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BORATES OF N-HYDROXYALKYL-NITROGEN-HETEROCYCLIC SATURATED COMPOUNDS

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ABSTRACT OF THE DISCLOSURE

Borate of N-hydroxyalkyl-nitrogen-heterocyclic compound free of unsaturation in the heterocyclic ring, exemplified by a borate of N-hydroxyethyl-N'-sec-octyl-piperazine. The compounds are useful as weathering stabilizers for organic substrates normally subject to deterioration by weathering, such as plastics, also as antioxidants for hydrocarbon distillates.

This invention relates to a novel composition of matter comprising a borate of an N-hydroxyalkyl-heterocyclic saturated compound, and to the use thereof as an additive to organic substrates.

In a preferred embodiment the novel compound of the present invention is a borate of N-hydroxyalkyl-piperazine and preferably of N-hydroxyalkyl-N'-alkyl-piperazine. In a particularly preferred embodiment the N'-alkyl substituent is of secondary alkyl configuration. Accordingly, particularly preferred compounds of the present invention include

borate of N-hydroxyethyl-N'-isopropyl-piperazine, borate of N-hydroxyethyl-N'-sec-butyl-piperazine, borate of N-hydroxyethyl-N'-sec-pentyl-piperazine, borate of N-hydroxyethyl-N'-sec-hexyl-piperazine, borate of N-hydroxyethyl-N'-sec-heptyl-piperazine, borate of N-hydroxyethyl-N'-sec-octyl-piperazine, borate of N-hydroxyethyl-N'-sec-nonyl-piperazine, borate of N-hydroxyethyl-N'-sec-decyl-piperazine, borate of N-hydroxyethyl-N'-sec-undecyl-piperazine, borate of N-hydroxyethyl-N'-sec-dodecyl-piperazine, borate of N-hydroxyethyl-N'-sec-tridecyl-piperazine, borate of N-hydroxyethyl-N'-sec-tetradecyl-piperazine, borate of N-hydroxyethyl-N'-sec-pentadecyl-piperazine, borate of N-hydroxyethyl-N'-sec-hexadecyl-piperazine, borate of N-hydroxyethyl-N'-sec-heptadecyl-piperazine, borate of N-hydroxyethyl-N'-sec-octadecyl-piperazine, borate of N-hydroxyethyl-N'-sec-nonadecyl-piperazine, N-hydroxyethyl-N'-sec-eicosyl-piperazine, etc.

In still another embodiment the novel compound is a borate of N-hydroxyethyl-N'-cycloalkyl-piperazine, the cycloalkyl preferably being cyclohexyl, although it may be cyclobutyl, cyclopentyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl, etc. In still another embodiment the piperazine may be substituted on the ring by alkyl, cycloalkyl or aryl groups. It is understood that the hydroxyethyl group may be replaced by hydroxypropyl, hydroxybutyl, hydroxypentyl, hydroxyhexyl, hydroxyheptyl, hydroxyoctyl, etc.

The particular compounds set forth above are derivatives of piperazine in which the nitrogen atoms are in a position para to each other. Another embodiment comprises the borates of corresponding compounds prepared from hexahydropyrimidine, in which the nitrogen atoms are in a position meta to each other, and from hexahydropyridazine, in which the nitrogen atoms are in a position ortho to each other. Illustrative compounds in this embodiment include borate of N-hydroxyalkyl-N'-sec-alkyl-hexahydropyrimidine, in which the hydroxyalkyl moiety

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contains from 1 to 8 or more carbon atoms and in which the sec-alkyl group contains from 3 to 20 or more carbon atoms, borate of N-hydroxyalkyl-N'-cycloalkyl-hexahydropyrimidine, in which the cycloalkyl preferably is cyclohexyl, although it may contain from 4 to 12 or more carbon atoms in the cycloalkyl group and the hydroxyalkyl moiety contains from 1 to 8 carbon atoms, borate of N-hydroxyalkyl-N'-sec-alkyl-hexahydropyridazine, in which the hydroxyalkyl moiety contains from 1 to 8 or more carbon atoms and in which the sec-alkyl group contains from 3 to 20 or more carbon atoms, borate of N-hydroxyalkyl-N'-cycloalkyl-hexahydropyridazine, in which the cycloalkyl preferably is cyclohexyl, although it may contain from 4 to 12 or more carbon atoms in the cycloalkyl group and the hydroxyalkyl moiety contains from 1 to 8 carbon atoms. Here again, the ring may be substituted by alkyl, cycloalkyl or aryl groups.

