Kirk-Othmer Encyclopedia of Chemical Technology.

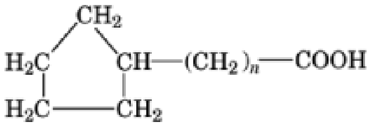
NAPHTHENIC ACIDS

The term naphthenic acid, as commonly used in the petroleum industry, refers collectively to all of the carboxylic acids present in crude oil. Naphthenic acids [1338-24-5] are classified as monobasic carboxylic acids of the general formula RCOOH, where R represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives. Naphthenic acids are composed predominantly of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic (paraffinic or fatty) acids. Aromatic, olefinic, hydroxy, and dibasic acids are considered to be minor components. Commercial naphthenic acids also contain varying amounts of unsaponifiable hydrocarbons, phenolic compounds, sulfur compounds, and water. The complex mixture of acids is derived from straight-run distillates of petroleum, mostly from kerosene and diesel fractions (see Petroleum).

Naphthenic acids have been the topic of numerous studies extending over many years. Originally recovered from the petroleum distillates to minimize corrosion of refinery equipment, they have found wide use as articles of commerce in metal naphthenates and other derivatives. A comprehensive overview of the uses of naphthenic acid and its derivatives can be found in References 1 and 2. A review of the extensive research on carboxylic acids in petroleum conducted up to 1955 is available (3), as is a more recent review of purification, identification, and uses of naphthenic acid (4).

1. Chemical Structure

The name naphthenic acid is derived from the early discovery of monobasic carboxylic acids in petroleum, with these acids being based on a saturated single-ring structure. The low molecular weight naphthenic acids contain alkylated cyclopentane carboxylic acids, with smaller amounts of cyclohexane derivatives occurring. The carboxyl group is usually attached to a side chain rather than directly attached to the cycloalkane. The simplest naphthenic acid is cyclopentane acetic acid [1123-00-8], (**1**, n = 1).



(1)

Naphthenic acids are represented by a general formula $C_nH_{2n-z}O_2$, where *n* indicates the carbon number and *z* specifies a homologous series. The *z* is equal to 0 for saturated, acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids. Typical structures for the homologues of naphthenic acids are shown in Figure 1. Naphthenic acids in the range of C-7 to C-12 consist mainly of monocyclic acids. The more complex acids contain larger proportions of multicyclic condensed compounds.

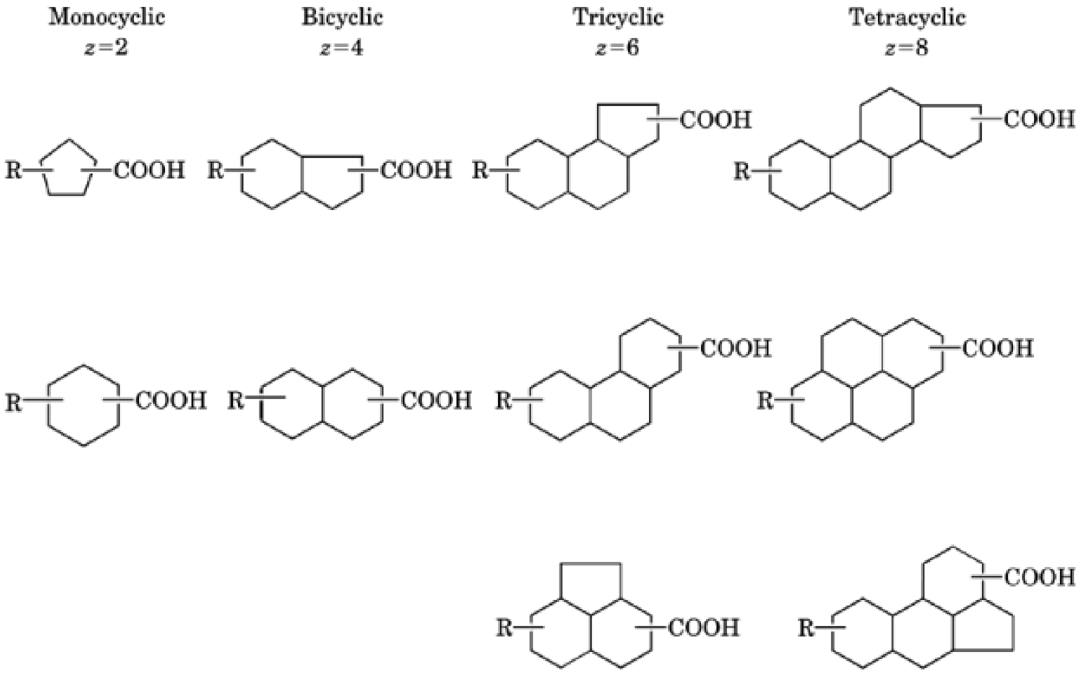


Fig. 1. Typical naphthenic acid structures, where R=alkyl. For the acyclic case $z=0$ and the structure is simply R–COOH.

