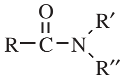
# AMIDES, FATTY ACID

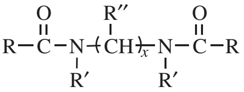
## 1. Introduction

Fatty acid amides are of the general formula



$$R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}R'\\R''\end{matrix}$$

in which R may be a saturated or unsaturated alkyl chain derived from a fatty acid. They can be divided into three categories (1). The first is primary monoamides in which R is a fatty alkyl or alkenyl chain of $C_5-C_{23}$ and $R' = R'' = H$. The second, and by far the largest category, is substituted monoamides, including secondary, tertiary, and alkanolamides in which R is a fatty alkyl or alkenyl chain of $C_5-C_{23}$; R′ and R″ may be a hydrogen, fatty alkyl, aryl, or alkylene oxide condensation groups with at least one alkyl, aryl, or alkylene oxide group. The third category is bis(amides) of the general formula:



$$R-\overset{\overset{O}{\|}}{C}-\underset{R'}{N}-(\overset{R''}{CH})_x-\underset{R'}{N}-\overset{\overset{O}{\|}}{C}-R$$

where R groups are fatty alkyl or alkenyl chains. R′ and R″ may be hydrogen, fatty alkyl, aryl, or alkylene oxide condensation groups. Other amides include halogenated amides and multifunctional amides such as amidoamines and polyamides. A more detailed description of the synthesis, properties, and reactions of amides can be found in (2). Examples of fatty acid amides and common nomenclature for primary amides can be seen in Table 1.

Table 1. **Primary Fatty Amide ($RCONH_2$) Nomenclature**

| Carbon atoms[a] | Common name | Molecular formula | IUPAC name | CAS Registry Number |
|---|---|---|---|---|
| | | *Alkyl* | | |
| 12 | lauramide | $C_{12}H_{25}NO$ | dodecylamide | [1120-16-7] |
| 14 | myristamide | $C_{14}H_{29}NO$ | tetradecylamide | [638-58-54] |
| 16 | palmitamide | $C_{16}H_{33}NO$ | hexadecylamide | [629-54-9] |
| 18 | stearamide | $C_{18}H_{37}NO$ | octadecylamide | [124-26-5] |
| | | *Alkenyl* | | |
| 16(1) | palmitoleamide | $C_{16}H_{31}NO$ | hexadecenamide | [b] |
| 18(1) | oleamide | $C_{18}H_{35}NO$ | 9-octadecenamide | [301-02-0] |
| 18(2) | linoleamide | $C_{18}H_{33}NO$ | 9,12-octadecadienamide | [3999-01-7] |

[a] The number in parentheses designates double bonds in the carbon chain.
[b] Not available.

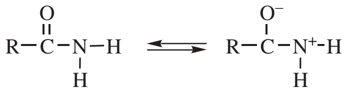
Table 2. **Fatty Amide Melting Points**

| | RCONH$_2$ Amide | | RCONHCH$_2$CH$_2$OH MEA | | RCON(CH$_2$CH$_2$OH)$_2$ DEA | |
|---|---|---|---|---|---|---|
| Alkyl(R) length | CAS Registry Number | mp, °C | CAS Registry Number | mp, °C | CAS Registry Number | mp, °C |
| 12 | [1120-16-7] | 103 | [142-78-9] | 78.2 | [120-40-1] | 38.7 |
| 14 | [638-58-4] | 104 | [142-58-5] | 87.4 | [7545-23-5] | 47.9 |
| 16 | [629-54-9] | 108 | [544-31-0] | 94.4 | [7545-24-6] | 65.1 |
| 18 | [124-26-5] | 109 | [111-57-9] | 96.1 | [93-82-3] | 69.7 |

For alkanolamides the abbreviation MEA and DEA are used after the common name as seen in Table 2 to signify monoethanolamide (MEA) and diethanolamide (DEA) according to INCI (The International Nomenclature of Cosmetic Ingredients) as wellas in this article.

## 2. Physical Properties

Many of the physical properties of fatty acid amides have been explained on the basis of the tautomeric structures:



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-H \rightleftharpoons R-\overset{\overset{O^-}{|}}{C}-\underset{\underset{H}{|}}{N^+}-H$$

Primary and secondary amides show strong hydrogen bonding that accounts for their high melting points and low solubilities in most solvents. With tertiary amides (disubstituted amides), hydrogen bonding is not possible as exhibited by their increased solubility and lower melting points as shown in Table 2 (3).

Many fatty acid amides are essentially insoluble in water. Polar solvent solubilities decrease with longer alkyl chain lengths. Amides with alkyl chain lengths $>C_{12}$, with the exception of alkanolamides, have low solubility in all solvents. In nonpolar solvents, solubility is low and varies irregularly with chain length (4).

Solubility is influenced by the production procedure used resulting in different by-product composition. As an example the following can be mentioned. Equimolar quantities of diethanolamine with a fatty acid results in water insoluble products and high levels of ester amide. Wolff Kritchevsky in 1937 (5,6) observed that reaction between 2 mol of diethanolamine and 1 mol of fatty acid led to a water soluble product with good surface activity. These were found to be complex mixtures of free diethanolamine, fatty acid amine soap, fatty amide (50–60%), ester amide, diester amide, amine ester, amine diester, and *N,N′*-bis(2-hydroxyethyl) piperazine. Later, the so-called superamides were developed by Meade in 1949 (7), which contain fatty acid amide up to 95%. It is a two-stage process via triglyceride reacted with 3 mol methanol to form the methyl ester and then the methyl ester is reacted with diethanolamine to give fatty acid diethanolamide