In another embodiment the novel compound of the present invention is a borate of N-hydroxyalkyl-piperidine and preferably of N-hydroxyalkyl-piperidine containing hydrocarbon substituents attached to the ring. Illustrative compounds in this embodiment include borate of p-sec-alkyl-N-hydroxyalkyl-piperidine in which the sec-alkyl group contains from 3 to 20 or more carbon atoms and in which the hydroxyalkyl moiety contains from 2 to 8 or more carbon atoms. In another embodiment the alkyl substituent may be in the ortho- or meta-position. In still another embodiment, two alkyl substituents are attached to the piperidine ring and these may be in the 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-positions. The alkyl groups preferably are sec-alkyl of from 3 to 20 or more carbon atoms each, although, in another embodiment, one of the alkyl groups may be a primary alkyl group of from 1 to 20 carbon atoms and the other is a sec-alkyl group of from 3 to 20 carbon atoms.

In still another embodiment the novel compound of the present invention is a borate of an N-hydroxy-alkyl-heterocyclic saturated five membered ring. Borates of N-hydroxyalkyl-N'-sec-alkyl-imidazolidine and N-hydroxyalkyl-N'-cycloalkyl-imidazolidine are the preferred compounds. In the imidazolidine ring the nitrogens are in 1,3-positions in the five membered ring. Other compounds include borate of N-hydroxyalkyl-pyrrolidine, borate of N-hydroxyalkyl-pyrazolidine, borate of N-hydroxyalkyl-hydrogenated 1,2,3-triazole, borate of N-hydroxyalkyl-hydrogenated 1,2,4-triazole, etc., and preferably these compounds containing a substituent, preferably sec-alkyl or cycloalkyl, attached to the ring and/or to one or more of the nitrogen atoms in the compounds containing more than one nitrogen atom. In still another embodiment the novel compound comprises a borate of N-hydroxy-hydrogenated indole, borate of N-hydroxyalkyl-hydrogenated carbazole, borate of N-hydroxyalkyl-hydrogenated quinoline, borate of N-hydroxyalkyl-hydrogenated acridine, borate of N-hydroxyalkyl-hydrogenated phenazine, etc. Here again, it is understood that the hydroxyalkyl moiety may contain from 2 to 8 or more carbon atoms and that alkyl, cycloalkyl or aryl substituents may be attached to the ring or to one of the nitrogen atoms for compounds containing more than one nitrogen atom.

The novel compounds of the present invention are prepared in any suitable manner. In some cases, the N-hydroxy-alkyl-heterocyclic saturated compound may be purchased in the open market and then is reacted with suitable borylating agent as will be hereinafter described. When the N-hydroxyalkyl-heterocyclic compound is not available commercially, it may be prepared in any suitable manner. For example, piperazine may first be subjected to oxyalkylation and, when a substituent is to be attached to the other nitrogen atom, this is effected by reductive alkylation. In another method, piperazine

may first be subjected to reductive alkylation and then is subjected to oxyalkenylation. The oxyalkenylation is effected in any suitable manner and may be accomplished by charging the piperazine or N-alkyl-piperazine into a reaction zone and passing alkylene oxide, particularly ethylene oxide, into the reaction zone. The alkylene oxide is used in a proportion of one mole thereof per each nitrogen atom to be oxyalkenylated. In the case of piperazine, equal mole proportions of alkylene oxide and piperazine are employed. When desired, an excess of one of the reactants may be present in order to insure complete reaction. The oxyalkenylation reaction readily occurs at a low temperature which may range from room temperature to 150° C. in the absence of a catalyst. As hereinbefore set forth, ethylene oxide is preferred. Other alkylene oxides include propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, etc., as well as styrene oxide, epichlorohydrin, etc. When oxyalkenylation is conducted first, the reaction products are fractionated or otherwise treated to separate the mono-oxyalkenylated product from the reaction mixture.

