

NAPHTHENIC ACIDS. II

MANUFACTURE, PROPERTIES, AND USES

EDWIN R. LITTMANN AND J. R. M. KLOTZ

Stanco Incorporated, New York, New York

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The expanding uses for naphthenic acids have made desirable a compilation of information regarding their occurrence, manufacture, composition, properties, analysis, and uses. The material presented in this paper is illustrative of and organized according to the above topics and has been collected mainly from the patent literature. Since, in a presentation of this type, a detailed discussion of every reference is precluded, a supplementary bibliography has been appended.

The true naphthenic acids are probably normal constituents of all crude oils, in which they occur to the extent of about 0.03 to 3.0 per cent (52, 54, 64, 78, 82). By using an average acid content of 0.1 per cent, Ellis (26) has estimated the potential annual production at 50,000 tons or 12,000,000 gallons. It is rather doubtful whether such a volume of production could be attained, since this would require the treatment of all crude oils produced. It is more probable that certain crude oils or distillates rich in acids will continue to be used as a source of the naphthenic acids.

I. RECOVERY OF NAPHTHENIC ACID

The extraction of naphthenic acid from petroleum products is based upon the formation of sodium naphthenate by the neutralization of naphthenic acid with caustic soda or soda ash. The low concentration of naphthenic acid in crude oil or distillate and the tendency of sodium naphthenate to promote emulsions impose practical difficulties on the apparently simple operation of extracting an acid from a neutral oil. In practice, naphthenic acid is recovered as sodium naphthenate from three different sources. Crude oil or a straight-run distillate is distilled from caustic soda, yielding a residue containing resins, asphalts, oils, and sodium naphthenate. Distillates of the gas-oil and kerosene type are extracted with aqueous solutions of caustic soda or soda ash, yielding an aqueous solution rich in sodium naphthenate. The third source of naphthenic acid is soda sludge, obtained by neutralizing the residual acidity in a sulfuric-acid-treated oil after the acid sludge has been separated. The true naphthenic acids remain unsulfonated during the acid treatment of the oil.

By choosing the sources of naphthenic acid in which it is normally concentrated during the refining operation, one of the difficulties in the recovery operation has been largely overcome. While the difficulty of the formation of emulsions was not so easily eliminated and is associated with sodium naphthenate irrespective of its source, there are distinct differences in the handling of the salt from each of the above sources. In view of these differences the following

illustrative methods of recovery of naphthenic acid are presented in relation to the source material.

The alkaline residue from the stills in which oil has been distilled from caustic soda contains resins, asphaltic materials, oil, and sodium naphthenate. Two general methods have been reported for the handling of the still residue: In one, the residue is first diluted with a light oil or solvent before recovery of the sodium naphthenate, while in the other the residue is acidified directly with a mineral acid. Accordingly, Powell (69) dilutes the still bottoms with an oil and extracts the sodium naphthenate from the hot mixture by discharging it on a stream of flowing water. In place of oil, Becker and Sloane (8) use a relatively low boiling naphtha as the diluent for the still bottoms.

A somewhat different scheme has been devised by Andrews and Lauer (4), who extract the still bottoms with 80–95 per cent ethyl alcohol in which the soaps are soluble, but which is not a solvent for the oil. Other low-molecular-weight alcohols, such as methyl and isopropyl, may be used. The choice of alcohol is largely dependent upon its cost.

The direct acidification of alkaline still bottoms with a mineral acid is the simplest method of recovery for naphthenic acids, though acids so prepared often contain oil which must later be removed. Despite the obvious steps involved in the acidification process, several patents have been issued covering minor improvements in the operation. Cook (18) dilutes the still bottoms with about ten parts by weight of water and acidifies the mixture with strong hydrochloric acid. Kaufman and Lauer (46) also record essentially the same process as above, as well as the direct acidification of the alkaline residues with dilute acid. The recovery of naphthenic acid and its simultaneous incorporation into an asphalt composition have been disclosed by Swerissen (85), who acidifies a mixture of alkali naphthenates and asphalt as obtained in still bottoms with sufficient acid just to free the naphthenic acids. The recovery of naphthenic acid and its incorporation into a cutting oil by a unified process have also been recorded by Terrell, Hughes, and Carter (89). The mixture of alkali naphthenates and asphalt is acidified, mixed with an oil of lower boiling point than the asphalt, and distilled. The distillate, containing oil and naphthenic acid, is then neutralized to form a cutting oil. This patent is of further interest in that it illustrates the distillation of naphthenic acids through the medium of a carrier liquid, thereby minimizing decarboxylation.

In general, the removal of oil from alkali-naphthenate-containing still bottoms is incidental to the recovery of the acids. Wunsch (93), however, has devised a process specifically for this purpose. The sludge is dispersed in water, thinned with water, and deëmulsified by the addition of water-soluble compounds, such as alcohols, ketones, and salts, while the temperature is maintained at 90–100°C. The acids may be recovered by acidification of the purified aqueous solution. Experience has shown that this method is quite effective when combined with a solvent extraction of the deëmulsified oil.