Table 3. **Physicochemical Properties of Selected Alkyl Amide Ethoxylates**

| Chemical substance[a] | HLB (Griffin) | Cloud point, °C | Surface tension mN/m 0.1% | Foam, Ross Miles (mm), 50°C, 0 and 5 min 0.05% | Draves wetting (s) 0.1% |
|---|---|---|---|---|---|
| OMA 2 | 6.4 | | 28 | 14/12 | 580 |
| OMA 4 | 8.8 | 69[b] | 30 | 20/18 | 280 |
| OMA 7 | 10.5 | | 30 | 26/23 | 210 |
| OMA 13 | 15.1 | 68[c] | 37 | | |
| CMA 2 | 7.7 | | 27 | 113/108 | 22 |
| CMA 5 | 11.1 | 80[b] | 30 | 125/122 | 20 |
| CMA 8 | 13 | 60–70[c] | 33 | | |
| CMA 12 | 14.6 | 72[c] | 34 | | |
| HTMA 5 | 8.8 | | 31 | 39/33 | 220 |
| HTMA 13 | 13.4 | | 37 | 65/66 | 560 |
| HTMA 50 | 17.7 | | 39 | 84/32 | >600 |
| Cocamide DEA | 8.5 | | 27 | 90/85 | 27 |

[a] OMA = Oleylmonoethanolamide, CMA = Cocomonoethanolamide, HTMA = Hydrogenated tallow monoethanolamide.

[b] A 5-g product in 25 mL 25% butyl glycol.

[c] 1 % in 10% NaCl, pH < 3 (HCl).

*Source:* Akzo Nobel internal reports and product data sheets. The figures show the number of ethylene oxide.

and methanol. The superamides are high foamers and foam stabilizers and exhibit synergistic effects with other surfactants. They are easily solubilized by other surfactants and soap. They gradually have taken over from Kritchevski amides in personal care products, hard surface cleaners, and higher quality liquid detergents Table 3.

Amides have a strong tendency to reduce friction by adsorption on surfaces. This coating action may be attributed to their hydrophobic character and strong hydrogen bonding. Hydrogen bonding between amide groups lead to higher surfactant crystal stability and higher Krafft point (8,9).

The question arises whether hydrogen bonding occurs in aqueous solution? The role of the amide linkage in the molecular structure when it comes to physicochemical properties in aqueous solution has been investigated lately by Folmer (10,11) and Kjellin (12). Their focus is on alkyl amide ethoxylates that are compared to alkyl ethoxylates. The discussion concerns hydrogen-bond formation on one hand and increase in hydrophilicity and hydrophilic head group size on the other. These two functional properties may be expected to influence the physicochemical behavior in opposite directions, with hydrogen bonding causing denser packing and hydrophilicity resulting in less tendency to aggregate.

The general conclusion is that an amide linkage renders the surfactant more hydrophilic and increases the CMC and the cloud point. (13). However, the surface tension at CMC is higher. Attractive interactions could be found between amide groups in an adsorbed layer (13,14), which is all explained in terms of changes in the packing in several ways and not necessarily depending on direct hydrogen bonding between the amide groups.

The amide group also changes the form of the micelle to a more prolate shaped structure (15), which would mean a tendency to form rodlike structures at higher concentrations. This in turn points at the uses of alkyl amides for rheology control. The existence of rodlike micelles in a typical alkyl amide ethoxylate has been shown by Khan and co-workers (16) for an octadecylamide, poly(oxyethylene)ether, made from rapeseed oil fatty acid according to the superamide route described above. A special application for the threadlike micelles formed is as drag reducing agents in cold water distribution systems (17).

## 3. Chemical Properties

Amides in general are stable to elevated processing temperatures, air oxidation, and dilute acids and bases. Stability is reduced in amides containing unsaturated alkyl chains; unsaturation offers reactive sites for many reactions. Hydrolysis of primary amides catalyzed by acids or bases is rather slow compared to other fatty acid derivatives. Even more difficult is the hydrolysis of substituted amides. More information can be found in Table D under Applications. The dehydration of amides that produce nitriles is of great commercial value (18). Amides can also be reduced to primary and secondary amines using a copper chromite catalyst (19) or metallic hydrides (20).

## 4. Synthesis and Manufacture

**4.1. Amides.** Fatty amides are prepared from fatty acids by reaction with ammonia at elevated temperature and pressure followed by dehydration, or from fatty esters by ammonolysis. Catalysts for the amidation of fatty acids include boric acid, alumina, titanium and zinc alkoxides, and various metallic oxides (21,22). Partially dehydrated metal hydroxides of zirconium, titanium, and tin have also been described (23). A low-pressure process from alkyl esters utilizes a soluble tetravalent tin catalyst (24). Purification of the crude amides to remove residual fatty acid and nitrile is achieved by neutralization of the amide with an alkali metal hydroxide followed by distillation using a thin-film evaporator. Antioxidants can be included in the purification process to stabilize the color and odor of the product, particularly for unsaturated amides (25,26).

Substituted amides can be made directly from triglycerides by the base-catalyzed reaction with amines (27). The process may also be run under high pressure in the absence of catalyst (28). Phenyl substituted amides can be made using boric acid or boronic acid catalyst in the presence of a chelating agent (29), and alkenyl substituted amides by dehydration of 2-hydroxyalkyl substituted amides (30).

**4.2. Alkanolamides.** The methods for manufacture of alkanolamides are well known and comprise the reaction of an alkanolamine, such as ethanolamine, diethanolamine, or monoisopropanolamine, with a fatty acid, fatty acid ester, or triglyceride (17,21). The reaction of fatty acid with diethanolamine yields a mixture of DEA and diethanolamine esteramide. The milder conditions used with fatty acid esters leads to improved selectivity and better color.