As hereinbefore set forth, in a preferred embodiment the piperazine or N-hydroxyalkyl-piperazine is subjected to reductive alkylation. In one embodiment the reductive alkylation is effected using a ketone in order to prepare the corresponding N-hydroxyalkyl-N-sec-alkyl-piperazine. Any suitable ketone may be used and will be selected to produce the desired substituent. Illustrative preferred ketones include acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, methyl pentyl ketone, methyl hexyl ketone, methyl heptyl ketone, methyl octyl ketone, methyl nonyl ketone, methyl decyl ketone, etc., diethyl ketone, ethyl propyl ketone, ethyl butyl ketone, ethyl pentyl ketone, ethyl hexyl ketone, ethyl heptyl ketone, ethyl octyl ketone, ethyl nonyl ketone, etc., dipropyl ketone, propyl butyl ketone, propyl pentyl ketone, propyl hexyl ketone, propyl heptyl ketone, propyl octyl ketone, etc., dibutyl ketone, butyl pentyl ketone, butyl hexyl ketone, butyl heptyl ketone, butyl octyl ketone, etc., dipentyl ketone, pentyl hexyl ketone, pentyl heptyl ketone, pentyl octyl ketone, etc., dihexyl ketone, hexyl heptyl ketone, hexyl octyl ketone, etc., diheptyl ketone, heptyl octyl ketone, dioctyl ketone, etc. It is understood that the ketone may be of straight or branched chain configuration. Cycloalkyl ketones include particularly cyclohexanone. Ketones are available commercially or may be synthesized as required. A number of ketones and particularly the higher boiling ketones are available as mixtures which are either products or byproducts of commercial operations. These mixtures generally are available at comparatively low cost and, as another advantage of the present invention, the mixtures may be used without the added time and expense of separating specific compounds in pure state. One such mixture available commercially is "Stearone" which is diheptadecyl ketone.

The reductive alkylation of the ketone and piperazine or hydroxyalkyl-piperazine is effected in any suitable manner. The reaction is effected using at least one mole of ketone per mole of nitrogen atom to be reductively alkylated. In the case of piperazine, this means equal mole proportions of ketone and piperazine. When reacting hydroxyalkyl-piperazine an excess of ketone, which may range up to about 20 mole proportions of ketone per 1 mole proportion of heterocyclic nitrogen compound, generally is employed to insure complete reaction. In one embodiment the reaction is effected in the presence of hydrogen and a suitable reductive alkylation catalyst in one step, which may be either continuous or batch type operation. Any suitable reductive alkylation catalyst is employed including those containing nickel, platinum, palladium, etc., preferably composited with a suitable support. A particularly preferred catalyst comprises a composite of platinum and alumina, which may or may not contain combined halogen. The platinum generally is

present in the catalyst in a concentration of from about 0.1 to about 2% by weight of the final catalyst and the halogen, when present, is in a concentration of total halogen of from about 0.01% to about 1% by weight of the final catalyst, the halogen preferably comprising fluorine and/or chlorine. Another suitable catalyst comprises an intimate mixture of copper oxide, chromium oxide and barium oxide. When using the platinum catalyst, the temperature generally will be within the range of from about 90° to about 260° C. and a hydrogen pressure of from about 100 to about 3000 pounds per square inch or more.

In a continuous type operation, the catalyst is disposed as a fixed bed in a reaction zone and the N-hydroxy-alkyl-piperazine, ketone and hydrogen, at the required temperature and pressure, are passed through the catalyst in either upward or downward flow. The reactor effluent is separated into a hydrogen stream and unreacted products, all or part of which may be recycled to the reaction zone, and the alkylated N-hydroxyalkyl-piperazine is separated from the other products. In a batch type operation, the N-hydroxy-alkyl-piperazine, ketone and catalyst are disposed in a reaction zone which is pressured with hydrogen and then heated to the desired temperature. After cooling, the products are separated to recover the alkylated N-hydroxy-alkyl-piperazine. While the one-step process generally is preferred, it is understood that the reaction may be effected in two steps. In the first step, effected in the absence of hydrogen, the Schiff base is first prepared and then is dehydrogenated in a separate step to form the alkylated N-hydroxyalkyl-piperazine.