The recovery of naphthenic acid under anhydrous conditions has been described by Brunck, Kreutzer, and Boeck (14), who treat the alkaline still bottoms

with concentrated (98 per cent) sulfuric acid in the presence of a light solvent for the naphthenic acids. It is claimed that the asphaltic materials resinify and precipitate out along with the alkali sulfates. The acids so obtained may, under certain conditions, be contaminated with oil-soluble sulfonic acids.

II. PURIFICATION OF NAPHTHENIC ACIDS

For many practical uses the naphthenic acids as obtained from petroleum are too impure. The impurities associated with the acids are chiefly oil, phenols, basic nitrogen compounds and, to a minor extent, sulfur-containing compounds. While numerous methods of purification have been suggested, only those which combine relatively simple operations and low cost are of importance commercially. As a rule, simple distillation under reduced pressure yields an acid of sufficient purity for most purposes. Table 1 shows the results obtained on two samples of naphthenic acid distilled commercially.¹ According to these results it appears that single distillations will yield a product of 92 to 93 per cent total acid content and having a pale color. Although distillation yields marked improvement in color and acid number, there is a lesser improvement in odor.

TABLE 1
Properties of original and distilled naphthenic acids

ACID	ORIGINAL		DISTILLED	
	Acid No.	Unsaponifiable <i>per cent</i>	Acid No.	Unsaponifiable <i>per cent</i>
A.....	256	8.0	263	7.4
B.....	205	13.5	235	7.9

A distillation process claiming the decolorization as well as deodorization of naphthenic acid has been reported by Ewing (27), who first distills the crude acids and then redistills the distillate from a metallic oxide such as cupric oxide or other non-volatile oxidizing agents to remove phenols and odoriferous materials. Volatile oxidizing agents such as air have also been used, both in the presence and in the absence of catalysts or of non-volatile oxidizing agents (28). The formation of color in naphthenic acids, particularly after distillation, has been attributed to the oxidation of phenols and the above processes are designed to remove them. Merrill and Blount (61) separate phenols and naphthenic acid by means of a selective neutralization with soda ash or caustic soda. This mixture is then distilled with steam to remove the phenols and oils.

Several investigators have reported on the treatment of naphthenic acids with strong sulfuric acid as a method of purification. While it was originally thought that sulfuric acid changed the properties of naphthenic acids even to the extent of sulfonating them (81), later work by Charitschkoff (17, 37), Gurwitsch (37), and Tanaka and Nagai (87) on acids from different sources indicates that the acids remain unattacked. The treatment with sulfuric acid serves to precipitate

¹ Private communications.

sludge-forming materials from the naphthenic acids as well as to carry down with the sludge some phenols and basic impurities. In general, sulfuric acid of higher concentration than 85 per cent is miscible with naphthenic acid, though its solubility is markedly decreased by the presence of petroleum solvents. Such solvents decrease the viscosity of the naphthenic acid and facilitate the separation of sludge and acid. Such a process has been reported by Rutherford (77).

Carr (15) found, however, that sulfuric acid of at least 100 per cent concentration could be used without the difficulty of solubility arising if 0.5 to 5.0 per cent of acid, based on the naphthenic acid, were used. With this quantity sludge separated readily, while if 10 to 15 per cent was employed mutual solubility and no purification resulted. Hendrey (40) prefers to treat partially purified naphthenic acids with about 5 per cent of 98 per cent sulfuric acid and then dilute the mixture to throw out the sludge. The naphthenic acid is then distilled for final purification. A combination treatment of naphthenic acids with sulfuric acid of 50 to 83 per cent concentration and then activated clay has been reported by Ewing (29). A slightly different process has also been suggested by Rabinovich and Osenova (70), who treat a 50 per cent solution of naphthenic acids in gasoline with concentrated sulfuric acid. This solution is then treated with an adsorbing material (clay), after which it is washed with an aqueous solution of zinc chloride or calcium chloride.

III. COMPOSITION OF NAPHTHENIC ACIDS

The commercially available naphthenic acids are at present identified by origin and acid number. The lack of a more definite and scientific classification is probably due to the complexity of the mixtures of acids now known as naphthenic acid and to the absence of information correlating the properties of the acids from different sources. Chemically, the naphthenic acids have been classified (25) as carboxylic acids of the formulas $C_nH_{2n-2}COOH$ and $C_nH_{2n-4}COOH$, with the largest group falling into the former class. Several attempts to demonstrate the presence of cyclohexane derivatives (12, 94, 95) in more than traces indicate that such compounds are probably present in very minute quantities.

In the absence of cyclohexane derivatives the commercial naphthenic acids may be said to be essentially mixtures of small quantities of low-molecular-weight fatty acids and cyclopentane acids. The latter may be considered as the real naphthenic acids. According to Schutze, Shive, and Lochte (83), the products of the index of refraction and density "show that aliphatic acids have products ranging from 1.280 to 1.350 with most values between 1.300 and 1.310, the naphthenic acids range from 1.390 to 1.470 with most values between 1.410 and 1.440, while phenols have nd products above 1.500 and hydrocarbon values below 1.300 and usually below 1.280." Temperatures of $20^\circ C. \pm 2^\circ$ were used. The application of this rule to naphthenic acids from different sources and of different molecular weights is illustrated in table 2.

