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2,820,053

TEREPHTHALAMATES

Bruce W. Hotten, Orinda, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

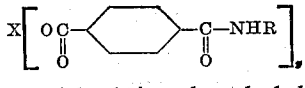
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14 Claims. (Cl. 260—471)

This invention relates to terephthalamic acids and the derivatives thereof as new compounds. These new compounds, particularly the metal soaps thereof, are useful as oil-thickening agents. For example, these metal soaps can thicken lubricating oils to the consistency of greases, and the resulting greases are unusually stable to oxidation, and they also have unusually high melting points.

The new compounds of the present invention contain a benzene nucleus having substituents thereon which are in positions para to each other, which positions impart new characteristics and properties to these compounds. The para position of the substituents of the benzene nucleus imparts thermal stability to this new compound. When the same substituents on a benzene ring are present in the ortho position, the compounds derived therefrom are not as thermo-stable. For example, lubricants thickened with the new compounds of this invention have greater heat stability than lubricants to which the latter compounds have been added. The new compounds of the present invention have properties characterizing them as plasticizers, wetting agents, detergents, surface-active agents, etc., and, in addition, these new compounds are useful as thickening agents for lubricating oils, for example, as thickening agents for the formation of grease compositions.

The general formula for these new compounds is as follows:



wherein R is a straight-chain or branched-chain, saturated or unsaturated hydrocarbon radical having from 1 to 22 carbon atoms, and X is hydrogen, a metal, a salt-forming radical, or an ester radical containing from 1 to 22 carbon atoms, and y is a number having a value equal to the valence of X.

Examples of R include the following radicals: methyl; ethyl; propyl; n-butyl; tertiary butyl; pentyl, 2-methylbutyl; 2,3-dimethylbutyl; 2,3-dimethylhexyl; 2-ethylhexyl; hexyl, heptyl; octyl; decyl; decenyl; dodecyl; tetradecyl; hexadecyl; hexadecenyl; octadecyl; octadecenyl; eicosyl; docosyl; cyclohexyl; etc.

Examples of X as ester radicals include the following: methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, isooctyl, octenyl, nonyl, decyl, decenyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, etc.

Examples of X as metals include lithium, sodium, potassium, copper, silver, magnesium, calcium, zinc, strontium, cadmium, barium, aluminum, tin, antimony, chromium, molybdenum, manganese, iron, cobalt, nickel, lead, etc. In the thickening of lubricating oils, it has been found that the metals lithium, sodium, and barium are particularly effective in thickening lubricating oils to grease compositions having increased melting points and improved texture.

As a salt-forming radical, X can be an ammonia radical, a nitrogen base radical, etc.

Examples of the new compounds of this invention include: methyl N-methyl terephthalamate, methyl N-butyl terephthalamate, methyl N-phenyl terephthalamate, methyl N-octadecyl terephthalamate, ethyl N-dodecyl terephthalamate, octyl N-dodecyl terephthalamate, decyl N-tetradecyl terephthalamate, dodecyl N-ethyl terephthalamate, octadecyl N-octadecyl terephthalamate, N-methyl terephthalamic acid, N-ethyl terephthalamic acid, N-butyl terephthalamic acid, N-hexyl terephthalamic acid, N-octyl terephthalamic acid, N-decyl terephthalamic acid, N-octyl terephthalamic acid, N-tetradecyl terephthalamic acid, N-hexadecyl terephthalamic acid, N-octadecyl terephthalamic acid, N-eicosyl terephthalamic acid, N-docosyl terephthalamic acid, sodium N-octyl terephthalamate, sodium N-decyl terephthalamate, sodium N-tetradecyl terephthalamate, sodium N-hexadecyl terephthalamate, sodium N-octadecyl terephthalamate, potassium N-octadecyl terephthalamate, potassium N-methyl terephthalamate, potassium N-octyl terephthalamate, potassium N-eicosyl terephthalamate, potassium N-docosyl terephthalamate, lithium N-decyl terephthalamate, lithium N-octadecyl terephthalamate, lithium N-eicosyl terephthalamate, lithium N-docosyl terephthalamate, calcium di(N-butyl terephthalamate), calcium di(N-octyl terephthalamate), calcium di(N-tetradecyl terephthalamate), calcium di(N-octadecyl terephthalamate), barium di(N-hexyl terephthalamate), barium di(N-octyl terephthalamate), barium di(N-octadecyl terephthalamate), barium di(N-eicosyl terephthalamate), barium di(N-docosyl terephthalamate), etc.