The N-hydroxyalkyl-heterocyclic compound now is reacted with a borylating agent to form the borate. Any suitable borylating agent may be used. A particularly preferred borylating agent is boric acid. Other borylating agents include trialkyl borates in which the alkyl groups preferably contain from 1 to 4 carbon atoms each. In the use of the latter type borylating agent, the reaction is effected by transesterification and, accordingly, there is no advantage to using trialkyl borates containing more than 4 carbon atoms in each alkyl group, although the higher boiling trialkyl borates may be used when satisfactory and advantages appear therefor. Still other borylating agents include alkyl boric acid, dialkyl boric acid, boric oxide, boric acid complex, cycloalkyl boric acid, aryl boric acid, dicycloalkyl boric acid, diaryl boric acid, or substitution products of these with alkoxy, alkyl and/or halo groups, etc.

The reaction of the borylating agent and the N-hydroxy-alkyl-heterocyclic compound is effected in any suitable manner. The ortho-borates are formed by heating and stirring the reactants at a temperature up to about 100° C. and thus within the range of from about 60° to about 100° C. when using boric acid. The meta-borates are formed at temperatures above about 100° C. and thus may be within the range of from about 100° to about 200° C. or more. The higher temperature of from about 100° to about 200° C. is used when employing trialkyl borates in order to effect the transesterification reaction. In one method the reactants are refluxed in the presence of a solvent. Any suitable solvent may be used and advantageously comprises an aromatic hydrocarbon solvent including benzene, toluene, xylene, ethylbenzene, cumene, etc. Other solvents include n-hexane, n-heptane, n-octane, chlorinated hydrocarbons, etc., or mixtures thereof. The use of a solvent is particularly preferred when boric acid is used as the borylating agent. When using a trialkyl borate as the borylating agent, the solvent may be omitted. While no catalyst normally is required, a catalyst may be used when employing the trialkyl borate. Any suitable catalyst may be employed including sodium hydrogen sulfate, potassium hydrogen sulfate, tin oxide, polyalkyl tin derivatives, alkoxy tin derivatives, polyalkyl titanium derivatives, alkoxy titanium derivatives, trialkyl or tri-

alkoxy aluminum, etc. The borylating agent and N-hydroxyalkyl-heterocyclic compound generally are used in a mole proportion within the range of from about 0.3 to 1 mole proportions of borylating agent per one mole proportion of N-hydroxyalkyl-heterocyclic compound.

In another embodiment, an alcohol, including aliphatic or aromatic alcohol, or mercaptan, including aliphatic or aromatic mercaptan, is included in the reaction charge to satisfy one or two of the valences of the boron. When used, the alcohol or mercaptan is employed in an amount of from about 1 to 2 mole proportions thereof per 1 mole proportion of the N-hydroxyalkyl-heterocyclic compound. Preferred aliphatic alcohols include methanol, isopropanol, butanol, sec-butyl alcohol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol, eicosanol, etc. Preferred aromatic alcohols include phenol, cresol, xyleneol, etc. The alcohol or aromatic phenol moiety may be substituted with alkoxy groups or thioalkoxy groups. Preferred mercaptans include butyl mercaptan, pentyl mercaptan, hexyl mercaptan, heptyl mercaptan, octyl mercaptan, nonyl mercaptan, decyl mercaptan, undecyl mercaptan, dodecyl mercaptan, etc., and thiophenol, thiocresol, thioxyleneol, etc.

As hereinbefore set forth, the reaction is readily effected by refluxing the borylating agent and N-hydroxyalkyl-heterocyclic compound, with or without solvent and/or catalyst as required. Refluxing is continued until the required amount of water when using boric acid or alcohol when using trialkyl borate is collected. Following completion of the reaction, the solvent and alcohol, if any, are removed by vacuum distillation. The borated N-hydroxyalkyl-heterocyclic compound is recovered as a liquid and used as such or, when desired, the product may be retained in the solvent and used as such or the product may be prepared as a solution in a different solvent and used in this manner.