The fundamental nature of naphthenic acids was determined by the 1960s (3, 5, 6). As recently as 1955, only two naphthenic acids with as many as 10 carbon atoms had been positively identified. Later, more extensive laboratory studies revealed an astonishing variety of organic acids present in crude oil, including fatty acids as low in molecular weight as acetic acid, as well as saturated and unsaturated acids based on single and multiple five- and six-membered rings. One study identified ~ 1500 different organic acids in a single California crude oil, ranging in molecular weight between 200 and 700. The peak of the molecular weight distribution is between 300 and 400 (7). Early studies concentrated on identification of individual low molecular weight acids; more recent work has focused largely on geochemical correlations and biodegradation mechanisms of petroleum (8). C-14 to C-20 acyclic isoprenoid acids and C-10 to C-11 monocyclic naphthenic acids have been isolated from California crude petroleum (9–12). California crudes have also yielded C-22 to C-24 steroid acids, affirming the biological origin of petroleum (13).

2. Physical and Chemical Properties

Naphthenic acids are viscous liquids, with phenolic and sulfur impurities present that are largely responsible for their characteristic odor. Their colors range from pale yellow to dark amber. An odor develops upon storage of the refined acids. Naphthenic acids have wide boiling point ranges at high temperatures (250–350°C). They are completely soluble in organic solvents and oils but are insoluble (<50 mg/L) in water. Commercial naphthenic acids are available in various grades and are marketed by acid number, impurity level, and color. Typical compositions and properties of three grades of naphthenic acids are given in Table 1. The product of refractive index and specific gravity, approximately 1.40–1.45, can be used to distinguish naphthenic acids

Table 1. Properties of Commercial Naphthenic Acid

	Grade		
Property	Crude	Refined	Highly refined
acid number, mg KOH/g	150–200	220–260	225–310
acid number (oil-free)	170–230	225–270	230–315
unsaponifiables, wt %	10–20	4–10	1–3
phenolic compounds, wt %	2–15	0.1–0.4	0.05–0.4
water, wt %	0.3–1.0	0.01–0.1	0.01–0.08
specific gravity at 20°C	0.95–0.98	0.95–0.98	0.95–0.98
viscosity at 40°C, mPa s (=cP)	40–80	40–100	50–100
color, Gardner	black	6–8	5–6
refractive index, n_D^{20}	1.482	1.478	1.475
avg. mol wt (oil-free)	240–330	210–250	180–250

from unsaponifiables (ca 1.2) and from other acidic compounds found in petroleum such as aliphatic acids (ca 1.3) and phenols (>1.5) (14).

Chemically, naphthenic acids behave like typical carboxylic acids with similar acid strength as the higher fatty acids. Dissociation constants are on the order of 10^{-5} to 10^{-6} (15). They are slightly weaker acids than low molecular weight carboxylic acids such as acetic, but are stronger acids than phenol and cresylic acid. Whereas the principal use of naphthenic acids has been in the production of metal salts, they also can react to form esters, amine salts, amides, imidazolines, and many other derivatives (see Esters, organic; Amides). Derivatives of naphthenic acid often have advantageous physical properties over fatty acid derivatives, particularly their high stability to oxidation and solubility in hydrocarbons.

Naphthenic acid corrosion has been a problem in petroleum-refining operations since the early 1900s. Naphthenic acid corrosion data have been reported for various materials of construction (16), and correlations have been found relating corrosion rates to temperature and total acid number (17). Refineries processing highly naphthenic crudes must use steel alloys; 316 stainless steel [11107-04-3] is the material of choice. Conversely, naphthenic acid derivatives find use as corrosion inhibitors in oil-well and petroleum refinery applications.

