Beta-Amines

MILES R. McCORKLE, PAUL L. DuBROW, and BYRON E. MARSH,
Armour Industrial Chemical Company, Chicago, Ill.

Abstract

Petroleum-based olefins are the source of a new series of alkylated amines. These constitute a series of more liquid, more soluble secondary alkyl primary amines and assorted cationic derivatives. Isomer distribution, physical property and application data are presented.

"Beta-Amines"

LONG-CHAIN AMINES have been articles of commerce since the early 'forties. They now command a mass market as chemical intermediates and as specialty chemicals, entering into all phases of a broad spectrum of industrial and consumer markets and applications.

These materials are manufactured and sold by several companies, including General Mills, Archer-Daniels-Midland, Foremost, HumKo, and Armour Industrial Chemical Company, who first introduced these products as commercial chemicals.

Another Series of Amine Products

With the advent of petroleum-based olefin hydrocarbons, a related series of alkylated amines became possible and practical. This, combined with the capability of a new continuous manufacturing process, allowed Armour to introduce them as development chemicals in 1965.

Defined as "*beta*-amines," the parent compounds are actually secondary alkyl primary amines. They offer new approaches and alternatives for solving many long-standing problems of the chemical industry.

The basic structure, as distinguished from the *alpha*-amines, is represented in Fig. 1:

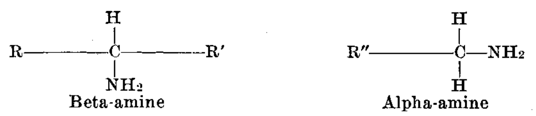

FIG. 1. Basic structure.

R′ can be methyl, ethyl, propyl, etc. The bulk of the substituent amino grouping is actually in the 2 + 3 positions (R′ is methyl and ethyl), but other positional isomers do occur. The hydrocarbon moiety, although composed of straight chains, therefore contains a secondary carbon atom.

R can consist of even carbon chains alone or of even plus odd chains, with chain lengths running from C_6 to C_{21}. A typical analysis of products now being offered is shown in Table I.

Reproducibility from batch to batch is excellent and analysis by thin-layer and gas chromatography is easily accomplished.

The secondary alkyl configuration, plus the large number of chain and positional isomers, lends to liquid characteristics and solubility properties unique in saturated compounds. Melting points are quite low and solubility in most common solvents is excellent. The following data shown in Table II, comparing the *beta* primary amines, with the corresponding *alpha*-amines, are typical.

All the *beta* primary amines are soluble to the extent of 2% in water and are completely soluble at 77F in acetone, isopropyl alcohol, ethanol, ethylene glycol, fuel oil, kerosene, mineral spirits and mineral oil.

Starting with the primary amines as the parent compounds, a complete line of derivatives is currently available. These include the following types (Fig. 2):

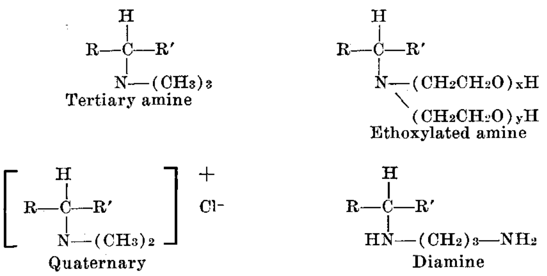

FIG. 2. Types of derivatives.

Some differences in reactivity between the *beta*- and *alpha*-amines do exist, which is to be expected from the higher degree of hindrance of the *beta* structure. Heavy substituent bulking around the nitrogen atom is difficult to obtain. Symmetrical secondary amines, for example, containing greater than seven carbons in the chains are difficult to prepare: quaternization of the ethoxylated amines cannot be carried out completely. Most other reactions go smoothly.

The *beta*-amines, as cationic chemicals, ionize normally, so that the segment containing the functional group has the long hydrocarbon chain or chains attached to it and is positively charged. Monomolecular film formation becomes feasible and easily applied from solution. The natural advantages of cationics are therefore inherent in these products, namely, the ability to form quick breaking oil/water emulsions and directed attraction to and adsorption onto negatively charged surfaces. These include plastics, metals, stone aggregate, etc. Modification of such surfaces by the adsorbed chemical contributes properties not generally exhibited by these substrates.

For example, a nonconducting polymer can be made static-free; difficult-to-coat filler materials can be asphalt- or oil-treated; metals can be given corrosion-inhibiting films; selective flotation separation of potash and phosphates becomes economically feasible and fabrics can be treated to supply softness.