Recent developments in alkanolamides have focused on improving the product quality in terms of color, odor, and ester content. Avoiding excess fatty acid in the system by a controlled addition of fatty acid with efficient mixing has been claimed to improve the purity of alkanolamides (31). However, others believe that a stepwise addition of the alkanolamine to fatty acid is beneficial in improving purity and color while reducing reaction times (32). Conducting the reaction in the presence of an inert gas or steam (33), or using a reducing agent comprising a mixture of alkali metal borohydride and alkali metal hydride (34) are claimed to improve both quality and odor. A product with reduced esteramide content is obtained when the reaction is run at 70–150°C at 10–400 Torr with a very specific amount of an alkali metal catalyst (35). Monoalkanolamides with low color, odor, and ester content can be made from fatty acid ester and monoethanolamine with an alkali metal catalyst and posttreating the product with water (36). Pretreatment of the alkanolamines with alkali metal hydroxide or alkoxide has been claimed to improve color (37). Novel alkanolamides, useful as thickeners, are obtained from the reaction of branched fatty acids with monoisopropanolamine (38).

Polyoxyalkylene amides are made either by alkoxylation of alkanolamides or by direct alkoxylation of amides using well-documented procedures (21). Monoethanolamides are typically solids but by alkoxylating with branched alkylene oxides such as propylene oxide liquid products with surfactant properties similar to DEA are obtained (39,40). The product distribution obtained when ethoxylating alkanolamides is impacted by esteramide impurities, increased levels of esteramide giving rise to increased amounts of polyglycol ethers in the product (17). Other by-product formation during the alkoxylation can be controlled by reducing the water content of the alkanolamide prior to alkoxylation, either by using a dehydrating agent such as a metal alkoxide (41), or by thermal processes (42).

**4.3. Sugar Amides.** The increased demand for biodegradable surfactants, particularly in the detergent industry, promoted the development of amide surfactants derived from sugars, notably glucamides and lactobionamides. Of these, glucamides are the most studied (17). Glucamides are prepared by the reductive amination of glucose, typically with methylamine to give the *N*-methylglucamine, followed by amidation with a fatty acid ester. The amidation step may be catalyzed by a variety of metal salts or aluminosilicates. Residual fatty acid can be reduced by reaction with a more reactive amine such as ethanolamine (43). Improvements in yield and quality are claimed if the glucamide is recovered from solution by crystallization (44). Amidation with akoxylated triglycerides has been claimed to provide a useful surfactant composition of *N*-methylglucamide and alkoxylated mono- and diglycerides (45), while a synergistic blend of *N*-methylglucamide and *N*-propylglucamide was prepared by blending the corresponding amines prior to the base-catalyzed amidation with a fatty acid ester (46). Lactobionamides are made by oxidation of lactose to lactobionic acid followed by amidation with an amine (47).

**4.4. Amidoamines.** The established process for making amidoamines is to react a fatty acid, ester, or triglyceride with a polyamine, usually without a catalyst, although several have been suggested (48). Common polyamines include ethylenediamine (EDA), diethylenetriamine (DETA), dipropylenetriamine (DPTA), aminoethylethanolamine (AEEA), and dimethylaminopropylamine

(DMAPA). The addition of fatty acid to DETA has the potential to proceed to give the 1,2-diamide or the 1,3-diamide, however, in the absence of solvent the reaction proceeds to give the 1,3-adduct in high yield. Amidoamines derived from DETA and AEEA cyclize at elevated temperatures, 200−300°C, to form imidazolines. The imidazolines tend to be unstable and care has to be exercised during

Table 4. **Fatty Amides, Producers, and Trade Names**

| Product category, trade name | Company | Web site |
|---|---|---|
| *Alkyl amides* | | |
| Armid | Akzo Nobel Surface Chemistry AB | www.surface.akzonobel.com |
| Petrac Vyn-Eze Addit. | Ferro Corp./Polymer Additives Divison | www.ferro.com |
| *Ethylene bis(stearamide)* | | |
| Alkamide STEDA | Rhodia Home, Personal Care, Industrial Ingreds. (HPCII), | www.rpsurfactants.com |
| Glycowax 765 | Lonza Inc. | www.lonza.com |
| Advawax | Rohm and Haas Co. | www.rohmhaas.com |
| Kemamide W-39 | Crompton Corp./Olefins & Styrenics | www.uniroyalchemical.com |
| *Amido amines* | | |
| Indulin QTS | Westvaco Corp., Chemical Division | www.westvaco.com |
| *Ethoxylated amides* | | |
| Schercoterge 140 | Scher Chemicals, Inc. | |
| Bermodol Amadol | Akzo Nobel Surface Chemistry AB | www.bermodol.com www.surface.akzonobel.com |
| *Alkanolamides* | | |
| Ablumide | Taiwan Surf. | www.taiwansurfactant.com.tw |
| Amidex | Chemron Corp. | www.chemron.com |
| Alkamide | Rhodia Home, Personal Care, Industrial Ingreds. (HPCII) | www.rpsurfactants.com |
| Mackamide | McIntyre | www.mcintyregroup.com |
| NINOL Manromid STEPANOL | Stepan Co Stepan UK Ltd. | www.stepan.com |
| Monamid | Uniqema | www.uniqema.com |
| Surfonamide Empilan | Huntsman Corp. | www.huntsman.com |
| Aminol Amidet | Kao Corp. | www.kao.co.jp |
| Calamide | Pilot Chemical Co. | www.pilotchemical.com |
| Chimipal Rolamid | Cesalpinia Chemicals SpA | www.cesalpinia.com |
| Comperlan | Cognis Deutschland GmbH | www.es.cognis.com |
| Witcamide | Akzo Nobel Surface Chemistry AB | www.surface.akzonobel.com |
| Foamid | Alzo International Inc. | www.alzointernational.com |
| Incromide | Croda Chemicals (SA) (Pty) Ltd | www.croda.com |
| Mazamide. | BASF Corp./Performance Chemicals | www.basf.com/businesses/chemicals/performance |

*Source: Industrial Surfactants Electronic Handbook*, 2002 ed.

manufacture and storage to minimize color degradation and hydrolysis. Hydrolysis of imidazolines can give a mixture of 1,2- and 1,3-amidoamines (49). The hydrolysis of imidazolines in the presence of metal salts and sodium borohydride has been described for making amidoamines of good color (50). Amidoamines with reduced odor and irritation properties can be obtained by using thin-film distillation or reverse osmosis [] to remove impurities (51,52). The manufacture of amidoamines from volatile amines like DMAPA often requires the use of an excess of the amine. Conducting the reaction under pressure with periodic venting to remove the water reduces the need for excess reagent (53). Alternatively, the reactor can be fitted with a membrane device to allow for continuous removal of the water (54).