The exact structure of the borated product will vary with the proportions of reactants employed, with the particular borylating agent, with the conditions under which the borylation is effected and whether an extraneous alcohol or mercaptan is used. For example, when reacting 3 mole proportions of N-hydroxyethyl-N'-alkyl-piperazine with 1 mole proportion of boric acid, it is believed that the triester is formed in which all valences of the boron are satisfied by the piperazyl ethoxy radical formed by the liberation of water. When equal mole proportions of the N-hydroxyethyl-N'-alkyl-piperazine and boric acid are reacted at a higher temperature, the metaborate is formed. When the reaction is effected using an extraneous alcohol or mercaptan in addition to the N-hydroxyethyl-N'-alkyl-piperazine, the resulting borate will be a mixed borate in which one or two valences of the boron are satisfied by the hydroxyalkyl-piperazine and the remaining valence or valences of the boron are satisfied by the alcohol or mercaptan. When employing a trialkyl borate as the borylating agent, either complete or partial transesterification occurs, depending upon the proportions of reactants and conditions of operation.

From the above discussion, it will be seen that the exact structure of the borate may vary and also that the product may consist of a mixture of compounds. Accordingly, the additives of the present invention are being claimed generically. It is understood that the different borated compounds meeting the requirements as hereinbefore set forth may be used for the purposes of the present invention but that the different additives are not necessarily equivalent in their effectiveness in the same or different substrates.

The novel compounds of the present invention possess varied utility. They are of especial utility in substrates exposed to weather and in this embodiment the compounds of the present invention serve as weathering stabilizers. Although the mechanism in which these compounds func-

tion is not completely understood, these compounds serve to protect substrates which undergo ultraviolet light induced oxidation. In addition, the compounds of the present invention possess anti-static properties and adhesion improving properties. The compounds are also effective as antioxidants, peroxide decomposers and bactericides, especially for petroleum products. Also, they may serve as dye sites in plastics. Furthermore, they are of ready solubility in most substrates. The substrates normally subject to exposure to weather include plastics, resins, paints, varnishes, other coatings, fibers, textiles, etc.

Illustrative plastics which are stabilized by the novel compounds of the present invention include polyolefins and particularly polyethylene, polypropylene, polybutylene, mixed ethylene propylene polymers, mixed ethylene butylene polymers, mixed propylene butylene polymers, etc. The solid olefin polymers are used in many applications including electrical insulation, light weight outdoor furniture, awnings, cover for greenhouses, fibers, etc. In many of these applications the solid olefin polymer is exposed to sunlight and air.

Another plastic being used commercially on a large scale is polystyrene. The polystyrene type resins are particularly useful in the manufacture of molded or machined articles which find application in such goods as windows, optical goods, automobile panels, molded household articles, etc. One disadvantage of polystyrene is its tendency to deteriorate when exposed to direct sunlight and air for extended periods of time.

Another class of plastics available commercially is broadly classed as vinyl resins and is derived from monomers such as vinyl chloride, vinyl acetate, vinylidene chloride, etc. Polyvinyl chloride plastics are available commercially on a large scale and undergo deterioration when exposed to sunlight. Other vinyl type resins include copolymers of vinyl chloride with acrylonitrile, methacrylonitrile, vinylidene chloride, alkyl acrylates, alkyl methacrylates, alkyl maleates, alkyl fumarates, polyvinyl butyral, etc., or mixtures thereof.

Other plastics being used commercially on a large scale are in the textile class and include nylon (polyamide), Perlon L or 6-nylon (polyamide), Dacron (terephthalic acid and ethylene glycol), Orlon (polyacrylonitrile), Dynel (copolymer of acrylonitrile and vinyl chloride), Acrilan (polyacrylonitrile modified with vinyl acetate), Saran (copolymer of vinylidene chloride and vinyl chloride), rayon, etc. Here again, deterioration occurs due to ultraviolet light and oxidation. In addition, the additives of the present invention may serve as dye sites in plastics. This is especially desirable in plastics used for textiles as, for example, use of plastics for carpeting, fabrics, etc. Furthermore, the additives of the present invention inhibit discoloration and, therefore, the color of the product will remain true, which also is of considerable advantage in the case of clear products.

Still other plastics are prepared from other monomers and are available commercially. Illustrative examples include polyurethanes, both the urethane foams and the rigid resins, epoxy resins, polycarbonates, etc. Still other illustrative examples include phenol-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, acryloid plastics which are derived from methyl, ethyl and higher alkyl acrylates and methacrylates as monomers used in the polymerization. Other polymers include polyacetals, especially polyformaldehydes such as "Delrin" and "Celcon." Still other substrates include vinyl, acrylic, nitrocellulose based coatings; especially cellulose acetate, cellulose acetate butyrate, ethyl cellulose, etc. Still other substrates are polyesters, including linear or cross-linked, reinforced polyesters, laminate polyesters, etc., various latexes, lacquers, alkyds, varnishes, polishes, stains, pigments, dyes, textile finishing formulations, etc.

