TABLE I

Mid-1980 Prices of Detergent Builders

Builder	Price ($/lb) (100% solids basis)
Citric acid (50% LIQ-W)	0.56
Sodium citrate (white powder)	0.685
NTA	0.385
STPP	0.30
TSPP	0.31
Zeolite NaA	0.22
Sodium silicate 2.0 ratio (44% solids)	0.123
Sodium silicate 2.4 ratio (47% solids)	0.126
Sodium carbonate	0.040-0.043

Nitrilotriacetic Acid (NTA)

NTA, sodium salt, is an excellent Ca and Mg ion chelating agent, in fact, better than STPP. In the late 1960s, NTA was beginning to appear in some U.S. detergents, but a voluntary cessation of large-scale use in detergents in the U.S. occurred in late-1970 at the urging of the U.S. Surgeon General, when concerns arose over the material's safety, based on some animal testing. In May 1980, in a letter from EPA Assistant Administrator Steven Jellinek to the Procter and Gamble Company, EPA announced that it saw no reason, based on present information, to regulate the use of NTA in detergents. This was not an endorsement, Jellineck said, and did not preclude future action in the event of new findings (23).

NTA is made commercially from the reaction of hydrogen cyanide, ammonia, and formaldehyde, and is used in detergents in the form of the sodium salt.

1980 VOLUMES AND PRICES

The detergent builder business is expected to take ca. 2.5 billion lb/year of products for 1980 in the U.S. Industry estimates (23) that phosphates (primarily STPP) have ca. 60% of the market, or ca. 1.5 billion lb/year; silicates (primarily 2.0-to-2.4 ratio products) are a distant second in volume with ca. 400 million lb/year; zeolite A and carbonates roughly are at 300 million lb/year each; and relatively little citrate and NTA are presently used. Major growth is expected in the use of zeolite A, in the USA and on a worldwide basis (3,4,7,24).

Industry sources in mid-1980 gave approximate prices for these builders as shown in Table I. These are bulk prices, F.O.B., point of manufacturing.

REFERENCES

1. Hollingsworth, M., JAOCS 55:49 (1978).
2. Crutchfield, M., Ibid. 55:58 (1978).
3. Savitsky, A., HAPPI 14:52 (1977).
4. Berth, P., JAOCS 55:52 (1978).
5. Lowe, E., W. Adair and E. Johnston, Ibid. 55:32 (1978).
6. Vail, J., "Soluble Silicates," Vols. I and II: ACS Monograph 116, Reinhold, New York, NY, 1952,
7. Schweiker, G., JAOCS 55:36 (1978).
8. Campbell, T., J. Falcone and G. Schweiker, HAPPI 15(3):31 (1978).
9. Curll, D., U.S. Patent 2,239,880 (1941).
10. DeLiedekerke, M., German Offen. 2,519,265 (1975).
11. Breck, D., "Zeolite Molecular Sieves," John Wiley and Sons, New York, NY, 1974.
12. Milton, R., U.S. Patent 2,882,243 (1959).
13. Sensel, E., U.S. Patent 2,841,471, (1958).
14. Estes, J., U.S. Patent 2,847,280 (1958).
15. Weber, H., U.S. Patent 3,058,805 (1962).
16. Michael, M., and D. Paper, U.S. Patent 3,433,588 (1969).
17. Kettinger, F., J. Laudone and R. Pierce, U.S. Patent 4,150,100 (1979).
18. Sensel, E., U.S. Patent 3,009,776 (1961).
19. Maher, P., U.S. Patent 3,185,544 (1965).
20. Maher, P., and E. Nealon, U.S. Patent 3,205,037 (1965).
21. Veda, T., 0. Sato and Y. Nakamura, U.S. Patent 3,535,975 (1970).
22. Williams, L., R. Mays and J. Wagner, Belgian Patent 844,473 (1977).
23. Layman, P., Chem. Week, July 23, p. 44 (1980).
24. Whalen, H., Review and Forecast, Chem. Marketing Res. Assoc. Meeting, May 8-10, 1978, p. 343.

Update on Surfactants: What Do We Have to Work with?