3. Occurrence

Naphthenic acids are normal constituents of nearly all crude oils, but not all crudes contain sufficient quantities of usable acids to make recovery an economic process. Heavy crudes from geologically young formations have the highest acid content, and paraffinic crudes usually have low acid content. The acid content of crude petroleum varies from 0–3%, with crudes from California, Venezuela, Russia, and Romania having the highest content. Smaller amounts are found in U.S. Gulf Coast crudes, whereas little or no naphthenic acids are found in Pennsylvania, Iraq, or Saudi Arabia crudes. Typical concentrations are shown in Table 2. Minor amounts of naphthenic acids are also found in bituminous oil sands, but these are not economically recoverable. Identification of naphthenic acids in water from oil-bearing strata is being examined as a potential method of petroleum exploration (18).

Naphthenic acids occur in a wide boiling range of crude oil fractions, with acid content increasing with boiling point to a maximum in the gas oil fraction (ca 325°C). Jet fuel, kerosene, and diesel fractions are the source of most commercial naphthenic acid. The acid number of the naphthenic acids decreases as heavier petroleum fractions are isolated, ranging from 255 mg KOH/g for acids recovered from kerosene and 170 from

Table 2. Acid Content of Various Crudes[a]

Crude oil source	Petroleum acids, wt %
Pennsylvania	0.03
West Texas	0.4
Gulf Coast	0.6
California	1.5
Russia, Balakhany light	1.0
Russia, Balakhany heavy	1.6
Romania, waxy	0.2
Romania, asphaltic	1.6
Venezuela, Lagunillas	1.2

[a] Ref. 3.

diesel, to 108 from heavy fuel oil (19). The amount of unsaturation as indicated by iodine number also increases in the high molecular weight acids recovered from heavier distillation cuts.

4. Manufacture

The commercial production of naphthenic acid from petroleum in based on the formation of sodium naphthenate. Although the separation of naphthenic acids from hydrocarbon fractions is a relatively simple process, extraction from crude petroleum is not feasible because of the low percentage of acids in the oil, the large volumes of fluids to be handled, and the abundance of other caustic-extractable compounds found in most crudes. The low water solubility of high molecular weight naphthenate soaps and the tendency of sodium naphthenate to emulsify also contribute to making direct recovery of acids from crude oil difficult. Although naphthenic acids can be removed from crude oil and heavy fractions by reaction with caustic soda prior to and during their distillation, the acids are probably unusable since they are mixed (as salts) with large quantities of asphalt or residual pitch. The numerous patents on this subject are basically modifications to an early patent for distilling oil in the presence of sodium hydroxide (20). The alkali residues are extracted with alcohol to remove unsaponifiables, followed by acidification to recover the naphthenic acids (21).

Naphthenic acids are generally obtained by caustic extraction of petroleum distillates boiling between 200 and 370°C. A continuous process has been developed for removing naphthenic acids from refinery streams by caustic washing (22). Caustic extraction also removes other acidic components of the petroleum fraction, including phenol and cresols (cresylic acid), mercaptans, and thiophenols. In addition to reducing corrosion in the refinery, the caustic wash is necessary to improve the burning qualities, storage stability, and odor of the finished kerosene and diesel fuels. The petroleum fractions are extracted with dilute (2–10%) sodium hydroxide since the sodium naphthenate salts are emulsifying agents. Stronger caustic strengths increase the solubility of hydrocarbon oils (unsaponifiables) in the sodium naphthenate. The Fiber-Film contacting process patented by Merichem reduces emulsification and caustic carryover during removal of naphthenic acid from petroleum fractions and achieves low acid number specifications in a single stage (23, 24). Noncaustic processes for recovery of naphthenic acids from petroleum distillates, including ammonia (qv) (25), triethylene glycol (26), ion-exchange resins (27), and aluminosilicate zeolites (28), have also been reported but not commercialized (see Ion exchange).

The aqueous sodium naphthenate phase is decanted from the hydrocarbon phase and treated with acid to regenerate the crude naphthenic acids. Sulfuric acid is used almost exclusively, for economic reasons. The wet crude naphthenic acid phase separates and is decanted from the sodium sulfate brine. The volume of sodium sulfate brine produced from dilute sodium naphthenate solutions is significant, on the order of 10 L per L of crude naphthenic acid. The brine contains some phenolic compounds and must be treated or disposed of in an environmentally sound manner. Sodium phenolates can be selectively neutralized using carbon dioxide and recovered before the sodium naphthenate is finally acidified with mineral acid (29). Recovery of naphthenic acid from aqueous sodium naphthenate solutions using ion-exchange resins has also been reported (30).