A method of preparing the new compounds of this invention includes dissolving a dialkyl ester of terephthalic acid in a solvent (e. g., benzene), to which solution is further added a basic substance (e. g., an alcohol solution of potassium hydroxide). The resulting reaction mixture is then heated for a time sufficient to complete the reaction. The salt of terephthalic acid thus formed immediately precipitates from the solvent blend upon formation, and the product is recovered as a precipitate.

The recovered metal salts of monoalkyl esters of terephthalic acid thus formed are hydrolyzed to form the acids. The corresponding terephthaloyl chlorides are then formed by treating the acids with thionyl chloride in a solvent (e. g., benzene). The resulting mixture is refluxed for a period sufficient to complete the reaction, after which any excess chlorinating agent and solvent are removed by distillation. The acid chloride is then treated wtih an amine (e. g., "octadecyl" amine) to form the corresponding monoester of terephthalamic acid, which can be treated with a basic substance to form the salt thereof.

Another method of preparing the new monoesters of terephthalamic acids includes the addition of a phosphorus halide (e. g., phosphorus trichloride) to a tertiary amine (e. g., triethylamine) solution of a monoester of terephthalic acid and a primary amine.

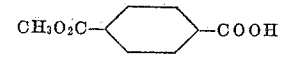
The following examples serve to illustrate the preparation of the new compounds of this invention.

EXAMPLE 1.—PREPARATION OF METHYL N-"OCTADECYL" TEREPHTHALAMATE

A mixture of 45 lbs. of dimethyl terephthalate and 255 lbs. of benzene was heated to 55° C. until all of the dimethyl terephthalate was dissolved, after which a solution of 12.3 lbs. of potassium hydroxide in 58.5 lbs. of absolute alcohol was added. The heating was continued at 55° C. for an additional 50 minutes.

It is to be particularly noted that in this reaction only one methyl group is saponified, and when this saponification has been completed, the salt precipitates from the benzene-alcohol mixture.

Ten gallons of water was added to the above mixture to dissolve the potassium salt of monomethyl terephthalate thus formed. The aqueous layer of the salt was separated, and to this aqueous layer was added 3.5 liters of concentrated sulfuric acid at room temperature to form the free monomethyl ester of terephthalic acid having the following formula:



This acid was filtered, washed with water, and dried in vacuuo. After purification, the neutralization equivalent of the acid thus formed was 180, which is equal to the theoretical neutralization equivalent.

28 lbs. of the acid was dispersed in 37 lbs. of benzene and heated to about 85° C., after which 20.5 lbs. of thionyl chloride was added over a period of 2 hours at this temperature. After the complete addition of the thionyl chloride, the mixture was refluxed for four hours. The excess thionyl chloride and benzene were then removed by distillation. The product obtained at this point had the formula:



A mixture of 25 lbs. of this acid chloride, 9.5 lbs. of triethylamine, and 26.6 lbs. of "octadecyl" amine was heated at about 70° C. until the amine had substantially wholly dispersed, after which the mixture was heated at about 80° C. for 15 minutes.

To the above mixture was added 15 gallons of water at 90° C., after which the mixture was filtered.

The methyl N-"octadecyl" terephthalamate thus prepared was washed three times with hot water and dried. The saponification equivalent of the final product was 471 (the average of four determinations), and the melting point was 115° C.

The "octadecyl" amine used herein was a commercial preparation of amines known as "Armeen HT," sold by the Armour Company, Chicago, Illinois, and containing 25% hexadecylamine, 70% octadecylamine, and 5% octadecenylamine. 85% of this mixture consists of N-primary amines.

EXAMPLE 2.—PREPARATION OF METHYL N-"OCTADECYL" TEREPHTHALAMATE

180 grams (1 mole) of monomethyl terephthalate, 300 grams (1 mole) of "octadecyl" amine, 300 ml. (2.16 moles) of triethylamine, and 500 ml. of toluene were charged to a glass resin flask. The whole mixture was heated with agitation to 45° C. to form a solution, after which 44 ml. (0.5 mole) of phosphorus trichloride was added dropwise over a period of 30 minutes at temperatures ranging from 45° C. to 60° C. The whole mixture was then heated at reflux temperature (115° C.) for a period of 2.5 hours, after which the mixture was cooled slightly and 2 liters of toluene were added. The mixture was washed with water at temperatures of about 65° C. to about 95° C. until the water was negative to the chloride ion test. After the separation of the toluene layer from the water layer, the toluene solution was cooled to room temperature to precipitate out the monomethyl-N-octadecyl terephthalamate. The precipitate was recovered and washed with diethyl ether and dried. The saponification number (milligrams of KOH per gram of sample) of the product was 441. (The theoretical value is 440.) A 78% of theoretical yield was obtained. Further quantities of the product can be recovered by working up the water washings.