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ABSTRACT

The number of commercially available surfactants continues to grow, but at a slower pace than in the past decade. Low-cost raw material continues to guide the market. Several surfactants, such as AOS, have yet to reach their potential volumes. The class, structure and chemistry of the major and developing surfactants are reviewed and some unique application examples are described.

INTRODUCTION

To answer the rhetorical question posed by the title of this paper, at the present time, the surfactant chemist or formulator can "work with" over 600 surface-active agents manufactured by about 160 producers in the U.S. These 600-plus surfactants represent a production volume of ca. 5 billion lb of products (1). The major portion is consumed as packaged soaps and detergents (i.e., cleaning products) for household and industrial use. The balance is used in such diverse applications as agricultural sprays, cosmetics, ore flotation, foods, lubricants, pharmaceuticals, textile processing, oil well drilling, leather manufacture, inks, synthetic elastomer production, and oil recovery operations.

The three primary sources of raw materials for surfactants are natural fats and oils (2-4), silvichemicals, such as lignin and tall oil, and coal tar and petrochemical stocks. The first two sources are renewable whereas the petroleum and coal chemical stocks are in a relatively limited supply. The issue of renewability, though obviously important, is not discussed in this paper. Surfactants generally are

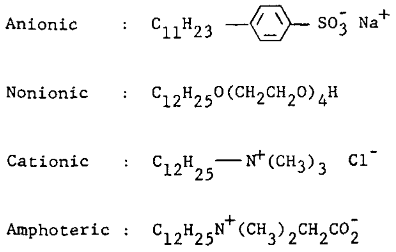

FIG. 1. Typical examples of surfactants.

$CH_3(CH_2)_{12}CH{=}CH{-}CH_2{-}SO_3Na$

Sodium 2,3-alkenylsulfonate

$CH_3(CH_2)_{12}CH(OH){-}CH_2{-}CH_2{-}SO_3Na$

Sodium 3-hydroxyalkanesulfonate

FIG. 2. Commercial α-olefin sulfonate (AOS).

classified as to their chemical type (ionic class), which is how these materials will be covered in this discussion. Typical examples of the four general types of surfactants are shown in Figure 1.

Marketing

In the U.S., anionic surfactants continue to dominate the market with greater than 65% of production (1). Nonionic surfactants, the next largest volume, account for another 30% of production. Cationics represent most of the remaining production with a relatively small volume for amphoterics.

The impact of government regulations probably will reduce the number of "new" commercial surfactants introduced into the marketplace. Possibly, this could lead to major changes in basic materials as happened in the past when the rapid conversion occurred from branched chain alkylbenzene sulfonate (ABS) to straight chain linear (LAS) in the 1964-66 period (5).

In developing detergent-based products or an industrial surfactant end-use, three prime considerations must be balanced: availability, cost and properties. A surfactant can have the best properties for a formulated product, but may not be commercially available in the quantities required at the desired price to produce an economically viable product. One must recognize, in evaluating available surfactants, that low-priced materials with reasonable surface active performance tend to dominate the market. In selecting surfactants, the chemical and physical properties such as physical form and activity, pH, specific gravity, flash point, cloud point, surface tension, color, viscosity, odor, stability, solubility and HLB value are important for the formulation and performance.

Viscosity is a good example to consider. From a manufacturing/commercial view, the handling of a raw material has both technical and economic overtones. For every 3 lb of sodium lauryl sulfate that is shipped, handled and stored in liquid form, 7 lb of water and inert materials accompany the 3. For every 4 lb of C14-16 α-olefin sulfonate (AOS), there are only 6 lb of water and inert material. (These proportions are inherent in the solubility and viscosity of the particular surfactant). Thus, AOS is less costly to ship than the lauryl sulfate based on 100% actives.