It is understood that the plastic may be fabricated into

any desired finished product including moldings, castings, fibers, films, sheets, rods, tubing or other shapes.

Rubber is composed of polymers of conjugated 1,3-dienes, ether as polymers thereof or as copolymers thereof with other polymerizable compounds, and the rubbers, both natural and synthetic, are included as solid polymers in the present specifications and claims. Synthetic rubbers include SBR rubber (copolymer of butadiene and styrene), Buna N (copolymer of butadiene and acrylonitrile), butyl rubber (copolymer of butadiene and isobutylene), neoprene rubber (chloroprene polymer), Thiokol rubber (polysulfide), silicone rubber, etc. The natural rubbers include hevea rubber, caoutchouc, balata, gutta percha, etc. It is well known that rubber undergoes deterioration due to oxygen and, when exposed to direct sunlight for extended periods of time, also undergoes deterioration from this source.

The above are illustrative examples of various plastics and resins which are improved by the additives of the present invention. As hereinbefore set forth, still other substrates include paints, varnishes, drying oils, pigments, rust preventive coatings, wax coatings, protective coatings, etc. It is understood that the compounds of the present invention may be used in any coating which is subject to exposure to ultraviolet light, oxidation, heat, etc. While the compounds are especially useful in materials subject to such exposure, it is understood that the compounds of the present invention also may be used advantageously in other coatings, plastics, resins, paints, etc., which normally are not exposed outdoors.

The compounds of the present invention also are of utility as additives in other organic substrates including, for example, hydrocarbon distillates. Illustrative hydrocarbon distillates include gasoline, naphtha, kerosene, jet fuel, solvents, fuel oil, burner oil, range oil, diesel oil, marine oil, turbine oil, cutting oil, rolling oil, soluble oil, drawing oil, slushing oil, lubricating oil, fingerprint remover, wax, fat, grease, etc. In the oils, the compounds of the present invention serve to inhibit oxidative deterioration, thermal deterioration, etc., thereby retarding and/or preventing sediment formation, dispersion of sediment when formed, preventing and/or retarding discoloration, rust or corrosion inhibitor, detergent, etc. In gasoline, the additive improves the combustion characteristics of the gasoline.

In many applications it is advantageous to utilize the compounds of the present invention in conjunction with other additives. For example, particularly improved results are obtained in the stabilization of plastics, apparently due to a synergistic effect, when the compound of the present invention is used in admixture with a phenolic antioxidant including particularly 2,6-ditertiarybutyl-4-methylphenol. Other inhibitors which may be used generally will be of the phenolic or amine type and include phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, phenothiazine, Nonox WSP, Nonox C1, dialkylated phenols, trialkylated phenols including 2,4-dimethyl-6-tertiarybutylphenol, etc., Santonox R, Santowhite, alkyl-alkoxyphenols, 2246 (2,2' - methylene-bis-(4-methyl-6-tertiarybutylphenol) and 425 (2,2' - methylene-bis-(4-ethyl-6-tertiarybutylphenol) (American Cyanamid), diphenyl-p-phenylene-diamine, 1,1,3 - tris - (2-methyl-4-hydroxy-5-*t*-butylphenyl) - butane, 703 (2,6 - di-*tert*-butyl-alpha-dimethyl-amino-*p*-cresol) (Ethyl Corporation), 4,5'-bis-(2-methyl-6 - *tert*-butylphenol); 4,4'-thio-bis-(6-*tert*-butyl-*o*-cresol); 4,4'-bis-(2,6-di-*tert*-butylphenol); 4,4'-methylene-bis-(2,6-di-*tert*-butylphenol); Salol (salicylic acid esters), *p*-octylphenylsalicylate, various phosgene alkylated phenol reaction products, various alkoxyalkyldihydroxybenzophenones, polyalkyldihydroxybenzophenones, tetrahydroxybenzophenones, 2,4,5-trihydroxybutyrophenone, etc., and especially such hydroxybenzophenones as 2,2'-dihydroxy-4 - octoxybenzophenone, 2,2' - dihydroxy-4-decoxybenzophenone, 2,2'-dihydroxy-4-dodecoxybenzophenone, 2,2'-