EXAMPLE 3.—PREPARATION OF METHYL N-"OCTADECYL" TEREPHTHALAMATE

3880 grams (21.6 moles) of monomethyl terephthalate, 6000 grams (20 moles) of "octadecyl" amine, 4157 grams (41.2 moles) of triethylamine, and 6000 grams of toluene were charged to an iron vessel and heated, with agitation,

to temperatures in the range 65° C. to 100° C. until a solution was obtained. The mixture was cooled to about 40° C., and 1400 grams (10.2 moles) of phosphorus trichloride were added slowly during a period of 45 minutes. The temperature of the mixture was increased to reflux temperature and maintained at that temperature for 2.5 hours, after which the mixture was cooled to 90° C. and washed with hot water until the water washings were negative to the chloride ion test. The toluene was removed by distillation, leaving a light tan solvent as the product. The saponification number of this crude product was 500.

EXAMPLE 4.—PREPARATION OF METHYL N-"OCTADECYL" TEREPHTHALAMATE

229 grams (1 mole) of potassium methyl terephthalate, 300 grams (1 mole) of "octadecyl" amine, 111 grams (1.1 mole) of triethylamine, and 750 ml. of toluene were charged to a resin flask and heated to 80° C. until complete solution for the reactants in the triethylamine and toluene. The mixture was cooled to 40° C., at which temperature the mixture was a smooth, soft paste. 48 ml. (0.55 mole) of phosphorus trichloride was added dropwise, over a period of 25 minutes, during which time the temperature was maintained below 60° C. After the addition of the phosphorus trichloride, the temperature was increased to 115° C. (reflux temperature) and maintained at that temperature for 6 hours. At this point, melting point determination of a sample of the product indicated that the reaction was incomplete. Therefore, the toluene was removed by distillation, and 750 ml. of xylene was added. The mixture was heated at reflux temperature (140° C.) for 6 hours, after which the reaction mixture was washed alternately with water, aqueous acetic acid solutions, and triethylamine solutions. The xylene solution was cooled, and methyl N-"octadecyl" terephthalamate was separated from the xylene by filtration. The product thus recovered had a saponification number of 455. The yield was 88% of theory.

EXAMPLE 5.—PREPARATION OF METHYL N-"DECYL" TEREPHTHALAMATE

122 grams of "decyl" amine, 158 grams of methyl terephthaloyl chloride, and 85 grams of triethylamine were charged to a reaction flask and heated to temperatures as high as 120–130° C. for a period of about 10 minutes. The reaction product was water washed three times with vigorous agitation to remove the water-soluble triethyl ammonium chloride, after which the product was crystallized twice from 95% ethanol and dried. The reaction product had a saponification number of 324 (theory equals 336).

The "decyl" amine was obtained from "Armeen 10D," a product sold by the Armour Company, Chicago, Illinois, and containing 90% decylamine, 3% octylamine, and 7% dodecylamine.

EXAMPLE 6.—PREPARATION OF METHYL N-"TALLOW" TEREPHTHALAMATE

A mixture of 244 grams of "tallow" amine, 180 grams of methyl terephthaloyl chloride, 95 grams of triethylamine, and 35 ml. of benzene was heated to temperatures of about 120–130° C., with agitation, for a period of about 10 minutes, after which the product was thoroughly water washed to remove the triethyl ammonium chloride. The reaction product had a saponification number of 468 (theory equals 472).

EXAMPLE 7.—PREPARATION OF METHYL N-"OCTADECYL" TEREPHTHALAMATE

A mixture of 107 grams of methyl terephthaloyl chloride, 138 grams of "octadecyl" amine, 55 grams of triethylamine, and a small amount of benzene was heated to 120–130° C. for a period of about 10 minutes. After the reaction product was water washed, the benzene was removed by distillation. The product, which was crystal-

lized from alcohol, had a saponification number of 409 (theory equals 438), and a melting point of 117° C. The "octadecyl" amine was a product known as "Armeen 18D," which is sold by the Armour Company, Chicago, Illinois and contains 98% octadecylamine.