How do the *beta*-amines differ from the *alpha*-amines from an applications viewpoint?

A marked effect has been noted in the flotation upgrading of low grade nonmagnetic ores. Increased selectivity allows more complete removal of contaminating silica and, consequently, greater recovery of purer iron for pelletizing and conversion in the modern steel furnace.

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TABLE I
Armeen L-15

Carbon chain length	% Present
14	1
15	18
16	17
17	16
18	16
19	14
20	13
21	5

TABLE II
Melting Points

Beta-amines	mp (°F)	Primary amines	mp (°F)
Armeen L-17	−162	Octyl amine	+10
Armeen L-11	−20	Coco amine	+55
Armeen L-15	+50	Hydrogenated tallow amine	+125

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NOVEL GEL EMULSIONS. T. G. Kaufman and R. J. Tkaczuk (Drew Chem. Corp.). *U.S. 3,341,465.* A clear gel emulsion consists essentially of 10–40% by wt. of at least one ester having the following general formula: R_1COOR_2, where R_1 is a C_8–C_{24} fatty acid residue and R_2 is a C_1–C_4 lower alkyl radical; 20 80% water; 3–15% of at least one alkylolamide having the general formula: $R_3CONR_4R_5$, where R_3 is a C_8–C_{14} fatty acid residue, R_4 is either hydrogen or a C_1–C_4 monohydric alkyl radical and R_5 is a C_1–C_4 monohydric alkyl radical; 1–25% of a polyoxyethylene surfactant having one of the two following general formulas: $R_6O(C_2H_4O)_nH$ and $R_6COO(C_2H_4O)_nH$, where R_6 is a C_8–C_{24} aliphatic radical and n is an integer between 2 and 40; and 1 8% of a partial oleic acid ester of a polyglycerol.

DETERGENT COMPOSITION. G. G. Corey and E. J. Kennedy (Colgate-Palmolive Co.). *U.S. 3,342,739.* A clear hard surface cleaning composition characterized by high flash foam during dilution and low residual foam at use concentration consists essentially of about one part of a polyethenoxy nonionic detergent, 0.4–3.0 parts of an ethoxylated fatty acid alkylolamide condensate with 10–14 C atoms in the acyl group and 0.05–0.3 parts of C_{10}-C_{14} fatty acids, and the remainder water. This mixture of ingredients, having a pH of 6.9–7.5, forms a clear solution with a viscosity between 125 and 1,000 centipoises.

WINDOW CLEANER. J. E. Kazmierczak, A. B. Herrick and A. Carlo (Armour & Co.). *U.S. 3,342,740.* A window cleaner composition consists essentially of 0.1 to 2.5% by wt. of a water soluble silicone glycol copolymer, 10–30% of a C_1 to C_4 alcoholic solvent, 0.1–0.5% of a nonionic surfactant, and the rest water.

THIOETHER SULFONATES. E. P. Antoniades (Chevron Research Co.). *U.S. 3,342,741.* A detergent composition is claimed, consisting essentially of 10 to 40%, by wt., of a water soluble guanidinium 2-thioalkoxyethanesulfonate having 8–20 C atoms in the alkyl groups, and 60–90% of water soluble inorganic detergency builders.

PROCESS FOR PREPARING DETERGENT TABLETS. E. D. Wilcox, Jr. (Lever Bros. Co.). *U.S. 3,344,076.* An improvement is claimed in the process of preparing strong, abrasion-resistant, fast dissolving, low sudsing detergent tablets by blending together a mixture of (1) 4–13% by wt. of a synthetic nonionic detergent, and (2) 20–95% of a mixture of Form I and Form II pentasodium tripolyphosphate, and compressing the resulting granular mixture into tablets. The improvement claimed consists in chilling the compressed tablets to 10–45F for a period of 5 to 20 minutes to accelerate their strengthening.