## 5. Economic Aspects

Several large chemical producers make alkyl amides and derivatives today. In Table 4, typical brand names for alkyl amides, alkanol amides, amido amines, and alkyl bis(stearamides) and the companies producing them are listed together with the web addresses. Extensive product information can be found on the web sites and it is unneccessary to give more detailed information in this article. Approximate volumes for alkanolamides are estimated to be 90,000 tons/year for 2003 by Colin A. Houston & Associates, Inc.

## 6. Analytical Methods

Amides can be titrated directly by perchloric acid in a nonaqueous solvent (52,53) and by potentiometric titration (54), which gives the sum of amide and amine salts. Infrared (ir) spectroscopy has been used to characterize fatty acid amides (55). Mass spectroscopy (ms) has been able to indicate the position of the unsaturation in unsaturated fatty amides (56).

Alkyl glucamides have been analyzed by liquid chromatography coupled with ms with electrospray ionization (I) and fatty acid amides were separated and determined as trimethylsilyl derivatives by gas chromatography (gc) with mass spectrometric detection (II). Configurational and conformational nuclear magnetic resonance (nmr) analysis of sugar amides have been described (III), which also is a generally applicable technique to characterize fatty acid amides.

Typical specifications of some primary fatty acid amides and properties of bis(amides) are shown in Tables 5 and 6.

## 7. Health and Safety Factors

### 7.1. Environmental Properties.

Products contributing to sustainable development are becoming more and more important. The alkyl amides are derived directly from fatty acids that come from renewable sources and are thus seen as an attractive surfactant type (17). The biodegradability of some representative structures is shown in Table 7. Most of the amide-based

Table 5. **Amide Specifications**[a]

| Primary amide | CAS Registry Number | Iodine number[b] | Fatty acid max% | Mp, °C | Gardner color[b] |
|---|---|---|---|---|---|
| coco fatty amide | [61789-19-3] | 10 | 4.0 | 85 min | 10 |
| hydrogenated tallow amide | [61790-31-6] | 5 | 5.0 | 98–103 | 7 |
| stearamide | [124-26-5] | 95[c] | 3.5 | 68 min | 7 |
| oleamide | [361-02-0] | 2 | 5.0 | 99–109 | 7 |

[a] Amide, 90% minimum.
[b] Maximum.
[c] Minimum = 80.

products that are sold in this area are considered to be easily biodegradable. Their aquatic toxicity is also rather low, with a fish toxicity $LC_{50}$ value of 1–10 mg/L or above.

The positive environmental profile makes them a good alternative to the nonyl phenol ethoxylates as emulsifiers or dispersants. Their structure with delocalized $\pi$-electrons over the amide function is similar to the phenol ring with its aromatic structure. This in combination with an alkyl chain-containing conjugated unsaturation affords effective dispersants for pigments, see, eg, the Bermodol series from Akzo Nobel.

### 7.2. Nitrosamines in Alkanol Amides.

Cosmetics are controlled in the EU by Council Directive 76/768/EEC and its subsequent amendments and adaptations. The 15th adaptation, Council Directive 92/86/EEC was implemented in many EU states in the mid 1990s, eg, in the United Kingdom by the Cosmetic Products (Safety) (Amendment) Regulations of 1993. The 15th adaptation includes certain requirements in respect of fatty acid dialkanolamides, the most commonly used in cosmetics being diethanolamides. The Directive specifies a maximum 50 ppb level of *N*-nitrosodiethanolamine, commonly referred to as "NDELA", a maximum of 5% free diethanolamine in fatty acid diethanolamides and a maximum 0.5% free diethanolamine in formulated products containing them. The directive did not provide or refer to any analytical procedures for the determination of ppb levels of NDELA in fatty acid diethanolamides,

Table 6. **Substituted Amide Properties**

| Substituted amides | CAS Registry Number | Molecular formula | Melting range, °C | Flash point[a], °C | Gardner color |
|---|---|---|---|---|---|
| ethylenebis-stearamide (EBS) | [110-30-5] | $C_{38}H_{76}N_2O_2$ | 140–145 | 304 | 3 |
| methylenebis-stearamide (MBS) | [109-23-9] | $C_{37}H_{74}N_2O_2$ | 135–140 | 260 | 5 |
| oleyl stearamide | [b] | $C_{36}H_{71}NO$ | 70–75 | 260 | 3 |
| stearyl stearamide | [13276-08-9] | $C_{36}H_{73}NO$ | 92–95 | 246 | 4 |

[a] Tag closed cup.
[b] Not available.