The other acidic compounds extracted by caustic remain in the crude naphthenic acid after acidification of the sodium naphthenate has occurred. These phenolic and sulfur compounds are objectionable because of their odor and color-forming properties. Although numerous methods for naphthenic acid purification have been suggested, only those which combine low cost and relatively simple operation are used commercially. Crude naphthenic acids are dried and distilled under reduced pressure to produce the refined products. Distillation removes some of the phenolic and unsaponifiable impurities, but the refined products still contain significant levels of impurities boiling at the same temperature. Because it is difficult and costly to remove all of the hydrocarbon impurities, commercial refined naphthenic acids typically contain 5–10% unsaponifiables. Unsaponifiables can be reduced to $<5\%$ by distilling the hydrocarbons from the alkali salts of the naphthenic acids (31). Naphthenic acids can also be purified by treatment with concentrated sulfuric acid to precipitate sludge-forming materials, which reduces the content of phenolics (32). The naphthenic acid is then distilled for final purification. Liquid–liquid extraction processes reduce unsaponifiable content by extracting naphthenic acids into water–alcohol mixtures (33, 34).

Interest in synthetic naphthenic acid has grown as the supply of natural product has fluctuated. Oxidation of naphthene-based hydrocarbons has been studied extensively (35–37), but no commercially viable processes are known. Extensive purification schemes must be employed to maximize naphthene content in the feedstock and remove hydroxy acids and nonacidic by-products from the oxidation product. Free-radical addition of carboxylic acids to olefins (38, 39) and addition of unsaturated fatty acids to cycloparaffins (40) have also been studied but have not been commercialized.

5. Production

Nameplate capacities of naphthenic acid producers in North America are 9000 metric tons of crude and refined acid at Merichem (Tuscaloosa, Ala.), and 3600 t of crude acid at Hewchem (Gulfport, Miss.) (41). However, actual production capacity may vary widely as a result of the mix of feedstocks being processed. Some feedstocks require significantly greater processing time to achieve high grade finished product. Naphthenic acid products are shipped in tank cars, tank trucks, and drums under DOT 9137/UN 3082 identification numbers. Principal producers in Japan are Sanko Yuka Kogyo, Yamato, Taniguchi Oil, and Union Oil (a subsidiary of Idimitsu); in Europe, Nord Import, Oleochimie, Imperial Oil, and Corn Van Loocke.

6. Economic Aspects

Roughly 5500–6000 t of naphthenic acid were consumed in North America in 1992. Less than 500 t of finished product demand was met by imports in spite of the large quantities of naphthenic acid produced overseas. The average unit value was \$1.56/kg. After much price volatility in the late 1970s and early 1980s, prices have risen moderately in the 1990s. For fob bulk shipments, current refined acid prices range from \$1.94–2.09/kg for acid numbers 220 to 300. Crude acid prices range from \$0.99–1.17/kg for acid numbers 150 to 180 (41).

Naphthenic acid availability exceeds demand, although some minor market disruptions occurred in North America during the early 1990s. In 1990, the U.S. Environmental Protection Agency (EPA) put into place low sulfur requirements for highway diesel fuel to be met by October 1993. To meet the specification, several feedstock producers were prompted to hydrotreat their diesel fractions, since caustic extraction does not reduce sulfur to the required level. Hydrotreating destroys naphthenic acids, so the result was a decrease in feedstock availability. Raw materials from previously unused feedstock sources in Asia, Europe, and South America were then imported into North America to achieve market balance. Long-term yearly feedstock supply is expected to meet market growth projections with large discoveries of high naphthenic-content oil.

7. Analysis

Naphthenic acid concentration in crude oil and distillates is typically measured by titrating with potassium hydroxide for neutralization number using potentiometric (ASTM D664) or colorimetric (ASTM D974) methods. The same procedures are used to measure the acid number of crude or refined naphthenic acids after recovery from the petroleum fraction. The neutralization or acid numbers are expressed numerically as mg KOH (formula $\mathrm{wt} = 56.1$) required to neutralize the acidity in 1 g of sample. This value for the acid on an impurity-free basis is readily converted to equivalent weight by dividing $100\times$ the formula weight of KOH (56,100) by the acid number. Naphthenic acid having a high acid number indicates a low molecular or equivalent weight product. Crude oil or a petroleum fraction would have a very low acid number, since the acid content is low.

Naphthenic acids comprise a highly complex mixture containing hundreds of compounds that are impossible to separate into individual components, even by high resolution gas chromatography. Progress in obtaining information on the structure of naphthenic acids has been retarded because of this complexity. Analysis by gas chromatography of methyl esters is useful in detecting naphthenic acids adulterated with synthetic or vegetable oil-based fatty acids. Infrared spectroscopy is unable to distinguish clearly between naphthenic and fatty acids.