dihydroxy-4-octadecoxybenzophenone, etc., in general any alkoxy or cycloalkoxy substituted 2,2'-dihydroxybenzophenone, 2-hydroxy-4'-octoxybenzophenone, 2-hydroxy-4'-decoxybenzophenone, 2-hydroxy-4'-dodecoxy, etc., and in general any alkoxy or cycloalkoxy substituted 2-hydroxybenzophenone. Other ultraviolet light stabilizers include nickel-bisdithiocarbamates and especially nickel-bis-dibutyldithiocarbamate, nickel-bis-dihydroxypolyalkylphenol sulfides, especially [2,2'-thio-bis-(4-*t*-octylpheno-1-ato)]-*n*-butyl-amine nickel (II), dialkyl beta-mercaptodipropionate, dihydroxytetraalkyl sulfides, dihydroxytetraalkyl methanes, various trithiophosphites as trialkylthiophosphite, dialkylphosphites, trialkylphosphites, high molecular weight nitriles, various Mannich bases, various *N*-hydroxyphenylbenzotriazoles such as 2-(2'-hydroxy-5'-octylphenyl) - benzotriazole, 2 - (2'-hydroxy-5'-dodecylphenyl) - benzotriazole, 2-(2'-hydroxy-5'-octoxyphenyl)-benzotriazole, 2 - (2'-hydroxy-5'-dodecoxyphenyl)-benzotriazole, Tinuvin 326, etc., in general, any alkyl or alkoxyphenyl substituted benzotriazole, etc. The additional inhibitor may be used in a concentration of from about 1% to about 75% by weight of the compound of the present invention. Generally, the additional inhibitor will be used in a concentration within the range of from about 0.001% to about 3% and more particularly from about 0.01% to about 2% by weight of the substrate.

The additive of the present invention will be used in a stabilizing concentration which will depend upon the particular substrate. The additive may be used in a concentration as low as 0.001% to about 25% but generally will be used in a concentration of from about 0.01% to about 5% by weight of the substrate. When used in hydrocarbon distillate and particularly gasoline, the additive generally is used in a concentration of from about 0.0001% to about 0.5%. The additive is incorporated in the substrate in any suitable manner. For example, when it is incorporated into a plastic, resin or the like, it may be added to the hot melt with stirring, generally in a Banbury mixer, extruder or other device. When it is added to a liquid, it is incorporated into the liquid with intimate stirring. When it is added to a multicomponent mixture as, for example, grease, it may be added to one of the components and, in this manner, incorporated into the final mix or it may be added directly into the final mix.

The additive of the present invention may be utilized as such or prepared as a solution in a suitable solvent including alcohols and particularly methanol, ethanol, propanol, butanol, etc., hydrocarbons and particularly benzene, toluene, xylene, cumene, Declin, etc.

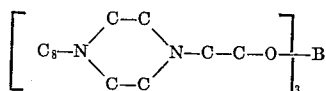
The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

The compound of this example was prepared by the reaction of 3 mole proportions of *N*-hydroxyethyl-*N*'-sec-octyl-piperazine with 1 mole proportion of boric acid. The *N*-hydroxyethyl-*N*'-sec-octyl-piperazine was prepared as follows. Hydroxyethyl-piperazine, which is available in the open market, was subjected to reductive alkylation by reacting 240 g. of hydroxyethyl-piperazine and 500 g. of methyl hexyl ketone at 160° C. in the presence of hydrogen and an alumina-platinum catalyst containing about 0.3% by weight of platinum. The resultant *N*-hydroxyethyl-*N*'-sec-octyl-piperazine was analyzed and found to have a basic nitrogen of 8.27 meq./g. and a basic mole combining weight of 121 which corresponds to the theoretical basic mole combining weight of 121. The product had an index of refraction n_D^{20} of 1.4787.