Table 7. **CAS Registry Numbers, EINECS/ELINCS, Physical, and Environmental Data**

| Compounds, INCI | CAS Registry Number | EINECS/ ELINCS | Physical form | Melting point, °C | Biodegradable | Fish toxicity 96 h $LC_{50}$; mg/L |
|---|---|---|---|---|---|---|
| lauramide MEA | [142-78-9] | 205-560-1 | cream wax | 85 | | |
| cocamide MEA | [68140-0-1] | 268-770-2 | flakes to solid | 70–74 | readily | 10–100 |
| lauramide DEA | [120-40-1] | 204-393-1 | solid | 39 | | |
| cocamide DEA | [8051-30-7] | 263-163-9 | liquid | | readily | 1–10 |
| oleamide DEA | [93-83-4] | 202-281-7 | liquid | | | 1–10 |
| tallamide DEA | [68153-57-1] | 268-949-5 | liquid | | | |
| soyamide DEA | [68425-47-8] | 270-355-6 | liquid | | | |
| erucamide | [112-84-5] | 204-009-2 | waxy beads | 75–80 | Not readily | |
| oleamide | [301-20-0] | 206-103-9 | waxy beads or powder | 72 | readily | |
| stearamide | [124-26-5] | 204-693-2 | flakes | 98–109 | | |
| hydrogenated tallow amide | [61790-31-6] | 263-123-0 | flakes | 98–103 | readily | |
| coco monoethanol amide ethoxylate | [68425-44-5] | | | | readily | 1–10 |
| cocamidopropyl dimethylamine | [68140-01-2] | 268-771-8 | soft solid to liquid | | | |
| ethylene distearamide | [110-30-5] | 203-755-6 | solid | 140–145 | | |

*Source: Industrial Surfactants Electronic Handbook*, 2002 ed., environmental data from company product information.

diethanolamine raw materials or formulated products containing fatty acid diethanolamides.

*N*-nitroso derivatives, including NDELA, $(HO{-}CH_2{-}CH_2)_2N{-}NO$, are well-known carcinogens (57,58). In the case of NDELA liver and nasal tumors are produced. The formation of potentially carcinogenic *N*-nitroso products has been recorded for virtually every kind of amino substrate, but the most extensive reactions relate to secondary amines and secondary *N*-acyl compounds (59). The nitrosation of secondary amines leads, of course, directly to *N*-nitrosamines (eq. 1) and under appropriate conditions these reactions can be both rapid and extensive (59).

$$R_2NH + NOX \rightarrow R_2NNO + HX \qquad (2)$$

Further, the *N*-nitrosamine products as well as being carcinogenic are usually stable and difficult to destroy (60). The principle sources of nitrosating agents are either $HNO_2$(nitrite salts) or nitrogen oxide ($NO_x$) pollutants (59). Exhaust fumes from a stacker truck passing an open drum of a fatty acid diethanolamide is sufficient to produce ppb levels of NDELA. The formation of *N*-nitrosamine in surfactants and related products has been extensively studied and reported by Challis and co-workers at the United Kingdom's Open University (61,62).

It is recommended that fatty acid DEA producers ensure DEA raw material suppliers provide DEA with a minimum level of NDELA, inorganic nitrite and organic nitrite esters and that DEA is carefully stored and transported to avoid NDELA formation. Fatty acid DEAs should not be stored long term at elevated temperature in the presence of air, likewise during blending by a formulator.

Commercial test houses in the United Kingdom, Germany, and the United States were found to be using variations based on the Eisenbrand-Preussmar cleavage reaction (63) and utilising headspace analysis. The levels of NDELA being measured are close to the limit of detection of these methods and explain the variations in results obtained from different test houses.

The anticipated difficulties with DEA-based amides has also initiated work to substitute them with combinations of other amides. Since MEA amides are less soluble they can only partly substitute the DEA based ones. A suggestion has been to combine them with suitable betaines (64).

## 8. Uses

The many applications of fatty acid amides and their ethoxylated derivatives are determined by their functional properties that include

Foam boosting and stabilization
Emulsification
Detergency
Viscosity modification
Lubricity

Antistatic properties
Corrosion inhibition
Wetting, etc

Alkanolamides enhance the foaming properties of detergents, personal care products, hard surface cleaners, hand cleaning gels and many general purpose cleaners by providing a more stable, finer foam. This is often accompanied by an increase in viscosity of the formulation by inclusion of alkanolamide; the nonethoxylated derivatives being the most effective. Enhanced detergency may also be observed. Their ability to emulsify a range of oils, waxes, solvents, and fuels affords application in metal working fluids/cutting oils, lubricants, fuels, textile auxiliaries, rust inhibitors, and plant protection formulations. Their antistatic properties are utilized to advantage in a range of plastics and polymers as well as in additives for fabric softener formulations.

The performance of alkanolamides will also depend on the choice of hydrophobe and their overall composition. Ethanolamines, such as DEA or monoisopropanol amine (MIPA) may be reacted 1:1 or 2:1 with fatty acids. Thus in a 2:1 fatty acid diethanolamide there will be an excess of DEA which may optionally be neutralized with another fatty acid. Wolff Kritchevsky in 1937 observed that reaction between 2 mol of DEA and 1 mol of fatty acid led to a water soluble product with good surface activity, whereas the 1:1 DEA/fatty acid reaction led to water insoluble products and high ester amide levels. In the 2:1 reaction of, eg, DEA and lauric acid, at 150–180°C with removal of water of condensation, $<5\%$ free fatty acid remains. In later years, analysis showed the 2:1 reaction products to be complex mixtures (65), including fatty amide (50–60%), free diethanolamine (20–30%), fatty amine soap (3–5%), ester amide (5–10%), and amine ester (5–10%).

In 1949, E. M. Meade (7) described the preparation of the so-called “superamides” with fatty alkanolamide contents up to 95%. They are prepared in a two-stage reaction, first by producing the fatty acid methyl ester from reaction of 3 mol of methanol with a triglyceride (at 80–95°C) with separation and removal of glycerol followed by reaction of the methyl ester with equimolar quantities of alkanolamine at 105°C using sodium methylate catalyst. The lower temperature reaction than the Kritchevsky process ensures far less by-products and improved product colors. Superamides may also be prepared directly from fats and oils, but in such cases the glycerol (8–10%) will remain in the product. Typical composition for a fatty acid DEA would be

| | % Component | |
|---|---|---|
| | Kritchevsky | “Superamide” |
| fatty acid diethanolamide | 60 | 90 |
| diethanolamine | 23 | 7 |
| fatty acid | 5 | 0.5 |
| ester amines/amides | 12 | 2.5 |

The higher fatty amide content of the superamides means that they are not as water soluble, but are readily solubilized by other surfactants and fatty acid additions to produce soap. The Kritchevsky amides are generally better wetters and detergents but poorer foam stabilisers. The superamides have excellent foam stabilizing properties and increase the viscosity of many anionic-based cleaning and personal care compositions. The superamides are also preferred in personal care products because of their higher purity and lower by product content.