Two mass spectrometric methods have been developed which improve the characterization of naphthenic acids. Chemical ionization using fluoride ion as a reactant gas (42) and fast-atom bombardment (43) both use the negative ion detection mode. The two methods detect the $(\mathrm{M}-1)^-$ ion in carboxylic acids, including high molecular weight species with no fragmentation. These methods allow the identification of naphthenic acids based on carbon number and z-series distributions, providing a fingerprint useful in correlating the sources of crude oils.

8. Health and Safety Factors

Naphthenic acids are only slightly toxic to mammals but are toxic to fish, bacteria, and wood-destroying insects. The lethal oral dose for humans is approximately 1 L (44), and the oral LD_{50} is 3.0–5.2 g/kg in rats (45). The deaths appeared to result from gastrointestinal disturbances. Naphthenic acid is nonmutagenic by the Ames mutagenicity test (46), and is not listed as a carcinogen by the International Agency for Research on Cancer, the National Toxicology Program, or the U.S. Occupational Safety and Health Act.

9. Commercial Uses

More than two-thirds of the naphthenic acid produced is used to make metal salts, with the largest volume being used for copper naphthenate, consumed in the wood preservative industry (see Wood). Metal salts used as paint driers accounted for only 16% of the naphthenic acid market in 1993 (see Paint). This is a dramatic contrast with 1977 usage, when 75% of the naphthenates went into the paint drier market. An overall view of the 1993 naphthenic acid market in North America shows the following uses:

Oil field uses are primarily imidazolines for surfactant and corrosion inhibition (see Petroleum). Besides the lubrication market for metal salts, the miscellaneous market is comprised of free acids used in concrete additives, motor oil lubricants, and asphalt-paving applications (47) (see Asphalt; Lubrication and LUBRICANTS).

Use	Percentage
wood	40.1
oil field	27.7
paint	15.8
tires	8.5
miscellaneous	7.9

Table 3. Metal Naphthenate Uses

Name	CAS Registry Number	Applications
copper naphthenate	[1338-02-9]	wood and textile preservative, catalyst
zinc naphthenate	[12001-85-3]	wood and textile preservative, lubricant, wetting agent
cobalt naphthenate	[61789-51-3]	paint drier, tires, ink drier, catalyst
manganese naphthenate	[1336-93-2]	paint drier, catalyst, fuel additive
lead naphthenate	[61790-14-5]	paint drier, wetting agent, lubricant additive
calcium naphthenate	[61789-36-4]	paint drier, catalyst, lube additive
iron naphthenate	[1338-14-3]	paint drier, fuel additive, catalyst
zirconium naphthenate	[72854-21-8]	paint drier, electrophotographic developer
cerium naphthenate	[68514-63-6]	paint drier, catalyst, fuel additive
vanadium naphthenate	[68815-09-8]	paint drier, catalyst, corrosion inhibitor
sodium naphthenate	[61790-13-4]	emulsifier, ore flotation, leather
potassium naphthenate	[66072-08-0]	emulsifier, plant growth modifier
aluminum naphthenate	[61789-64-8]	gelling agent, pigment wetting

Naphthenic acid has also been studied in ore flotation for recovery of rare-earth metals (48) (see Flotation; Lanthanides).

Naphthenic acid is ideal for synthesizing metal carboxylates that require a ligand with some oxidative stability, solubility in hydrocarbons and oils, and insolubility in water. The general chemical structure of the naphthenate salts is $M^{x+}({}^{-}OOCR)_x$ where x = metal charge and molar stoichiometry of naphthenic acid to the metal M. Table 3 lists commercially available metal naphthenates and their uses. Metal carboxylates are used in the oil-based (alkyd) paint industry as catalysts to accelerate the drying of coatings; hence the name driers was given to them (see Alkyd resins; Driers and metallic soaps). The metal naphthenates were originally used to replace the corresponding linoleates, resinates, and tallates. These naphthenate salts have the advantages of high metal content, low viscosity, better solubility in hydrocarbons and oils, and greater stability to oxidation. Each metal naphthenate has a specific function and is typically used in combination with other driers. This market is declining as a result of the 1990 Clean Air Act that reduces volatile organic compound (VOC) emissions. The paint industry is responding by replacing their oil-based paints with waterborne formulations.