While the data in table 2 are illustrative, calculations based on additional references give the same results. Data of this character are valuable from a

general viewpoint only, however, since they do no more than place the naphthenic acids within a certain group of compounds, the cyclopentane acids. Numerous efforts have been made to determine the structures of some of the major constituents of various naphthenic acids, but with little success. The difficulties involved in such studies are chiefly the location and identification of the type of substituents on the cyclopentane ring, the separation of optical and geometrical isomers, and the determination of the number of carbon atoms between the carboxyl group and the ring. von Braun devised a method for determining whether the carboxyl is primary, secondary, or tertiary by treating the naphthenic ethylamide with phosphorus pentachloride and measuring the chlorine present in the regenerated acid. This method is satisfactory for naphtheneacetic acids, but is inapplicable to homologs of acetic acid. Until further reactions of this type are discovered or until the acids are synthesized, it seems likely that the detailed structures of the acids will remain unknown.

TABLE 2
nd values for naphthenic acids

ACID	SOURCE	nd	REFERENCE
C ₈ H ₁₄ COOH.....		1.424	(5)
C ₉ H ₁₆ COOH.....		1.423	(5)
C ₁₀ H ₁₈ COOH.....	Baku	1.419	(51)
C ₁₂ H ₂₂ COOH.....	Nishiyama	1.421	(86)
C ₁₃ H ₂₄ COOH.....	Nishiyama	1.427	(86)
C ₁₄ H ₂₆ COOH.....	Nishiyama	1.444	(86)
C ₁₅ H ₂₈ COOH.....	Nishiyama	1.439	(86)

IV. ANALYSIS OF NAPHTHENIC ACIDS

The present uses for naphthenic acids are based mainly on the relatively high acidity of these compounds. As a result of this, acid number and saponification number are of primary importance. These determinations are carried out in alcohol solution by the usual methods, as is also a determination of the unsaponifiable matter. An improved method for the determination of the total acid content has been proposed by Klotz and Littmann (49). In some cases it is desirable also to determine the phenols present as well as the sulfur content.

V. THE USES OF NAPHTHENIC ACIDS

The unique properties of the metallic soaps of naphthenic acids account for the major uses of the acid at the present time. The alkali soaps are extremely soluble in water, and 50 per cent solutions of sodium naphthenates are now available commercially.² These solutions flow freely and show no tendency to gel. Since commercial naphthenic acids have acid numbers of 200 to 300, their molecular weights are of the order of those of the fatty acids and the low viscosity of the aqueous solutions of the alkali salts is quite remarkable. In general, also, the naphthenic acids are somewhat stronger acids than those derived from the fats

² Nuodex Products Company.

and oils. The pH of the neutral alkali naphthenates in dilute aqueous solution is of the order of 8 to 9, whereas that of sodium stearate is 10 to 11. The alkali naphthenates have been proposed as both emulsifying and demulsifying agents. Frizell (33), for example, uses sodium naphthenate in the preparation of an emulsifiable oil by mixing four parts of dry sodium naphthenate with one part of cresol and then dissolving the product in mineral oil. The oils are used in the treatment of wool, as orchard sprays, and as cordage oils. Alleman (2) proposes the use of sodium naphthenate for the preparation of a similar soluble oil, but uses no cresol. In general, the use of a coupling agent is desirable when the alkali naphthenates are used as emulsifiers. In addition to cresol, illustrated above, rosin and ethylene glycol may be used. Neukom (67) describes the preparation of a soluble oil of this type in which a mixture of sodium naphthenate and rosin is blended with ethylene glycol and this blend is then diluted with mineral oil. Alcohols may also function as coupling agents. Merrill (60) prepares a soluble oil by adding 17 parts of butyl alcohol to 70 parts of 92 per cent sodium naphthenate and then diluting this product with mineral oil. Hendrey (39) uses pine oil as a coupling agent in a soluble oil having the following typical composition:

	<i>per cent</i>
Light lubricating oil.....	78-82
Sodium naphthenate.....	14-18
Pine oil.....	2
Water.....	2

Where sodium naphthenate alone is used as emulsifying agent, as in cutting oils, a very high percentage is required. Hughes (43) reports the preparation of such a product by mixing essentially dry sodium naphthenate with oil in the ratio of about one part of oil to one part of soap.

The preparation of disinfectants of either the tar-acid-oil or pine-oil type is often accomplished by a hot process in which an aging at elevated temperatures is required to complete the saponification of fatty acids used as emulsifying agents. Because of the increased strength of the naphthenic acids as compared with higher fatty acids, the saponification is greatly accelerated and the aging process may be greatly reduced or entirely eliminated. The formulations given in table 3 are illustrative of the "cold process" type of disinfectants which are readily and completely dispersible in water. The ingredients are added, with agitation, in the order shown and the reaction is complete as soon as the solutions become homogeneous.