EXAMPLE 8.—PREPARATION OF METHYL N-BUTYL TEREPHTHALAMATE

A mixture of 225 grams (1 mole) of potassium methyl terephthalate, 146 grams (2 moles) of N-butylamine, and approximately 1 liter of toluene was charged to a 2-liter resin flask. To this mixture 43.6 ml. of phosphorous trichloride was added dropwise over a period of 35 minutes at temperatures ranging from 25° C. to 70° C. The whole mixture was heated at the reflux temperature of 110° C. for a period of 6 hours, after which it was cooled to room temperature, acidified with hydrochloric acid, and washed with hot water until the chloride ion test was negative. The mixture was then made basic with ammonium hydroxide and water washed until no methyl hydrogen terephthalate was obtained on acidification. The methyl N-butyl terephthalamate was recovered as white crystals. The saponification equivalent was 245 (theory equals 235), the percent nitrogen was 5.99 (theory equals 5.96), and the melting point was 121° C. This compound was soluble in hot toluene, in mineral oil at 300° F., and in phenylmethyl polysiloxane (Dow-Corning 550) at 300° F.

EXAMPLE 9.—PREPARATION OF METHYL N-PHENYL TEREPHTHALAMATE

A mixture of 146 grams of potassium methyl terephthalate, 150 grams of aniline, and 750 ml. of toluene was charged to a 2-liter resin flask. To this mixture 35.4 ml. of phosphorus trichloride were added dropwise over a temperature range of 25–70° C., after which the mixture was heated at 110° C. for a period of 6 hours. The mixture was cooled to room temperature, acidified with hydrochloric acid, and washed free of the chloride ion. The mixture was made basic with ammonium hydroxide, then water washed until the acidified extract yielded no precipitate (test for methyl hydrogen terephthalate) on acidification. The raffinate was cooled and filtered, and the crystals obtained therefrom were recrystallized from isopropanol. The crystals, which had a melting point of 193° C., contained 5.41% nitrogen (theory equals 5.49). These crystals were insoluble in toluene, and they were soluble in mineral oil and in phenyl methyl polysiloxane (Dow-Corning 550) at 400° F. When the mineral oil and the phenylmethyl polysiloxane solutions were cooled to ambient temperatures, a paste was obtained.

EXAMPLE 10.—PREPARATION OF SODIUM N-"OCTADECYL" TEREPHTHALAMATE

A mixture of 21 grams of a methyl N-"octadecyl" terephthalamate, 200 ml. of dioxane, 2 grams of sodium hydroxide (CP), and 50 ml. of water was heated at reflux temperature for one hour. The reaction mixture was diluted with ether, filtered, and washed with warm carbon tetrachloride. The crystals of sodium N-"octadecyl" terephthalamate contained 3.1% nitrogen (theory equals 3.19) and 16.9% sulfate ash (theory equals 16.2). The crystals, which had a melting point in excess of 500° C., were insoluble in water and common organic solvents. X-ray diffraction pattern analyses are set forth in Table I hereinbelow.

EXAMPLE 11.—PREPARATION OF BARIUM DI-(N-"OCTADECYL" TEREPHTHALAMATE

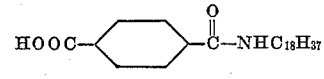
A mixture of 15 grams of methyl N-"octadecyl" terephthalamate, 8 grams of barium hydroxide octahydrate in 20 ml. of water, and 200 ml. of Carbitol (the monoethyl ether of diethylene glycol) was heated at reflux temperatures of 115° C. for a period of 4 hours. The reaction mixture was washed with hot dioxane. The resulting barium di-(N-"octadecyl" terephthalamate) had a melting point in excess of 500° C. The sulfate ash was 27.5% (theory equals 28.0%).

EXAMPLE 12.—PREPARATION OF OCTADECYL N-"OCTADECYL" TEREPHTHALAMATE

A mixture of 21 grams of methyl N-"octadecyl" terephthalamate, 16 grams of n-octadecanol, and 1 gram of sodium methylate was heated, with stirring, for 2 hours at 200° C. The methanol which was formed was removed by distillation, and the crystalline material was recrystallized from toluene.