An expanding market for naphthenic acid is in wood and textile preservatives (see Textiles; Wood). Copper and zinc naphthenate are used to prevent dry rot, as well as fungi and insect attack in wood. Zinc naphthenate is typically used in the log home industry because it provides a colorless coating on the wood. The naphthenates are environmentally preferred replacements for creosote, pentachlorophenol, and chromated copper–arsenic. Copper naphthenate prevents textile rotting at lower concentrations than copper oleates or tallates, in part because the naphthene moiety itself has fungicidal properties (49). In North America, the 1992 production of 8% copper naphthenate solution was estimated to be 2600–2900 t at a unit value of $2.20–2.45/kg. The estimated market growth for this application is 12–14%/yr.

Another market application for naphthenic acid is the tire industry, where cobalt naphthenate is used as an adhesion promoter (see Adhesives; Tire cords). Cobalt naphthenate improves the bonding of brass-plated steel cords to rubber, presumably by suppressing the de-zincification of brass (50). Its first reported use was in 1970 and the first patent for its use was issued in 1975 (51). About 900 t of cobalt naphthenate is used worldwide as an adhesion promoter, half of it in North America. The unit value fluctuates between $8.75–13.25/kg because of the volatility of cobalt prices. Although it is the industry standard, the use of cobalt naphthenate is declining with the advent of more economical high metal-containing substitutes.

In the other market areas, lead naphthenates are used on a limited basis in extreme pressure additives for lubricating oils and greases. Sodium and potassium naphthenates are used in emulsifiable oils, where they have the advantage over fatty acid soaps of having improved disinfectant properties. Catalyst uses include cobalt naphthenate as a cross-linking catalyst in adhesives (52) and manganese naphthenate as an oxidation catalyst (35). Metal naphthenates are also being used in the hydroconversion of heavy petroleum fractions (53, 54) and bitumens (55).

The surface-active properties of many naphthenic acid derivatives allow them to function in a variety of applications, including corrosion inhibitors, emulsifiers, and defoamers (see Corrosion and corrosion control; Emulsions; Foams). These properties can be exploited in performance-oriented applications such as petroleum recovery, asphalt emulsification, and concrete aeration where chemical composition is not critical (see Asphalt; Petroleum). Surfactants may be prepared from the acids themselves or from derivatives such as amides or esters. The general surfactant applications are dominated by the ethoxylated naphthenic acids and naphthenyl amides and alcohols. Ethoxylated and sulfated naphthenic acid derivatives are highly surface-active and have substantial detergency power. The petroleum industry utilizes naphthenic acid amine derivatives both as surfactants for enhanced (tertiary) oil recovery (56) and as corrosion inhibitors (57). Amides and imidazolines of naphthenic acid used as corrosion inhibitors are noted for oil solubility and flow characteristics that are superior to those of similar fatty acid-based derivatives. Naphthenyl amides and imidazolines based on polyamines such as diethylenetriamine are also reported in such diverse applications as bitumen emulsifiers, bactericides (58), and lubricant additives (see Lubrication and; Lubricants). The surfactant properties of naphthenyl amides improve adhesion of aggregate rock to the asphalt binder (59) and improve mechanical strength and plasticity in concrete (60). Alkaline flooding of oil sands improves bitumen extraction by producing anionic surfactants *in situ* from the naturally occurring naphthenic acids (61).

Simple esters are readily formed by the reaction of naphthenic acids with monohydric alcohols, olefins, or ethylene or propylene oxides. More complex esters are prepared by partial or complete esterification of polyhydric alcohols. Naphthenic acid esters have been repeatedly cited as replacements for phthalates as plasticizers for PVC resins. Alkyl and glycol naphthenate esters improve the flexibility and workability of resins and are valued for their low volatility, compatibility, stability, and resistance to kerosene extraction (62). Naphthenic acid esters of multifunctional alcohols such as pentaerythritol (63) and poly(ethylene glycol)s have been cited as lubricants or additives for fuels, and for improved oil recovery (64). Glycol esters and other esters of naphthenic acid are used as hydraulic fluids (65), plasticizers, and surfactants, and are finding increasing use in the fat-liquoring process in leather tanning (66) (see Hydraulic fluids; Leather; Plasticizers; Surfactants). Triethylene glycol naphthenate improves dispersion of carbon black in water-borne conductive primer coatings (67).

Naphthenyl alcohols are formed by reduction of the acids or their simple esters. They are valuable as surfactants, solvents, and components of lubricants. The acid halides are of value mainly as chemical intermediates (1).

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