Alkanolamides being derived from natural oils and fats, can vary in price depending on climatic conditions and harvest yields. Severe weather conditions in South East Asia, eg, can dramatically reduce the supply of coconut oil. Hence, compared to many petrochemical derived nonionic surfactants, their long-term price is less predictable. In some more price sensitive areas, such as detergent and personal care products, usage has diminished as a consequence. Their continued use is in areas where combinations of their unique properties (as listed above) are required and alternatives not readily available.

The following application sectors are considered in more detail.

### 8.1. Detergents and Personal Care Products.

It is reasonable to consider the use of alkanolamides together in all aspects of cleaning, whether in household detergents, personal care or industrial and institutional cleaning products, as their inherent properties of detergency, enhancement of foam properties and viscosity modification apply to all these sectors (66,67). Anionic surfactants including alkylbenzene sulfonates, fatty alcohol sulfates, and alcohol ether (2 or 3 mol EO) sulfates are frequently the prime component of a formulation selected to impart detergency. Hence, it is the interaction between these surfactants and the alkanolamides that is the key to enhancement of formulation properties. Table 8 illustrates the effect of a coconut diethanolamide on the foam properties of various anionic surfactants.

Ether sulfates are already high foamers and addition of alkanolamide is most marked in the case of alkyl sulfates, particularly when used in personal care products.

Table 8. **Effect of Coconut Diethanolamide on the Foaming of Anionic Surfactants**[a]

| | | Foam height (cm) at 45°C in hard water | | | |
|---|---|---|---|---|---|
| | | 100% Anionic | | 80% Anionic/20% diethanolamide | |
| Anionic surfactant | Active concentration, % | 0 min | 5 min | 0 min | 5 min |
| triethanolamine lauryl sulfate | 0.02 | 38 | 15 | 110 | 90 |
| monoethanolamine lauryl sulfate | 0.02 | 30 | 12 | 105 | 100 |
| sodium lauryl ether (3 EO) sulfate | 0.02 | 160 | 150 | 150 | 150 |
| sodium lauryl sulfate | 0.02 | 55 | 50 | 135 | 125 |

[a] See Ref. (67).

Table 9. **Plate Washing Test for Alkylaryl Sulfonate/Coconut Diethanolamide Blends**[a]

| Alkyl aryl sulfonate, % active | Coconut, diethanolamide % | Number of plates washed to foam end-point: Distilled water | 10 water hardness | 30 water hardness |
|---|---|---|---|---|
| 100 | 0 | 0 | 8 | 11 |
| 80 | 20 | 4 | 11 | 12 |
| 70 | 30 | 5 | 12 | 15 |
| 60 | 40 | 6 | 12 | 15 |

[a] See Ref. (67).

Alkyl aryl sulfonates are the base detergent used in washing up liquids and many general purpose cleaners. Although high foaming they generate a rather coarse, open structured foam and secondary surfactants, such as alkanolamides, fatty alcohol ether sulfates, or betaines are used to enrich the foam and enhance detergency. Table 9 illustrates partial substitution of an alkyl aryl sulfonate by a coconut DEA in a standard plate washing test for the evaluation of washing-up liquids. Here plates soiled with a standard fat-based soil are washed in 0.25-g/L active solutions of surfactant at 40°C until the surface foam disappears.

Both the Kritchevsky and superamides exhibit detergency in their own right, but they also exhibit a synergistic effect with other surfactants. This finding is illustrated in Table 10, where scouring tests on wool and cotton with a sodium alkyl aryl sulfonate alone and blended 3:1 in an alkyl aryl sulfonate/ coconut DEA blend are compared, the latter affording up to 30% improvement in fabric brightness.

Similar improvements in detergency can also be shown with nonionic/ alkanolamide blends.

Formulation of alkanolamides in both highly alkaline and acidic cleaning systems can be restricted by their limited hydrolytic stability. However, as illustrated in Table 11, some derivatives are more stable than others.

Table 11 clearly shows that the hydrolytic stability is in decreasing order lauric monoethanolamide ethoxylates > lauric monoisopropanolamide > lauric monoethanolamide > lauric diethanolamide. The monoalkanolamides have

Table 10. **Fabric Brightness Results from Alkyl Aryl Sulfonate/Coconut Diethanolamide Scouring Systems**[a]

| Concentration, g/L | Brightness: Sodium alkyl aryl sulfonate, Wool | Sodium alkyl aryl sulfonate, Cotton | 75 parts alkyl aryl sulfonate/25 parts high active coconut DEA, Wool | 75 parts alkyl aryl sulfonate/25 parts high active coconut DEA, Cotton |
|---|---|---|---|---|
| 0.75 | 38 | 39 | 51 | 39 |
| 1.0 | 44 | 42 | 58 | 43 |
| 1.25 | 48 | 45 | 61 | 51 |
| 1.5 | 50 | 47 | 64 | 52 |

[a] See Ref. 67.