The use of alkali naphthenates in the manufacture of asphalt emulsions and road-paving materials has been advocated by Limburg (55) and by Lichtenstern (53). The demulsifying action of alkali naphthenates is usually confined to water-in-oil type emulsions as encountered in petroleum-refining operations. While in most cases alkali naphthenates are reported as the demulsifying agents, other derivatives and mixtures of naphthenic acid and other materials are also used. For convenience all these materials are grouped together. For example, DeGroot (20) in one case uses a sulfonated condensation product between

naphthenic acid and an aromatic hydrocarbon; in another case (21), acids, salts, and esters (naphthenic) are said to accomplish the same purpose. In a third patent DeGroot and Wirtel (24) show the use of naphthenic acid derivatives in combination with salts of alkylated naphthalenesulfonic acids, and in a fourth (22) in combination with salts of polysulfonic acids. Other modifications are reported by DeGroot (23), Hendrey and Ebaugh (41), and Mead (57). The use of naphthenic acid esters alone as demulsifying agents has also been reported (19). In the breaking of water-in-oil emulsions the function of the various agents used seems to be one of phase reversal rather than a simple breaking of the two phases, though Wells and Southcombe (92) indicate that certain naphthenates give non-emulsifying oils when incorporated in a lubricating oil.

The use of various metallic naphthenates in lubricating compositions is usually confined to greases and to high-pressure and industrial lubricants. Becker (7) reports a lubricant composed of sodium naphthenate, petrolatum, and still wax.

TABLE 3
Disinfectants and deodorants

INGREDIENTS	PER CENT BY WEIGHT	
Tar acid oil (10 per cent).....	70	
Tar acid oil (75 per cent).....		70
Naphthenic acid (Acid No. 225).....	10	10
Oil-soluble petroleum sulfonate.....	13	13
Caustic soda (50 per cent).....	3.2	3.2
Water.....	3.8	3.8
Pine oil.....	67.7	70.6
Oil-soluble petroleum sulfonate.....	5.8	8.8
Naphthenic acid (Acid No. 225).....	19.3	11.8
Caustic soda (50 per cent).....	7.2	
Triethanolamine.....		8.8

Other sodium naphthenate compositions are reported by McKee and Eckert (56) and by Kaufman and Puryear (47).

In place of the alkali naphthenates, those of the alkaline-earth and heavy metals are also employed where a different effect is desired. In the case of castor machine oils, where increased "stringiness", viscosity, or oiliness is desired, various naphthenates have been employed. Frizell (34) describes such a product prepared from aluminum naphthenate dissolved in a mineral oil to which has been added a very small quantity of sodium naphthenate. The addition of the sodium naphthenate is claimed as an improvement over the use of aluminum naphthenate alone, as shown by Rebber (71). In addition to the metallic naphthenates, certain other derivatives have been advocated for the preparation of castor machine oils. Steik (84) uses the reaction product between castor oil and naphthenic acid, while Hagedorn (38) employs cellulose naphthenate in a composition containing either animal or mineral oil. Johnson (44) uses naphthenate esters of glycol ethers for the same purpose.

The addition of metallic naphthenates to crankcase lubricants is said to decrease the sticking of piston rings. There appears to be some doubt as to which naphthenate is the best to use. The Texas Company (90), for example, suggests the use of stannous naphthenate in quantities of 0.05 to 5.0 per cent. Evidence is presented that this compound is superior to zinc, iron, or aluminum naphthenate. Neely (66), on the other hand, states that aluminum, zinc, magnesium cobalt, cadmium, manganese, and tin (stannic?) naphthenates are all effective if used in conjunction with an organic acid. Nickel naphthenate has been advocated by Brandes (11), but the addition of this salt apparently also requires the use of an antioxidant. Substituted phenols were used for this purpose. Where aluminum naphthenate is used to prevent the sticking of piston rings, the basic product seems to be the best. Neely (65) proposes the aluminum dinaphthenate.

The soot-forming tendencies of fuel oil are materially reduced by the addition of metallic naphthenates to the oil. Adams, Ovitz, and Wiley (1) showed that

TABLE 4
Effect of naphthenates in fuels on the formation of soot

FUEL	WEIGHT PER CENT OF NAPHTHENATE ADDED	WEIGHT PER CENT OF METAL ADDED AS NAPHTHENATE	UNBURNED CARBONACEOUS MATERIAL (IN PER CENT OF THAT FORMED WHEN BURNING UNBLENDED FUEL)	
			Stack	Total (including tubes)
			<i>per cent</i>	<i>per cent</i>
Unblended fuel.....	0	0	62.6	100.0
Fuel plus zinc naphthenate.....	0.58	0.047	68.0	94.3
Fuel plus lead naphthenate.....	0.32	0.078	46.8	83.8
Fuel plus copper naphthenate.....	1.03	0.062	45.7	79.5
Fuel plus manganese naphthenate.....	1.27	0.076	38.4	68.0
Fuel plus cobalt naphthenate.....	1.23	0.074	32.6	67.4
Fuel plus iron naphthenate.....	1.13	0.068	29.5	62.6

the metallic salts of naphthenic acids or mahogany soaps could effect a reduction of as much as 540°F. in the ignition temperature of the soot. Quantities of added salt varied between 0.5 and 30 per cent, depending upon the frequency and constancy with which the modified fuel was used. A quantitative study of the effect of naphthenates as soot inhibitors has been reported by Fischer and Hulse (30). Table 4 shows the marked reduction in soot formation.