From a consumer product view, responsiveness and compatibility with various viscosity builders are critical to formulation of shampoos, liquid hand soaps, liquid dishwash and other products. Polymeric thickeners, alkanolamides, and various salts and cations have their specific

TABLE I

Surfactant Applications Where Foam Is Important

Industrial	Consumer products
Gas well cleaning	Hand dishwashing
Fire fighting	Car wash
Concrete	Hand soap
Gypsum wall board	Laundry detergent
Ore flotation	Hair shampoo
	Rug shampoo
	Bubble bath
	Tooth paste

TABLE II

Anionic Surfactants

225 Anionics	%
Alkylbenzene sulfonates	20.6
Lignin sulfonates	26.8
Other sulfonic acid derivatives	5.8
Alcohol sulfates	7.2
Ethoxylated alcohol sulfates	9.2
Other sulfates	1.4
Carboxylic acid salts	26.4
Phosphoric acid esters and salts	1.2
Other anionics	1.4

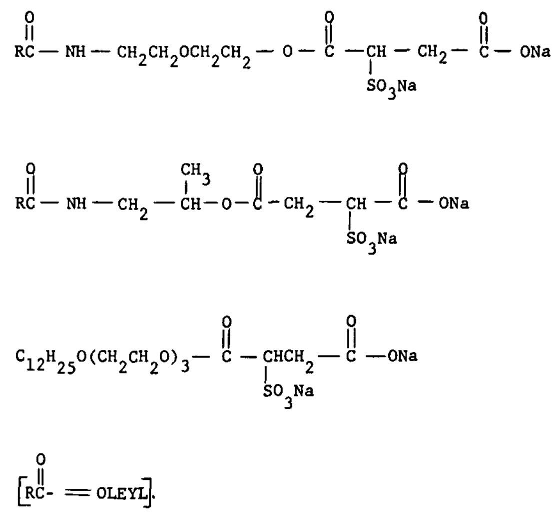

FIG. 3. The commercial sulfosuccinate half-esters.

$C_8F_{17}SO_3H$ $C_8F_{17}CO_2Na$

$(F_3C)_2CH-O-(CH_2)_6-OSO_3Na$

$F_3C-CF_2-(CH_2)_4-O-(CH_2-CH(CH_3)-O)_2SO_3Na$

$C_8F_{17}CO_2Li$

FIG. 4. Examples of perfluoro surfactants.

TABLE III

Some New Anionic Surfactants

Reference	Surfactant	Utility
27	$RCH(SO_3Na) - CO_2 - [CH_2CH(OH) - CH_2O]_nH$ Polyglyceride of α-sulfocarboxylic acid	Good surfactant
28	Sulfosuccinate half-esters of oxyethylated resin derivatives	Wetting agents for dyes and pigments
29	Telomers from acrylic acid or acrylamide and $C_{12}H_{25}SH$	Good Ca^{+2} sequesterant

TABLE IV

Nonionic Surfactants

200 Nonionics	%
Alkoxylated linear alcohols	42.9
Alkoxylated phenols	24.6
Carboxylic acid esters	18.2
Carboxylic acid amides	5.2
Other alkoxylated	6.5*
Other nonionics	2.6

TABLE V

Cationic Surfactants

150 Cationics	%
Quaternary ammonium salts	36.9
Amines without oxygen (and salts)	26.4
Amine oxides (non-amide links)	25.5
Amines and amine oxides (with amide links)	9.7
Other cationics	1.5

and varying effects on different surfactants (6).

In order to gain proper performance from a surfactant, often the ionic class predominates in its selection. However, for many applications the ionic class is less important. Properties which are often important for performance include foaming, wetting and emulsifiability. Table I lists a number of examples of industrial and consumer products in which foam plays important and diverse roles. The requirements for quality, quantity, stability (7) and manner of generation will differ significantly for many of these uses.

Anionic Surfactants

Surfactants in commercial use in the U.S. will be described in order of their commercial production volume. Of the more than 200 anionic surfactants listed by the U.S. Tariff Commission (1), sulfonic acids and their salts represent, by far, the largest volume (Table II). This includes alkylbenzene sulfonates, such as LAS (8), and lignin sulfonates. Alcohol sulfates and ethoxylated alcohol sulfates (8) make up the next largest volume of anionic surfactants. The large volume of carboxylic acid salts is mostly a result of their use in household bar soaps. Some of the newer anionic surfactants that have been developing markets are AOS, sulfosuccinates, acylglutamates, perfluoroalkyl acids and derivatives, and α-sulfo fatty acids.