Table 11. **Hydrolytic Stability of Alkanolamide Derivatives (% Breakdown after 2-h reflux at 100°C)**[a]

| | Sulfuric acid hydrolysis | | Caustic soda saponification | |
|---|---|---|---|---|
| Alkanolamide | 0.1 *N*, pH 1.2 | 1.0 *N*, pH 0.4 | 0.1 *N*, pH 12.4 | 1.0 *N*, pH 12.9 |
| lauric diethanolamide | 3.2 | 88.2 | 33.6 | 94.1 |
| lauric isopropanolamide | 4.3 | 83.7 | 0.6 | 1.8 |
| lauric monoethanol-amide | 9.5 | 71.9 | 2.7 | 22.2 |
| lauric monoethanol-amide + 2 EO | 2.8 | 22.5 | 0.0 | 6.2 |
| lauric monoethanol-amide + 5 EO | 0.0 | 6.8 | 0.0 | 0.0 |

[a] See Ref. 67.

better hydrolytic stability than the corresponding DEAs, with monoisopropanolamides being more stable than the monoethanolamides, most likely due to steric hindrance. Hydrolytic stability is further increased when the monalkanolamides are ethoxylated. The 5-mol ethoxylate of lauric monoethanolamide is extremely stable and hence suitable for both heavy duty acidic and alkaline cleaners.

The degree of ethoxylation, of, eg, lauric monoethanolamide, also influences the physical form, solubility, foaming, and wetting properties. Transition from 3 to 5 mol EO changes physical form from solid through paste to a liquid, with a minimum melting point at 5-6EO, optimum wetting at 4EO and highest foaming (Ross & Miles test) at 4-5EO.

**8.2. Personal Care.** The prime use of alkanolamides, most commonly diethanolamide superamides, is as foam boosters and stabilisers and to increase the viscosity of shampoo and bath products.

Table 12 illustrates the ability of alkanolamides to boost the viscosity of typical anionic surfactants used to formulate personal care products, namely, lauryl and lauryl ether sulfates. Not all anionics respond in this way, as illustrated by the alpha-olefin sulfonate. However, in the latter case small additions of sodium chloride will increase viscosity.

Table 12. **Viscosity Enhancement of Anionic Surfactant Solutions**

| Anionic surfactant, 15% solution | Viscosity[a] | | | |
|---|---|---|---|---|
| | Oleamide MIPA (1:1) | | | |
| | 1% | 3% | 5% | 5% + 0.75% NaCl |
| sodium lauryl ether (3 EO) sulfate | 3.5 | 34 | 2650 | |
| sodium lauryl sulfate | 3 | 18 | 2600 | |
| sodium $C_{14,16}$-alpha olefin sulfonate | 2 | 4.5 | 45 | 2500 |

[a] Brookfield viscometer model DVIII+, spindle #21 (1 rpm) at 25°C.

Table 13. **Ross & Miles Foam Heights for Anionic Surfactants Containing Alkanolamide**

| Blend | | Foam height (mm) | |
|---|---|---|---|
| anionic | :oleamide MIPA | initial | after 5 min |
| sodium lauryl ether sulfate | :oleamide MIPA | 155 | 154 |
| sodium lauryl sulfate | :oleamide MIPA | 150 | 150 |
| sodium $C_{14,16}$ alpha olefin sulfonate | :oleamide MIPA | 168 | 166 |

Ross and Miles foaming tests of 0.5% solutions of the blends in Table 12 afforded excellent foam stability, even at the 1% addition level of the oleamide MIPA, as shown in Table 13.

Anionic derivatives such as sulfated monoalkanolamide ethoxylates and monoester sulfosuccinates may also be used as major components in such products, the latter in part to being milder to skin and eyes compared to the frequently used alcohol ether sulfates. More specialized applications include lipsticks (68), medicated face washes (69) and a range of applications for the polyoxyethylated amides (70–73). Propoxylated $C_{10}$–$C_{18}$ fatty acid alkanolamides have also found application as foam stabilizers and thickeners in shampoos (74). Permanent wave setting lotions are frequently based on quaternary ammonium salts and alkanolamides (75).

**8.3. Detergents and Cleaners.** In the household sector, laundry detergents have been formulated based on combinations of polyoxyethylated amides with soaps (76), alkyl sulfates (77), fatty alcohol ethoxylates (78) and in combination with anionics and enzyme lipase (79–80).

*N*-Methyl lauric acid ethanolamide and *N*-Methyl cocoethanolamides have been found to enhance the stability of enzymes in liquid detergents (81) and may be incorporated in detergent tables without loss of strength and disintegration rate (82). They also enhance the foam profile of many anionic surfactants ($C_{12}$ methyl ester sulfonates, $C_{12}$ alkyl and alkyl ether phosphates, etc) (83) as well as mixtures of primary and secondary alcohol ethoxylates (84).

Polyoxyethylated rapeseed oil monoethanolamide + 5-7EO has also been formulated into low-foam laundry detergents (85). Ethoxylated oleic acid amides find application as textile softeners (86) and in fabric conditioners to improve antistatic properties (87–88).

Industrial cleaning and degreasing compositions containing various alkanolamides are used in many applications, including degreasing of metallic surfaces prior to painting or coating (89–92), degreasing to reduce corrosion (93), removal of deposits (94) or hydrocarbons from metallic surfaces (95), and removal and emulsification of many oily soils (96).

Ethoxylated amides in combination with glycol ethers are effective cleaners for glass and ceramic surfaces (97). These derivatives may be used in disinfectant-cleaner compositions in combination with quaternary ammonium compounds (eg, alkyltrimethylammonium chloride) for use in, say, the dairy industry (98–99). The polyoxyethylated coconut oil analogue when used in disinfectant-cleaners affords reduced eye irritation (100). Combinations of alkyl polyglucoside and polyoxyalkylated amide may be used in a variety of cleaning compositions for wool, dishwashing, etc.

Alkanolamides may be used as cosurfactants with quaternary ammonium compounds in the formulation of fabric conditioners and softeners (101,102). More recently, *N*-alkylglucamides have been used as cosurfactants in the formulation of detergents, syndet bars, and cosmetics because of their mildness and, like APGs, their synergistic effects with other surfactants (103–106, 111).