The metallic naphthenates have also found industrial application in the fields of preservatives and driers. As preservatives are included fungicides and insecticides. The use of sodium naphthenate in place of soap for the preparation of oil-cresylic acid emulsions as insecticides has been reported by Jones (45), who claims that such an emulsion has increased stability to calcium compounds. A similar product was also reported by Berry (9). An emulsion of copper naphthenate with mahogany soap oil, alcohol, and water has been patented by Rogers and McNeil (73), who advocate this composition for the treatment of seeds and plants.

Copper and zinc naphthenates are effective insecticides and fungicides, and solutions of these salts in petroleum solvents are available commercially. According to Trevor (91), good protection of wood against dry rot or mildew and termites is secured by the application of copper naphthenate. Protection against a wide variety of wood beetles is obtained through the use of zinc naphthenate. Attention is also called to the fact that sandbags are being treated in Britain with copper naphthenate to prevent their rotting. A six- to eight-fold increase in life was observed.³ Despite the volume of "popular" information on the mildew-proofing of textiles with copper and zinc naphthenates, little or no quantitative data have been heretofore presented. Illustrative of the effectiveness of zinc naphthenate are the results given in table 5, which were obtained on 6-oz. and 12-oz. duck treated with different quantities of zinc naphthenate and buried for

TABLE 5
Effectiveness of zinc naphthenate in mildew-proofing of textiles

DUCK WEIGHT	ZINC NAPHTHENATE	TENSILE STRENGTH			
		Initial		Final	
		Warp	Filling	Warp	Filling
<i>ounces</i>	<i>per cent</i>			Falling apart	
6	0	117.0	66.0		
	2			63.0	43.0
	4			105.0	82.7
	6			100.0	85.7
	8			116.0	82.3
12	0	216.0	201	13	12
	2			202.0	190.3
	4			202.9	192.7
	6			214.1	204.3
	8			217.0	212.3

2 weeks in mildew-infested soil maintained at 60–70°F. and about 25 per cent moisture content. The zinc naphthenate contained 12.5 per cent zinc.

General experience has shown that copper naphthenate is much more effective than zinc naphthenate over an extended period of time. This is best illustrated by the results obtained when the accelerated burial test is continued for 7 weeks. At the end of this time a sample of duck containing 0.5 per cent of zinc as naphthenate was falling apart, while the one containing the same amount of copper remained intact and showed only a trace of staining. A further illustration of the protective action of copper naphthenate is given by experiments on cotton seine twine, the results of which are given in table 6. The treated twine contained 0.5 per cent of copper as naphthenate.

The phenol esters of naphthenic acid (88), as well as the glyceryl esters (50), have also been proposed as insecticides. Naphthenic acid has been used to in-

³ Private communication.

crease the activity of certain insecticides and fungicides (72) for which a polar solvent is required.

Perhaps the largest present use for metallic naphthenates is in driers. Because of this application a brief description of the general methods of manufacture is given. In the first method, neutral sodium naphthenate solution is mixed with approximately an equivalent quantity of a water-soluble salt of the metal to be combined as naphthenate. Since most of the precipitated naphthenates are sticky, the reaction may be carried out in the presence of a solvent. After puri-

TABLE 6
Protective action of copper naphthenate on cotton twine

TIME	TENSILE STRENGTH		LOSS	
	Untreated	Treated	Untreated	Treated
<i>days</i>			<i>per cent</i>	<i>per cent</i>
0	44.5	47		
7	21.5	44	51.6	6.38
14	3.0	46	93.2	2.25
21	0.0	44	100	6.38
28	0.0	32	100	31.9

TABLE 7
Some patents pertaining to driers

INVENTOR AND REFERENCE	SUBJECT OF PATENT
Alleman (3).....	Metallic naphthenates from oil emulsions
Bogdan (10).....	Stabilizing metallic naphthenates
Fisher (31).....	Reaction of naphthenic acid and oxides
Fisher (32).....	Combination of lead and other naphthenates
Gardner and Hodge (35)...	Naphthenates of metals of sulfide group
Gerlach (36).....	Metallic naphthenates from acetates
Meidert (58).....	Flux for fusing metallic naphthenates
Meidert (59).....	Combination of wool grease and naphthenate driers
Minich (62).....	Stabilizing drier solutions
Minich (63).....	Insoluble naphthenate driers
Pohl and Insbeck (68).....	Washing precipitated naphthenates with hot water
Roon (74).....	Pale naphthenate driers
Roon and Gotham (75).....	Manufacture of naphthenate driers
Roon and Minich (76).....	Naphthenates as grinding agents

fication of the solvent solution, water and excess solvent are removed by distillation. In some cases the precipitated naphthenate may be purified by washing with water under controlled conditions of temperature and agitation. In the second method of manufacture the naphthenic acid is heated with the oxide or carbonate of the metal to be converted to the naphthenate. Since the general principle of manufacture and use of naphthenate driers are as outlined above, reference should be made to the following table of references for information on specific details (table 7).

Unlike esters of the fatty acids of comparable molecular weight, naphthenic acid esters are solvent plasticizers for cellulose derivatives. Schneider (80) proposes the use of naphthenic acid esters of ether alcohols, while Kirsthaller and Kaiser (48) and Barrett and Lazier (6) propose the use of esters of naphthenic alcohols.

