1953**, 132.
53. F. Bohlmann and H. G. Viehe, *Chem. Ber.*, **88**, 1347 (1955).
54. D. Barnard and L. Bateman, *J. Chem. Soc.*, **1950**, 926.
55. R. A. Raphael and F. Sondheiner, *J. Chem. Soc.*, **1951**, 2693.
56. A. M. Walborsky, R. H. Davis, and D. R. Howton, *J. Am. Chem. Soc.*, **73**, 2590 (1951)

57. S. S. Nigam and B. C. L. Weedon, *Chem. Ind. (London)*, **1955**, 1555.
58. S. S. Nigam and B. C. L. Weedon, *J. Chem. Soc.*, **1956**, 4049.
59. F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).
60. V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer, *J. Am. Chem. Soc.*, **64**, 580 (1942).
61. V. H. Wallingford and A. H. Homeyer (to Mallinckrodt Chemical Co.), U.S. 2,391,530 (1945).
62. V. H. Wallingford and A. H. Homeyer (to Mallinckrodt Chemical Co.), U.S. 2,438,241 (1948).
63. M. Conrad and C. A. Bischoff, *Ann. Chem.*, **204**, 121 (1880).
64. W. A. Noyes, *J. Am. Chem. Soc.*, **18**, 1105 (1896).
65. C. Daimler, *Chem. Ber.*, **20**, 203 (1887).
66. C. Daimler, *Ann. Chem.*, **249**, 173 (1888).
67. W. Bleyberg and H. Ulrich, *Chem. Ber.*, **64**, 2504 (1931).
68. H. W. Lemon, *Can. J. Res.*, **22F**, 191 (1944).
69. H. W. Lemon, *Can. J. Res.*, **27B**, 605 (1949).
70. H. A. Schuette, R. M. Christenson, and H. A. Vogel, *Oil and Soap*, **20**, 263 (1943).
71. A. Lieben and A. Rossi, *Ann. Chem.*, **159**, 58, 70 (1871).
72. A. Lieben and G. Janecek, *Ann. Chem.*, **187**, 126 (1877).
73. P. A. Levene and F. A. Taylor, *J. Biol. Chem.*, **59**, 163 (1924).
74. L. Wolff, *Ann. Chem.*, **394**, 23 (1912).
75. H. T. Harwood and A. W. Ralston, *J. Org. Chem.*, **12**, 740 (1947).
76. W. G. Dauben, *J. Am. Chem. Soc.*, **70**, 1376 (1948).
77. D. R. Howton, R. H. Davis, and J. C. Nevenzel, *J. Am. Chem. Soc.*, **74**, 1109 (1952).
78. D. R. Howton, R. H. Davis, and J. C. Nevenzel, *J. Am. Chem. Soc.*, **76**, 4970 (1954).
79. S. Bergstrom, K. Paabo, and M. Rottenberg, *Acta Chem. Scand.*, **6**, 1127 (1952).
80. Borodin, *Ann. Chem.*, **119**, 121 (1861).
81. H. Hunsdiecker and C. Hunsdiecker, *Chem. Ber.*, **75B**, 291 (1942).
82. J. C. Nevenzel and D. C. Howton, *J. Org. Chem.*, **22**, 319 (1957).
83. Henkel & Cie., G.m.b.H., French 832,546 (1938).
84. *Ibid.*, French 833,064 (1938).
85. Markischen Seifen-Industrie, French 818,796 (1937).
86. *Ibid.*, German 722,591 (1942).
87. E. Keunecke (to I.G. Farbenindustrie A.G.), U.S. 2,095,473 (1937).
88. *Ibid.*, German 626,787 (1936).
89. I.G. Farbenindustrie A.G., British 478,317 (1938).
90. H. Pardun, German 723,528 (1942).
91. B. N. Tyutyunnikov, Z. M. Nikishina, and A. A. Perchenko, USSR 166,438 (1964); *C.A.*, 8020d (1965).
92. F. Wittka, *Soap Chem. Specialties*, **16**, (8), 28 (1939).
93. *Ibid.*, **16**, (9), 34 (1940).
94. G. Wietzel, *Fette Seifen Anstrichmittel*, **46**, 21 (1939).
95. M. Aschenbrenner, *Fette Seifen Anstrichmittel*, **46**, 26 (1939).
96. F. Wittka, *Siefensieden-Ztg.*, **38**, 397 (1941); *C.A.* **37**, 3999 (1943).
97. F. Wittka, *Siefensieden-Ztg.*, **40**, 50, 68 (1943); *C.A.* **39**, 2211 (1945).
98. L. Mannes, *Die Chemie*, **57**, 6 (1944).
99. A. Imhausen, *Chemiker-Z.*, **62**, 213 (1938).
100. A. Imhausen, *Kolloid-Z.*, **85**, 234 (1938).
101. W. K. Griesinger, J. A. Nevison, and G. A. Gallagbee *J. Am. Oil Chemists' Soc.*, **26**, 241 (1949).
102. H. A. Goldsmith, *Chem. Rev.*, **33**, 257 (1943).
103. G. J. Stockburger and J. I. Brandner, "The Reaction of Ethylene Oxide with Oleic Acid," presented at 56th Annual Meeting of the American Oil Chemists' Society, April, 1965.
104. K. Nagase and K. Sakaguchi, *Kogyo Kagaku Zasshi*, **64**, 1035 (1961), *C.A.*, **57**, 3284 (1962).