Because the purpose of this paper is to update surfactants as well as to indicate what materials are available, it is of interest to cover some of these newer anionics. These materials are commercially available, and a number of manufacturers have developed profitable markets for selling some of them, even though they are used in smaller volumes than the surfactants shown in Table II.

AOS has been commercially available for 10-15 years, but has not yet reached the total volume that could be manufactured and used (9,10). The two major components in commercial products are shown in Figure 2. Light-colored AOS can be produced with good detergent performance properties, i.e., foaming, detergency, emulsion stability and good biodegradability. AOS exhibits low eye and skin irritation, thus making it useful in shampoos, liquid hand soaps and liquid dishwash (11).

Sulfosuccinates have been carving out a fair-sized market segment in the surfactant industry. Sulfosuccinates refer both to diesters of sulfosuccinic acid and to monoesters (half esters) of sulfosuccinic acid. The diesters have been in use for some time (12). The half esters are being used because of their low irritancy and generally low toxicity profile. The half ester sulfosuccinates (Fig. 3) are used in shampoos and in bubble baths, and foam exceptionally well. Also, sulfosuccinates have the ability to disperse hard water soaps.

The fatty acid acyl derivatives of amino acids, e.g., lauroyl glutamate, $C_{11}H_{23}CONHCH(CH_2CH_2CO_2H)CO_2^-Na^+$, have been gaining more interest and commercial use. These materials also have good detergency and lime soap dispersant properties. Because they are nonirritating to skin and have a mild feel, they also are useful for cosmetics and toiletries (13). The Na salts of the long chain acyl derivatives of glutamic acid have received acceptance, and a great deal of development work is underway in this area (14,15).

TABLE VI

Three Examples of Some of the Newer Cationic Surfactants

Reference	Surfactant	Utility
37	$CH_3(CH_2)_{10}CONH - CH_2CH(NHCOCH_2CH_3)(CONH(CH_2)_3 - N(CH_3)_2)$	Antibacterial activity, nonirritating
39	$[C_{15}H_{31}CONH(CH_2)_2NHCH_2CHOHCH_2N(C_2H_5)_3]^+\ OH^-$	Corrosion inhibitor
40	$RCONHCH_2CH_2CH_2N^+(CH_3)_3\ X^-$	Hair conditioner

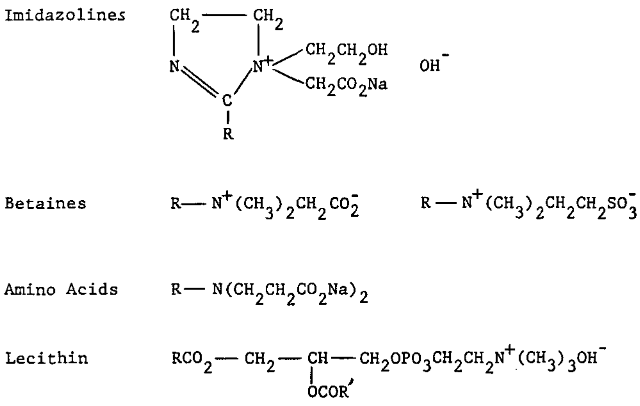

FIG. 5. Major types of commercial amphoteric surfactants.

Hydrolysates of various natural (and relatively cheap) proteins have been used, such as collagen protein (chrome leather shavings) leather scraps (16), fish scales (17), chicken feathers (18), vegetable soy protein (18) and casein (15).

Polyfluorochemical surfactants (Fig. 4) are relatively more expensive than other surfactants, but should be considered useful materials because of their unique properties conferred by the fluoro atoms. Because fluorine is the most electronegative atom, the perfluoroalkyl groups cause these surfactants to give the lowest surface tension in aqueous solution and to have other useful functions such as antistatic properties, antisoiling ability and unusually good wetting ability (19-23).

α-Sulfo fatty acids have been known to exist for a long time. Because improved processes for their manufacture have been developed, further utilization probably will occur (24,25). These surfactants are reported to have good washing and foaming properties, good biodegradability and low toxicity (26).

There is much literature, primarily foreign patents, covering many other new anionic surfactants. Although most of these materials are not gaining a commercial market, and probably will not, some are shown here (Table III) for academic interest (27-29).