Some unusual uses for naphthenic acid and some of its derivatives have also been reported. Schladebach and Hähle (79) advocate copper naphthenate in a rust-proofing paint, while Brizzolara (13) uses various naphthenates in promoting the dispersion of carbon black. Hintermaier (42) records the preparation of a naphthenic acid-silicic acid anhydride, and Cassidy (16) combines naphthenic acids with heterocyclic nitrogen compounds.

The foregoing discussion on the uses of naphthenic acids is probably far from complete, since their stability and acid character suggest many possible synthetic operations. As the composition and structure of the acids are more clearly understood, there is a possibility that they will find further application in synthetic organic chemistry as well as in the fields already developed.

REFERENCES

- (1) ADAMS, E. W., OVITZ, F. K., AND WILEY, E. G. (to Standard Oil Company of Indiana): U. S. patent 2,141,848 (December 27, 1938).
- (2) ALLEMAN, G. (to Sun Oil Company): U. S. patent 1,694,462 (December 11, 1928).
- (3) ALLEMAN, G. (to Sun Oil Company): U. S. patent 1,694,463 (December 11, 1928).
- (4) ANDREWS, T. M., AND LAUER, C. E. (to The Texas Company): U. S. patent 1,804,451 (June 6, 1925).
- (5) ASCHAN, O.: Ber. **23**, 871 (1890); **24**, 2723 (1891).
- (6) BARRETT, H. J., AND LAZIER, W. A. (to E. I. duPont de Nemours and Company): U. S. patent 2,047,664 (July 14, 1936).
- (7) BECKER, A. E. (to Standard Oil Development Company): U. S. patent 1,552,669 (September 8, 1925).
- (8) BECKER, A. E., AND SLOANE, R. G. (to Standard Oil Development Company): U. S. patent 1,785,242 (December 16, 1930).
- (9) BERRY, A. G. V. (to Trinidad Leaseholds, Ltd.): U. S. patent 2,017,391 (October 15, 1935).
- (10) BOGDAN, M. (to Shell Development Company): U. S. patents 2,199,828 and 2,199,829 (May 7, 1940).
- (11) BRANDES, O. L. (to Gulf Research and Development Company): U. S. patent 2,202,826 (June 4, 1940).
- (12) BRAUN, J. VON: Ann. **490**, 100 (1931).
- (13) BRIZZOLARA, R. T. (to E. I. duPont de Nemours and Company): U. S. patent 2,062,159 (November 24, 1936).
- (14) BRUNCK, R., KREUTZER, A., AND BOECK, W. (to Deutsche Gasolin A.-G.): U. S. patent 1,938,513 (December 5, 1933).
- (15) CARR, D. E. (to Union Oil Company of California): U. S. patent 2,081,475 (May 25, 1937).
- (16) CASSIDY, T. A. (to Frank J. Busser and Henry T. Hornidge, as trustees): U. S. patent 1,860,850 (May 31, 1932).
- (17) CHARITSCHKOFF, K. W.: Neft. Dyelo **1905**, 518.
- (18) COOK, L. W. (to The Texas Company): U. S. patent 1,802,336 (April 28, 1931).
- (19) DEGROOTE, M. (to W. S. Barnickel and Company): U. S. patent 1,596,597 (August 17, 1926).