105. A. N. Wrigley, F. D. Smith, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, **36**, 34 (1959).
106. R. L. Birkmeier and J. I. Brandner, *J. Agr. Food Chem.*, **6**, 471 (1958).
107. E. P. Wetterau, V. L. Olsanski, C. F. Smullin, and J. D. Brandner, *J. Am. Oil Chemists' Soc.*, **41**, 383 (1964).
108. A. N. Wrigley F. D. Smith, and A. J. Stirton, *J. Am. Oil Chemists' Soc.*, **34**, 39 (1957).
109. L. Schechter and J. Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).
110. C. Scholler and M. Wittwer (to I.G. Farbenindustrie A.G.), German 694,178 (1940).
111. A. T. Ballun, J. N. Schumacher, G. E. Kapella, and J. V. Karabinos, *J. Am. Oil Chemists' Soc.*, **31**, 20 (1954).
112. Ciba Ltd., Swiss 244,048 (1947).
113. Ciba Ltd., Swiss 248,685 (1948).
114. J. D. Malkemus (to Jefferson Chemical Co.), U.S. 2,910,490 (1959).
115. R. A. Wilson (to Monsanto Co.), U.S. 2,586,767 (1952).
116. V. Esposito (to Hollingshead Corp.), U.S. 2,610,966 (1952).
117. J. V. Karabinos and A. T. Ballun, *J. Am. Oil Chemists' Soc.*, **31**, 71 (1954).
118. J. A. Nevison (to Atlantic Refining Co.), U.S. 2,542,697 (1951).
119. J. D. Malkemus and J. I. Swan, *J. Am. Oil Chemists' Soc.*, **34**, 342 (1957).
120. G. J. Papariello, S. Chulkaratana, T. Highchi, J. E. Martin, and V. P. Kuceshi, *J. Am. Oil Chemists' Soc.*, **37**, 396 (1960).
121. M. J. Astle, B. Schaeffer, and C. O. Obenland, *J. Am. Chem. Soc.*, **77**, 3643 (1955).
122. E. W. Eckey (to Procter & Gamble Co.), U.S. 2,182,397 (1940).
123. R. Calvert (to Schaack Bros. Chemical Works), U.S. 1,807,304 (1931).
124. L. H. Flett (to National Aniline and Chemical Co.), U.S. 2,135,379 (1938).
125. E. Thielpape and A. Fulde, *Chem. Ber.*, **B66**, 1454 (1933).
126. F. A. Strauss (to E. F. Drew Co.), U.S. 2,469,446 (1949).
127. T. F. Bradley, *Ind. Eng. Chem.*, **29**, 579 (1937).
128. W. H. Kirkpatrick, V. L. Seale, A. Walker, and J. B. Love (to Visco Products Co.), U.S. 2,987,490 (1961).
129. C. Schoeller and M. Wittwer (to I.G. Farbenindustrie A.G.), U.S. 1,970,578 (1934).
130. R. H. Kienle and G. P. Whitcomb (to American Cyanamid Co.), U.S. 2,473,798 (1949).
131. H. Bennett, U.S. 2,275,494 (1942).
132. G. T. Pringle and J. H. K. Rixon (to Imperial Chemical Industries Ltd.), British 979,673 (1965).
133. S. Sussman, *Ind. Eng. Chem.*, **38**, 1228 (1946).
134. W. Schlutter, French 1,031,835 (1955).
135. I.G. Farbenindustrie A.G., German 556,658 (1932).
136. Montsanto Company, unpublished data, 1958–1962.
137. STEROX CD, Technical Bulletin I-129, Monsanto Co., St. Louis, Mo. (1958).
138. Technical Bulletin LG-60R, Atlas Chemical Industries.
139. E. M. Stoltz, A. T. Ballun, H. J. Erlin, and J. V. Karabinos, *J. Am. Oil Chemists' Soc.*, **30**, 271 (1953).
140. T. H. Vaughn and H. R. Suter, *J. Am. Oil Chemists' Soc.*, **27**, 249 (1950).
141. G. E. Kapella, G. E. Bartels, A. T. Ballun, and J. V. Karabinos, *J. Am. Oil Chemists' Soc.*, **31**, 392 (1954).
142. L. Shapiro, *Am. Dyestuff Reptr.*, **39**, 38, 62 (1950).
143. J. C. Harris, *Detergency Evaluation and Testing*, Wiley-Interscience, New York, 1954.
144, A. M. Schwartz, J. W. Perry, and J. Besch, *Surface Active Agents*, Vol. I, Wiley-Interscience, New York, 1949.
145. J. W. McCutcheon, *Detergent and Emulsifier, 1964 Annual*, J. W. McCutcheon Inc., Morristown, New Jersey.
146. P. J. Sisler, *Encyclopedia of Surface Active Agents* (English Translation), Chemical Publ. Co., New York, 1952.
147. N. Schoenfeldt, *Oberflaechenaktive Anlagerungs-produkte Des Aethylenoxyds*, Wissenschatliche Verlag, Stuttgart, 1959.
148. D. E. Anderson and W. F. Wegst (to Wyandotte Chemicals Corp.), U.S. 2,689,225 (1954).

149. *Etho-Chemicals*, Technical Bulletin, Armour & Co., Armour Chemicals Division, 1955.
150. *Renex 20*, Technical Bulletin, Atlas Chemical Industries, Chemical Division, 1960.
151. American Viscose Corp., British 798,192 (1958).
152. J. A. Dison and W. R. Saxton, German 1,033,842 (1958).
153. C. Schlatter (to American Viscose Corp.), U.S. 2,690,427 (1954).
154. O. Albrecht (to Ciba Ltd. Swiss), U.S. 2,576,896 (1951).
155. W. Ender, German 896,938 (1953).
156. J. Stadler, F. Engel, O. Roser, and A. Spaeth, German 1,007,289 (1957).
157. J. C. Wiedow (to Monsanto Co.), U.S. 2,893,913 (1959).