ORGANIC PHOSPHORUS COMPOUNDS. R. R. Irani and K. Moedritzer (Monsanto Co.). *U.S. 3,344,077.* A detergent composition is described, consisting of at least 5% of a water soluble inorganic alkaline builder or of an organic sequestering builder, and at least 10% of an organo-amine-di-alkylene phosphorus compound having the formula $(XO)_2POCR_1R_2NRCR_3R_4PO(OX)_2$, where R is selected from a group consisting of C_4 C_{30} aliphatic hydrocarbyl groups, C_4–C_6 alicyclic groups, C_6-C_{10} aryl groups, C_7–C_{30} alkaryl groups, C_7–C_{30} aralkyl groups; R_1, R_2, R_3 and R_4 are selected from the class consisting of hydrogen, C_1–C_{30} aliphatic hydrocarbyl groups, C_4–C_6 alicyclic groups, C_6–C_{10} aryl groups, C_7–C_{30} alkaryl groups and C_7 C_{30} aralkyl groups; and X is selected from the group consisting of hydrogen, alkali metal, alkaline earth metal, ammonium and lower molecular weight alkyl, alkylene and alkanol amines.

COATING COMPOSITIONS COMPRISING ALKYLOLATED ACRYLAMIDE-ETHER VINYL MONOMER-DRYING OIL INTERPOLYMER. H. H. Flegenheimer (Celanese Coatings Co.). *U.S. 3,344,097.* A coating composition consists of an interpolymer of (1) an N-alkoxymethyl acrylamide having less than 10 C atoms in its alkoxy portion, (2) 5–60% by wt. of a material selected from the group consisting of natural drying and semidrying oils, reaction product of dehydrated castor oil and pentaerythritol, linseed fatty acid ester of pentaerythritol, cyclopentadiene modified linseed oil and styrenated natural drying oil, and (3) at least one other vinyl monomer copolymerizable with (1) and (2).

DRYCLEANING PROCESS IN WHICH GARMENTS ARE INITIALLY CONTACTED WITH AN ORGANIC SOLVENT-WATER-DETERGENT CONCENTRATE. J. M. Chisholm (Emery Industries, Inc.). *U.S. 3,345,123.* An improvement is claimed in a dry cleaning process employing a mixture of organic solvent, oil-soluble

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25th Anniversary of Hormel Institute

Minnesota Univ. President Moos Addresses Group

The 25th anniversary of The Hormel Institute was celebrated on Nov. 8, 1967, with a luncheon at the Austin Country Club, Austin, Minn. Invited guests included Malcolm Moos, President of the University of Minnesota, and other University officials, former and present members of the Board of The Hormel Institute, various state, county, and city officials, and past and present employees of the Institute.

Following the luncheon, President Moos addressed the guests, speaking on "College Demonstrations Throughout the Nation."

Before the official celebration, W. O. Lundberg, Director of The Hormel Institute, R. T. Holman, and Herman Schlenk, senior staff members, appeared on the KAUS-TV program "Focal Point," and discussed various areas of research activities at the Institute. A question-and-answer period followed, with questions being telephoned in by people residing in the local area.

On Sunday, November 12, an open house was held at the Institute laboratories for the general public.

Beta-Amines . . .

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As for petroleum applications, increased hydrocarbon solubility, plus a high level of bactericidal activity toward anaerobic, corrosion-producing sulfate reducing organisms makes possible more efficient handling, storage and all-weather use in oil production usage. Excellent fuel oil additives, combining dehazing, corrosion inhibition and dispersancy, have been formulated; and chemicals which very effectively settle particulate matter from hydrocarbon systems have been developed.

Very promising anticaking formulations for hygroscopic particles, showing more even coating and easier application and better spreading characteristics, are now available. This is particularly true for mixed fertilizers, urea and ammonium sulfate.

Effective salts of the herbicidal acids, with low viscosities and pour points and high oil solubility have been prepared. Nonvolatility and low water loss are a characteristic of these. Invert emulsions for agricultural sprays have been readily prepared also.

Sound deadener formulations based on *beta* chemicals allow the preparation of coatings with good adhesion, even filler distribution and smooth, void-free films.

Excellent vapor-phase inhibitors, for protection in gas transmission lines and storage tanks, can be formulated.

In situ-prepared gelation systems for various polar and nonpolar solvents for a variety of uses are possible.

Toxicity data on these products are available and are in the same range of activity as the *alpha* amines, in terms of LD_{50} and skin and eye irritation levels.

Additional applications have been developed but are not yet available for publication because of patent filings. Process and product applications are also pending.

A large pilot plant installation, capable of producing all product lines in field development quantities is in full operation. Full plant capability should be available in about two years.

The February JAOCS will carry the AOCS abstracts for the AOCS-AACC Joint Meeting in Washington, March 31-April 4. A complete listing of titles and authors was published in the December 1967 issue.