Nonionic Surfactants

Of the nearly 200 nonionics commercially produced (1), alkoxylated linear alcohols make up the largest portion of this type (Table IV) (30). A large proportion of these alkoxylated alcohols is sulfated to produce anionic surfactants. Alkoxylated phenol is the next largest group in this type of surfactant (30).

Because of the ease in alkoxylating, e.g., alcohols and carboxylic acids, as well as the low price and availability of large amounts of ethylene oxide and propylene oxide, many new nonionic surfactants have been prepared, described and patented (31-35).

Cationic Surfactants

Quaternary ammonium salts (36) make up the largest part of the approximate 150 cationic surfactants available. Amines not containing oxygen and amine oxides each make up a quarter of the total volume (Table V). Because of the potential specialty applications of cationic surfactants, several newer materials (37-40) are being developed (Table VI).

Amphoterics

About 20 amphoteric surfactants in commercial production make up only ca. 1/2% of the total surfactants manufactured. Even though the volume is small, this class of surfactants is quite useful because of their unique properties which warrant their relatively higher cost. The major products in commercial use are the 2-alkyl-2-imidazolines, betaines (both sulfobetaines and carboxybetaines), amino acid derivatives and lecithins (Fig. 5). These various amphoteric surfactants perform well in shampoos and cosmetics (41-44), generally have good antistatic properties, are good in textile processing, perform well as lime soap dispersants and are good emulsifying agents (4,45-48).

An unusually large amount of development work is being done to prepare new types of amphoterics (49-52). Most of these mterials have to be considered academic, because their commercial cost probably would not be economical enough for the particular properties conferred by them. It is, however, interesting to see the variety of potential uses in Table VII.

New Applications

The versatility and uniqueness of surfactants lead to many new applications. In some cases the best, and most economical, solutions have not yet been reached.

Dewatering of coal (53-59). The use of surfactants reduces the surface tension and the water content of coal fines and controls coal dust. All types of detergent materials operate successfully, although the anionic type is best, according to the literature. Materials used included dodecylammonium bromide, sodium dodecylsulfate and high-molecular-weight poly(oxyethylene).

Fire-fighting. A fire-fighting foam has been reported based on a nonionic perfluoroalkyl derivative (60). A perfluoroalkyl sulfonate also was used in water-based fire extinguishers (61).

Foamed gypsum wallboard. Surfactants are used to create the bubbles needed to form foamed lightweight gypsum wallboard (62).

Enhanced oil recovery. Petroleum sulfonates differ from most of the previously discussed surfactants because of

TABLE VII

Some New Amphoterics

Reference	Material	Potential use
49	$HOCH_2CH_2N(C_{12}H_{25})CH_2CH_2SO_3H$ (taurine type)	Antimicrobial surfactant
50	$C_9F_{19}CON\langle\text{ring}\rangle N^+(CH_2CO_2^-)(CH_2CH_2OH)$	Very low surface tension, low CMC
51	$RCONH(CH_2)_2N^+(CH_3)_2CH_2CO_2^-$	Nontoxic to aquatic life
52	Amphoteric polymers of amino hydroxy aromatic acids	Blood preservatives, concrete plasticizers

their relatively low water solubility (63). They are of great current interest in micellar/polymer oil recovery systems, and represent a potentially large, new market (64,65). Large-scale use of totally new surfactant molecules has been inhibited by government regulations. Large volume potential can support the necessary human and environmental safety testing to make marketing possible. To the extent, however, that significant new use rules under the Toxic Substances Control Act relate to volume, rather than exposure, testing requirements may be more stringent as volume potential increases. As a result, the tendency will likely be to find ways to use known entities or variations of them before developing totally new molecules.