- (20) DEGROOTE, M. (to W. S. Barnickel and Company): U. S. patent 1,596,598 (August 17, 1926).
- (21) DEGROOTE, M. (to The Tretolite Company): U. S. patent 1,940,391 (December 19, 1933).
- (22) DEGROOTE, M. (to The Tretolite Company): U. S. patent 1,940,395 (December 19, 1933).
- (23) DEGROOTE, M. (to The Tretolite Company): U. S. patent 1,940,396 (December 19, 1933).
- (24) DEGROOTE, M., AND WIRTEL, A. F. (to The Tretolite Company): U. S. patent 1,940,392 (December 19, 1933).
- (25) ELLIS, C.: *The Chemistry of Petroleum Derivatives*, Volume I, pp. 1062, 1073. The Reinhold Publishing Corporation, New York (1937).
- (26) ELLIS, C.: *The Chemistry of Petroleum Derivatives*, Volume II, p. 1103. Reinhold Publishing Corporation, New York (1937).
- (27) EWING, F. J. (to Union Oil Company of California): U. S. patent 2,035,696 (March 31, 1936).
- (28) EWING, F. J. (to Union Oil Company of California): U. S. patent 2,035,741 (March 31, 1936).
- (29) EWING, F. J. (to Union Oil Company of California): U. S. patent 2,035,742 (March 31, 1936).
- (30) FISCHER, H. G. M., AND HULSE, S. H. (to Standard Oil Development Company): U. S. patent 2,230,642 (February 4, 1941).
- (31) FISHER, G. M. (to Socony-Vacuum Oil Company): U. S. patent 2,071,862 (January 20, 1936).
- (32) FISHER, G. M. (to Socony-Vacuum Oil Company): U. S. patent 2,116,884 (May 10, 1938).
- (33) FRIZELL, DE R. (to Union Oil Company of California): U. S. patent 1,582,257 (April 27, 1926).
- (34) FRIZELL, DE R. (to Union Oil Company of California): U. S. patent 1,582,258 (April 27, 1926).
- (35) GARDNER, R. H., AND HODGE, H. G. (to Sinclair Refining Company): U. S. patent 1,740,584 (December 24, 1929).
- (36) GERLACH, R. M.: U. S. patent 1,875,999 (September 6, 1932).
- (37) GURWITSCH, L., AND MOORE, H.: *Petroleum Technology*, p. 127. D. Van Nostrand Company, New York (1932).
- (38) HAGEDORN, M. (to Farbenindustrie A.-G.): U. S. patent 1,882,816 (October 18, 1932).
- (39) HENDREY, W. B. (to The Texas Company): U. S. patent 2,058,788 (October 27, 1936).
- (40) HENDREY, W. B. (to The Texas Company): U. S. patent 2,072,053 (February 23, 1937).
- (41) HENDREY, W. B., AND EBAUGH, I. A. (to The Texas Company): U. S. patent 2,014,936 (September 17, 1935).
- (42) HINTERMAIER, A. (to Henkel & Cie): U. S. patent 2,017,000 (October 8, 1935).
- (43) HUGHES, E. M. (to Sun Oil Company): U. S. patent 1,577,723 (March 23, 1926).
- (44) JOHNSON, J. W., JR. (to Atlantic Refining Company): U. S. patent 2,173,117 (September 19, 1939).
- (45) JONES, P. R. (to Balfour, Guthrie, & Company): U. S. patent 1,502,956 (July 29, 1924).
- (46) KAUFMAN, G., AND LAUER, C. E. (to The Texas Company): U. S. patent 1,986,775 (January 1, 1935).
- (47) KAUFMAN, G., AND PURYEAR, O. P. (to The Texas Company): U. S. patent 2,055,795 (September 29, 1936).
- (48) KIRSTHALER, A., AND KAISER, W. J. (to Henkel & Cie): U. S. patent 2,010,727 (August 6, 1935).
- (49) KLOTZ, J. R. M., AND LITTMANN, E. R.: *Ind. Eng. Chem., Anal. Ed.* **12**, 76 (1940).
- (50) KNIGHT, H. (to Standard Oil Company of Indiana): U. S. patent 1,949,799 (March 6, 1934).

- (51) KOMPPA, G.: Ber. **62**, 1562 (1929).
- (52) KRAEMER, G., AND BÖTTCHER, W.: Ber. **20**, 596 (1888).
- (53) LICHTENSTERN, R.: U. S. patent 1,671,284 (May 29, 1928).
- (54) LIDOW, A. P.: Seifensieder-Ztg. **32**, 834 (1905).
- (55) LIMBURG, H. (to Patent and Licensing Corporation): U. S. patents 1,984,023 and 1,984,024 (December 11, 1934).
- (56) MCKEE, J., AND ECKERT, S. B. (to Sun Oil Company): U. S. patent 1,530,386 (March 17, 1925).
- (57) MEAD, B. (to Standard Oil Development Company): U. S. patent 2,025,766 (December 31, 1935).
- (58) MEIDERT, F. (to I. G. Farbenindustrie A.-G.): U. S. patent 1,976,182 (October 9, 1934).
- (59) MEIDERT, F. (to I. G. Farbenindustrie A.-G.): U. S. patent 2,049,396 (July 28, 1930).
- (60) MERRILL, D. R. (to Union Oil Company of California): U. S. patent 1,695,197 (December 11, 1928).
- (61) MERRILL, D. R., AND BLOUNT, A. L. (to Union Oil Company of California): U. S. patent 2,000,244 (May 7, 1935).
- (62) MINICH, A. (to Nuodex Products Company): U. S. patent 2,081,407 (May 25, 1937).
- (63) MINICH, A. (to Nuodex Products Company): U. S. patent 2,116,321 (May 3, 1938).
- (64) NAPHTALI, M.: Fettchem. Umschau **7**, 149 (1933).
- (65) NEELY, G. L. (to Standard Oil Company of California): U. S. patent 2,144,078 (January 17, 1939).
- (66) NEELY, G. L. (to Standard Oil Company of California): U. S. patent 2,163,622 (June 27, 1939).
- (67) NEUKOM, O. W. (to Union Oil Company of California): U. S. patent 2,060,425 (November 10, 1936).
- (68) POHL, F., AND ISENBECK, B. (to I. G. Farbenindustrie A.-G.): U. S. patent 1,974,507 (September 25, 1934).
- (69) POWELL, R. E. (to Standard Oil Development Company): U. S. patent 1,694,280 (December 4, 1928).
- (70) RABINOVICH, A., AND OSENOVA, T.: Chem. Abstracts **29**, 8304 (1935).
- (71) REBBER, L. L. (to Union Oil Company of California): U. S. patent 1,582,227 (April 27, 1926).
- (72) REMY, T. P. (to The Texas Company): U. S. patent 2,045,925 (June 30, 1936).
- (73) ROGERS, F. M., AND McNEIL, C. P. (to Standard Oil Company of Indiana): U. S. patent 1,679,919 (August 7, 1928).
- (74) ROON, L. (to Nuodex Products Company): U. S. patent 2,139,134 (December 6, 1938).
- (75) ROON, L., AND GOTHAM, W. (to Nuodex Products Company): U. S. patent 2,113,496 (April 5, 1938).
- (76) ROON, L., AND MINICH, A. (to Nuodex Products Company): U. S. patent 2,180,721 (November 21, 1939).
- (77) RUTHERFORD, J. T. (to Standard Oil Company of California): U. S. patent 2,108,448 (February 15, 1938).
- (78) SCHELLER: Petroleum **13**, 731 (1917-18).
- (79) SCHLADEBACH, H., AND HÄHLE, H. (to I. G. Farbenindustrie A.-G.): U. S. patent 1,983,006 (December 9, 1934).
- (80) SCHNEIDER, G. (to Celanese Corporation of America): U. S. patent 2,016,392 (October 8, 1935).
- (81) SCHULTZ, F.: Chem.-Ztg. **55**, 729 (1908).
- (82) SCHULZ, F.: Chem.-Ztg. **32**, 596 (1908).
- (83) SCHUTZE, H. G., SHIVE, B., AND LOCHTE, H. L.: Ind. Eng. Chem., Anal. Ed. **12**, 262 (1940).
- (84) STEIK, K. T. (to National Oil Products Company): U. S. patent 2,068,088 (January 19, 1937).