Alkanolamides continue to be used as minor components (typically 5% by weight or less) or as optional cosurfactants in numerous detergent and personal care product patents, too many to list here.

**8.4. Textile Processing (67).** Outside the disinfectant and personal care sector, textile auxiliaries and fiber lubricants represents a major application sector for fatty acid amides. Coconut diethanolamide, eg, may be used as an antimigration agent in the dyeing of polyesters with dispersed dyes and as a setting agent (sometimes referred to as an antifrosting agent) in the dyeing of polyamides and cellulosics.

Alkanolamides are excellent emulsifiers for mineral oils and are used as coemulsifiers in coning oils to improve the shock emulsion and the scourability of the coning oil, as well as imparting antistatic properties. A typical formulation for a mineral oil-based coning oil would be

| | |
|---|---|
| 200 s mineral oil | 90 parts by weight (%) |
| fatty alcohol ethoxylate | 4 |
| PEG oleate | 4 |
| coconut diethanolamide | 2 |

Another example of textile auxiliary use is application in textile oversprays, where the alkanolamide assists wetting and spreading, as well as affording antistatic protection. A typical overspray would consist of

| | |
|---|---|
| coconut diethanolamide | 5–10 parts by weight (5) |
| PEG 400 monolaurate | 90–95 |

Fatty amides, mainly stearamide, are used in the production of water repellant fabrics (Zelan, Velan types) by reaction with formaldehyde, pyridine, and hydrochloric acid to produce a quaternary salt.

**8.5. Antistatic Agents for Plastics and Polymers.** Coconut diethanolamide is used widely as an antistatic agent in plastics, eg, in polyethylene film for food packaging and rigid Poly vinyl chloride (PVC). It has been employed in combination with metallic salts as an antistat for polystyrene and in impact resistant rubber–polystyrene blends. Lauric monoethanolamide is employed as an antistat for polyolefins, polystyrene, and acrylonitrile–butadiene–styrene (ABS) (107).

Alkylene bis (saturated higher fatty acid amides) are effective antistatic agents for films, sheets or moldings based on ethylene–styrene copolymers, as well as imparting antiblocking properties (108).

### 8.6. Metal Working Fluids / Cutting Oils.

Alkanolamides are used in the metal working industry as emulsifiers for mineral oils, but they also provide lubricant properties and good corrosion resistance. Oil soluble types such as groundnut oil derived alkanolamides are particularly effective both in mineral oil-based and semisynthetic cutting oils (109).

### 8.7. Lubricants and Antiblock Agents for Plastics and Polymers.

Alkanolamides are used as antiblock and mould release agents, lubricants, and slip agents for plastics and polymers (110). Applications include low density polyethylene (LDPE), polypropylene and linear low density polyethylene (LLDPE) polymers, especially in polymer films, incorporated at 0.05–0.4% levels. They have also been used in polyolefins, vinyl, and acrylic polymers and polystyrene as antiblock additives. Oleamide, and to a lesser extent, stearamide and erucamide are used as antislip and antiblock additives (via masterbatches) for polyethylene film used for packaging. Stearamide is also used as rubber mould release agent and, along with oleamide, as an ink additive to prevent printed pages sticking together after printing and stacking.

Ethylene bis(stearamide) is used as an internal lubricant in ABS and PVC plastics and is used as a lubricant in the manufacture of extrusion grade polyethylene.

### 8.8. Intermediates.

Ethoxylated fatty acid alkanolamides are used as intermediates for the production of anionic surfactants including amide ether sulfates and monoester sulfosuccinates.

Continuous, partial $SO_3$ sulfation of lauryl monoethanolamide +2EO, eg, can yield varying ratios of sodium lauryl monoethanolamide ether (2EO) sulfate / lauryl monethanolamide + 2EO blends suitable for use as a shampoo or bath product base. Here in a single product there is a combination of prime detergent component, foam booster–stabilizer, and viscosity modifier combined with low skin irritancy.

Likewise, conversion of this same ethoxylated alkanolamide intermediate to a monoester sulfosuccinate, by reaction first with maleic anhydride to produce a half ester maleate followed by reaction with sodium bisulfite, affords a mild anionic component for personal care applications. The lauric monoethanolamide ether (2EO) sulfosuccinate exhibits milder skin and eye irritation characteristics when compared to $C_{12}$-$C_{14}$ lauryl ether (2 or 3 mol EO) sulfates widely used in shampoos, shower, and bath products. This half ester also finds application in carpet shampoos.

The monoester sulfosuccinate derived from an undecylenic fatty acid amide is unique, in as much as it possesses antidandruff properties, and hence may be used in "medicated" shampoos.

Bis(amides), eg, *N*,*N*′-ethylenebis(stearamide), may be ethoxylated and then acrylated to produce acrylate intermediates for radiation ultraviolet(uv) or (EB) curable coatings.

Fatty amide ethoxylate phosphate esters may be used in conveyor lubricants (111) for the beverage industry.

Quaternary ammonium compounds containing fatty acid amido moieties are used in fabric finishing compositions (112) cosmetic formulations (113) and in nonwovens to improve long-term hydrophilicity (114).

**8.9. Miscellaneous Applications.** The claimed uses of alkanolamides and derivatives are many and varied but not necessarily all fully commercialized. Some of those applications where alkanolamide usage is established include the following:

Alkyd resin emulsions are unsaturated fatty acid amide ethoxylates, based on soybean- and linseed-based hydrophobes (115) or *N*-alkyl glucamides (116) may be used to prepare alkyd emulsions.

Asphalt compositions to prevent phase separation (117) or as release agents for paving equipment (118). Fat liquoring agents for leather (119).

"Spreader-stickers" in crop protection formulations (120).

Defoamer components, especially *N*, *N′*-ethylene bis(stearamide).

Demulsifiers for water-in-oil emulsions.

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INGEGÄRD JOHANSSON
Akzo Nobel Surface Chemistry AB

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