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REFERENCES

1. "Synthetic Organic Chemicals, U.S. Production and Sales, 1978," U.S. Govt. Printing Office, Washington, 1979, pp. 237-269.
2. Sonntag, N.O.V., JAOCS (in press).
3. Jungermann, E., Ibid. 56:827A (1979).
4. Linfield, W.M., Ibid. 55:87 (1978).
5. Haupt, D.E., and P.B. Schwin, Ibid. 55:28 (1978).
6. Schoenberg, T.G., Soap Cosmet. Chem. Spec. 56:54 (May 1980).
7. Beh, H.H., and K.C. James, Cosmet. Toiletries 92:21 (November (1977).
8. Matson, T.P., JAOCS 55:66 (1978).
9. Tuvell, M.E., G.O. Kuehnhanss, G.D. Heidebrecht, P.C. Hu and A.D. Zielinski, Ibid. 55:70 (1978).
10. Yamane, I., Ibid. 55:81 (1978).
11. Barker, G., M. Barabash and P. Sosis, Soap Cosmet. Chem. Spec. 54:38 (March (1978).
12. Longley, K.D., and A.J. Karalis, U.S. Patent 4,117,237 (1978); British Patent 1,523,644 (1978).
13. Takehara, M., R. Yoshida and M. Yoshikawa, Cosmet. Toiletries 94:31 (August 1979).
14. Shinoaga, T., and Y. Usuba, Jpn. Kokai Tokkyo Koho 78 132,007, November 17, 1978; Chem. Abstr. 90:139357y (1979).
15. Saito, S., Ibid. 79 45,311, April 10, 1979; Chem. Abstr. 91:93366r (1979).
16. Antos, K., E. Markusovska and P. Hodul, Kozarstvi 30(1):12 (1980); Chem. Abstr. 92:217049g (1980).
17. Chakrabarty, M.M., A.K. Basu, A.K. Samanta and A.K. Ghorai, J. Indian Chem. Soc. 56:885 (1979).
18. Sokol, P.E., Canadian Patent 1,072,952 (1980).
19. Nakamura, Y., M. Umemura and M. Yonekura, Jpn. Kokai Tokkyo Koho 77 35,184, March 17, 1977; Chem. Abstr. 87:70155z (1977).
20. Hayashi, T., and Y. Otoshi, Ibid. 79 147,184, November 17, 1979; Chem. Abstr. 92:148920v (1980).
21. Tatematsu, R., S. Ozaki, S. Nagase and K. Inukai, Yukagaku 29:23 (1980); Chem. Abstr. 92:148902r (1980).
22. "Zonyl Fluorochemical Intermediates," E.I. du Pont de Nemours & Co., Wilmington, DE.
23. "Lodyne Fluorochemical Surfactants," Ciba-Geigy Corporation, Ardsley, NY.
24. Kapur, B.L., J.M. Solomon and B.R. Bluestein, JAOCS 55:549 (1978).
25. Stein, W., and H. Baumann, Ibid. 52:323 (1975).
26. Bluestein, B.R., and B.L. Kapur in "Fatty Acids," edited by E.H. Pryde, AOCS Monograph 7, American Oil Chemists' Society, Champaign, IL, 1979, pp. 260-271.
27. Golovin, B.A., R.I. Obydenova, D.A. Zhukov, L.M. Averina, V.E. Kuban and V.V. Suchkov, USSR. Patent 709,622 (1980); Chem. Abstr. 92:131104j (1980).
28. Guntze, V., and H. Uhrig, German Offen. 2,840,113 (1980).
29. Yamada, K., S. Ikeda and H. Shosenji, Yukagaku 28:605 (1979); Chem. Abstr. 91:212885w (1979).
30. McKenzie, D.A., JAOCS 55:93 (1978).
31. Saito, H., M. Nozue and H. Takizawa, Jpn. Kokai Tokkyo Koho 79 79,229, June 25, 1979; Chem. Abstr. 91:142414r (1979).
32. Kuwamura, T., and S. Yoshida, Nippon Kagaku Kaishi 427 March (1980); Chem. Abstr. 93:26168e (1980).
33. Kuwamura, T., and T. Kawachi, Yukagaku 28:195 (1979); Chem. Abstr. 90:206248d (1979).