- (85) SWERISSEN, H. T. (to Shell Development Company): U. S. patent 2,026,073 (December 31, 1935).
 (86) TANAKA, Y., AND NAGAI, S.: J. Fac. Eng. Tokyo Imp. Univ. **16**, 1471 (1925).
 (87) TANAKA, Y., AND NAGAI, S.: J. Fac. Sci. Imp. Univ. Tokyo **16**, 117, 183 (1926); **20**, 2832 (1926).
 (88) TEICHMANN, C. F. (to The Texas Company): U. S. patent 2,015,045 (September 17, 1935).
 (89) TERRELL, H. T., HUGHES, E. M., AND CARTER, P. L. (to Sun Oil Company): U. S. patent 2,056,913 (October 6, 1936).
 (90) TEXAS COMPANY: British patent 510,496 (December 18, 1937).
 (91) TREVOR, J. S.: Chem. Industries **45**, 661 (1939).
 (92) WELLS, H. M., AND SOUTHCOMBE, J. E.: U. S. patent 1,319,129 (October 21, 1919).
 (93) WUNSCH, J. A.: U. S. patent 2,003,640 (June 4, 1935).
 (94) ZELINSKY, N., AND CHUKSANOV, A.: Ber. **57**, 42 (1924).
 (95) ZELINSKY, N., AND POKROVSKAIA, E.: Ber. **57**, 51 (1924).

Supplementary patent references

U. S. patents

1,286,179	R. E. Humphreys
1,425,882	H. T. Maitland (August 15, 1922).
1,425,883	H. T. Maitland (August 15, 1922).
1,425,884	H. T. Maitland (August 15, 1922).
1,425,885	H. T. Maitland (August 15, 1922).
1,474,933	R. E. Humphreys, F. M. Rogers, and O. E. Bransky (November 20, 1923).
1,482,416	W. O. Snelling (February 5, 1924).
1,529,658	J. McKee and S. B. Eckert (March 17, 1925). Grease.
1,681,657	O. E. Bransky (August 21, 1928).
1,694,461	G. Alleman (December 11, 1928).
1,720,821	S. P. Coleman (July 16, 1929).
1,784,262	R. C. Wheeler and P. W. Prutzman (December 9, 1930).
1,823,615	N. E. Lemmon and F. V. Grimm (September 15, 1931).
1,886,647	S. P. Coleman (November 8, 1932).
1,931,855	G. Alleman (October 24, 1933).
1,931,880	H. F. Angstadt (October 24, 1933).
19,179*	R. C. Wheeler and P. W. Prutzman (May 22, 1934).
1,984,432	J. Robinson (December 18, 1934).
1,998,765	W. B. Logan (April 23, 1935).
2,001,108	C. K. Parker (May 14, 1935). Transformer oil.
2,007,146	F. M. Rogers (July 2, 1935).
2,039,106	R. F. Nelson and L. Zapf (April 28, 1936).
2,093,001	A. L. Blount (September 14, 1937).
2,102,633	K. E. Long (December 21, 1937).
2,138,087	P. E. Burchfield (November 29, 1938).
2,157,766	K. E. Long (May 9, 1939).
2,157,767	K. E. Long (May 9, 1939).
2,157,768	K. E. Long (May 9, 1939).
2,191,449	A. L. Blount (February 27, 1940).
2,205,994	C. C. Towne (June 25, 1940). Manufacture of naphthenates.
2,206,002	A. J. Deutser and R. F. Nelson (January 25, 1940). Manufacture of naphthenates.

* Reissue.

Supplementary references

- CHERCHEFFSKY, N.: *Les acides de naphthe et leur applications*. H. Dunod et E. Pinat, Paris (1910).
- NAPHTALI, M.: *Naphthensäuren und Naphthensulfosäuren*. Wissenschaftliche Verlagsgesellschaft, Stuttgart (1934).
- NAPHTALI, M.: *Chemie, Technologie, und Analyse der Naphthensäuren*. Wissenschaftliche Verlagsgesellschaft, Stuttgart (1927).