EXAMPLE 13.—PREPARATION OF N-"OCTADECYL" TEREPHTHALAMIC ACID

In the preparation of N-"octadecyl" terephthalamic acid, 1 mole of the sodium N-"octadecyl" terephthalamate of Example 10, hereinabove, can be acidified with a molar amount of an acid (e. g., sulfuric acid or hydrochloric acid). The acid thus formed has the formula:



Interatomic distances of the sodium and barium salts of the above Examples 10 and 11 are set forth in Table I, hereinbelow. These interatomic distances, as determined by X-ray diffraction patterns, are as follows:

Table I

Compound	Sodium N-"octadecyl" terephthalamate		Barium di-(N-"octadecyl" terephthalamate)	
	I	II	I	II
Distances in angstrom units (I), and relative intensities (II) of lines of X-ray pattern	30.4	8	29.9	25
	29.4	8	19.8	18
	21.5	4	15.0	3
	20.0	6	11.9	7
	8.41	1.5	11.5	2
	5.21	7	9.93	4
	4.67	11	9.50	1.5
	4.50	11	8.50	9
	3.83	17	8.14	3
	3.08	4	7.46	4
	----------	----------	7.10	1.5
	----------	----------	6.63	5
	----------	----------	6.32	1
	----------	----------	5.96	2
	----------	----------	5.40	3
	----------	----------	5.16	1
	----------	----------	4.96	1.5
	----------	----------	4.65	2
	----------	----------	4.57	3
	----------	----------	4.53	2
	----------	----------	4.25	1.5
	----------	----------	3.98	1.5
	----------	----------	3.72	1

As noted hereinabove, the metal salts of terephthalamic acids of this invention are useful as thickening agents for lubricating oils. The following example illustrates the use of a metal salt of terephthalamic acid as a thickening agent in oil to form a grease composition.

EXAMPLE 14.—PREPARATION OF A GREASE THICKENED WITH A SODIUM N-"OCTADECYL" TEREPHTHALAMATE

A mixture of 66 lbs. of the N-"octadecyl" terephthalamic acid ester of Example 1, hereinabove, 0.6 lbs. of sodium hydroxide, and 132 lbs. of a California solvent-refined paraffin base oil having a viscosity of 1700 SSU at 37° C. was heated to 160° C. at a pressure of 73 p. s. i. for one hour. The mixture was then blown with air to remove the water, after which an additional 35 lbs. of the same base oil was added, and the mixture was heated to 315° C. For the purpose of preparing a grease containing 10% of this sodium terephthalamate, 4.4 lbs. of this mixture was diluted with 0.8 lb. of the same base oil. The whole mixture was then drawn into shallow pans and cooled, after which it was milled through a col-

loid mill. The grease thus prepared had a melting point (i. e., a dropping point) of 260° C.

This application is a continuation-in-part of Hotten application Serial No. 401,697, filed December 31, 1953 (now abandoned).

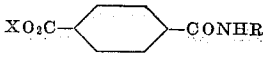
I claim:

1. Compounds having the general formula



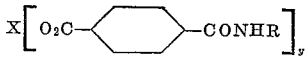
wherein R is an aliphatic hydrocarbon radical having from 1–22 carbon atoms, and X is a member of the group consisting of hydrogen, a metal selected from the group consisting of alkali metals and alkaline earth metals, and an aliphatic hydrocarbon radical having from 1–22 carbon atoms.

2. Compounds having the general formula



wherein R is an alkyl radical having from 1–22 carbon atoms, and X is a member of the group consisting of hydrogen, alkali metals, alkaline earth metals, and an aliphatic hydrocarbon radical having from 1–22 carbon atoms.

3. Compounds having the general formula



wherein R is an alkyl radical containing from 1 to 22 carbon atoms, X is a metal selected from the group consisting of alkali metals and alkaline earth metals, and y is a number having a value equal to the valence of the metal X.

4. The compound of claim 3, wherein X is an alkali metal.

5. The compound of claim 3, wherein X is sodium.

6. The compound of claim 3, wherein X is an alkaline earth metal.

7. The compound of claim 3, wherein X is barium.

8. Compounds having the general formula



wherein R is an alkyl radical containing from 1 to 22 carbon atoms.

9. Compounds having the general formula



wherein R is an alkyl radical containing from 1 to 22 carbon atoms, and X is an aliphatic hydrocarbon radical containing from 1 to 22 carbon atoms.

10. The compound, methyl N-decyl terephthalamate.

11. The compound, methyl N-octadecyl terephthalamate.

12. The compound, N-octadecyl terephthalamic acid.

13. The compound, barium di(N-octadecyl terephthalamate).

14. The compound, sodium N-octadecyl terephthalamate.

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