34. Kuo, P.-L., M. Miki, I. Ikeda and M. Okahara, JAOCS 57:227 (1980).
35. Rakhamankulov, D.L., S.S. Zlotskii, V.N. Uzikova, R.A. Karakhanov, I.L. Rakhmankulov and M.S. Klyavlin, Tr.-Mezhdunar. Kongr. Poverkhn.-Akt. Veshchestvam, 7th 1976, 1:402 (1977): Chem. Abstr. 91:59215f (1979).
36. Egan, R.R., JAOCS 55:36 (1978).
37. Ajisaka, K., E. Nagauchi and M. Honma, Jpn. Kokai Tokkyo Koho 79 145,608, November 14, 1979; Chem. Abstr. 92: 131103h (1980).
38. Yanagawa, T., Y. Kawada, D. Saika, T. Satsuki and S. Ota, Ibid. 79 87,709, July 12, 1979; Chem. Abstr. 91:212923g (1979).
39. Gawish, S.M., A.A.B. Hazzaa and B. El-Din Gebril, JAOCS 55:745 (1978).
40. Schoenberg, T.G., and A.A. Scafidi, Cosmet. Toiletries 94:57 (March 1979).
41. Kass, G.S., Ibid. 94:25 (August 1979).
42. Barker, G., Cosmet. Perfum. 90:69 (March 1975).
43. Schoenberg, T.G., HAPPI 16:60 (September 1979).
44. Hart, J.R., Cosmet. Technol. 2:41 (January 1980).
45. Kaminski, J.M., and W.M. Linfield, JAOCS 56:771 (1979).
46. Taki, M., H. Hidaka, S. Ishikawa, M. Takada and M. Moriya, Ibid. 57:183 (1980).
47. Fernely, G.W., Ibid. 55:98 (1978).
48. Lomax, E.G., Manuf. Chem. Aerosol News 39 (August 1979).
49. Kanetani, F., M. Kano and K. Negoro, Nippon Kagaku Kaishi 400 (1980); Chem. Abstr. 93:28167d (1980).
50. Hayashi, T., and Y. Otoshi, Jpn. Kokai Tokkyo Koho 79 62:998, May 21, 1979; Chem. Abstr. 91:125254w (1979).
51. Kersnar, P., and R.J. O'Conner, U.S. Patent 4,122,043, (1978).
52. Makhmudov, T.M., K. Kh. Khidoyatov and A.S. Khakimov, Tr.-Mezhdunar. Kongr. Poverkhn.-Akt. Veshchestvam, 7th 1976, 1:136 (1977); Chem. Abstr. 91:59211b (1979).
53. Baichenko, A.A., V.S. Kaminskii and V.S. Sokolova, Koks Khim. 11 January (1977); Chem. Abstr. 87:55533c (1977).
54. S.K. Nicol, Proc. Australas, Inst. Min. Metall. 260:37 (1976); Chem. Abstr. 87:70695a (1977).
55. Barker, A.F., Pap. Symp. Coal Prep. 2:175 (1976); Chem. Abstr. 87:104239x (1977).
56. Demchenko, P.A., V.P. Musienko, T.I. Zvyagina and I.P. Kosova, Visn. Akad. Nauk Ukr. RSR 51 April (1979); Chem. Abstr. 91:95793b (1979).
57. Sakuma, K., T. Ukigai, T. Yamashita, T. Ito and J. Yamada, Jpn. Kokai Tokkyo Koho 79 31,404, March 8, 1979; Chem. Abstr. 91:125960y (1979).
58. Stelma, G.J., (Syracuse Univ. thesis), Diss. Abstr. Int. B 40:404 (1979).
59. Glanville, J.O., and J.P. Wightman, Fuel 58:819 (1979).
60. Cooper, G.E., and R.E. Stratton, West German Offenlagenschrift 2,715,157 (1977).
61. Nakamura, Y., M. Umemura and M. Yonekura, Jpn. Kokai Tokkyo Koho 77 35,184, March 17, 1977; Chem. Abstr. 87: 70155z (1977).
62. Stiling, R.A., E.A. Burkard and R.M. Johnson, U.S. Patent 4,057,443 (1976).
63. Luisi, T.E., Soap Cosmet. Chem. Spec. 55:34 (May 1979).
64. Knaggs, E.A., and J.W. Hodge, Am. Chem. Soc., Div. Chem. Mktg. Econ. Rept. 95, (March 1980).
65. Oppenländer, K., M.H. Akstinat and H. Murtada, Tenside Deterg. 17:57 (1980).