Borylation of the *N*-hydroxyethyl-*N*'-sec-octyl-piperazine, prepared in the above manner, was effected by refluxing 72.6 g. (4.3 mole) thereof and 6.18 g. (0.1 mole) of boric acid in the presence of 100 g. of benzene at 85° C. Heating and refluxing was continued until a total of about 5 cc. of water was collected. Following completion of the

reaction, the benzene was removed by distillation at 160° C. under water pump vacuum, and the borated product was recovered as a liquid which contained 1.24% by weight of boron which corresponds to a theoretical boron content of 1.47% by weight for the triester. It is believed that the triester is of the following structure:



In the above structure the hydrogens attached to the carbon atoms have been omitted in the interest of simplicity.

Example II

The compound of this example is prepared by reacting N-hydroxyethyl-N'-sec-octyl-piperazine with tri-n-butyl borate. This is a transesterification reaction and is effected by heating and refluxing 3 mole proportions of N-hydroxyethyl-N'-sec-octyl-piperazine and 1 mole proportion of tri-n-butyl borate at a temperature of about 160° C. The refluxing is continued until the required amount of butanol is collected, the butanol resulting from the transesterification reaction. Following completion of the reaction, the borated product is recovered as a liquid.

Example III

The compound of this example is prepared by reacting boric acid with N-hydroxypropyl-N'-cyclohexyl-hexahydropyrimidine. Hexahydropyrimidine is oxypropylenated by reacting equal mole proportions of propylene oxide with hexahydropyrimidine, and the resulting N-hydroxypropyl-pyrimidine is subjected to reductive alkylation with cyclohexanone in the presence of an alumina-platinum catalyst. One mole proportion of the resultant N-hydroxypropyl-N'-cyclohexyl-hexahydropyrimidine is subjected to heating and refluxing with 0.33 mole proportions of boric acid in the presence of benzene solvent. Following completion of the reaction, the product is recovered as a solution in benzene.

Example IV

The compound of this example is the meta-borate formed by the reaction of p-octyl-N-hydroxyethyl-piperidine and boric acid. The reaction is effected by heating and refluxing equal mole proportions of p-octyl-N-hydroxyethyl-piperidine and boric acid in the presence of 100 g. of xylene. The temperature of reaction is above 120° C. and the refluxing is continued until the desired amount of water is collected.

Example V

The compound of this example is prepared by the reaction of N-hydroxyethyl-N'-decyl-hexahydropyridazine. Specifically, 2 mole proportions of N-hydroxyethyl-N'-decyl-hexahydropyridazine and 1 mole proportion of boric acid are heated and refluxed in the presence of benzene solvent. The refluxing is continued until the desired amount of water is collected. The borated product is recovered as a solution in benzene.

Example VI

The compound of this example is prepared by heating and refluxing a mixture of 1 mole proportion of boric acid, 2 mole proportions of N-hydroxyethyl-N'-hexyl-piperazine and 1 mole proportion of isooctyl alcohol in the presence of benzene solvent. The reaction is continued until the desired amount of water is collected, after which the borated product is subjected to vacuum distillation to remove the benzene solvent.

Example VII

The compound of this example is prepared by heating and refluxing 2 mole proportions of N-hydroxyethyl-N'-dodecyl-piperazine, 1 mole proportion of butyl mercaptan and 1 mole proportion of boric acid in the presence of benzene solvent. The heating and refluxing is continued

until the reaction is completed, after which the reaction mixture is subjected to vacuum distillation to remove the benzene solvent.

Example VIII

The compound of this example is prepared by first subjecting commercial 1-hydroxyethyl-2-heptadecenyl glyoxalidine to reduction with hydrogen in the presence of nickel hydrogenation catalyst to prepare 1-hydroxyethyl-2-heptadecyl imidazolidine, 3 mole proportions of which then is reacted with 1 mole proportion of boric acid by heating and refluxing the mixture in the presence of benzene solvent. Following completion of the reaction, the reaction mixture is subjected to filtration and the benzene is removed by distillation under vacuum. The resultant product is recovered as an ester of boric acid and 1-hydroxyethyl-2-heptadecyl imidazolidine.

Example IX

The borate of this example is prepared by subjecting 1-hydroxyethyl-2-methyl glyoxalidine to reductive alkylation with methyl hexyl ketone in the presence of hydrogen and alumina-platinum catalyst. The resultant product is reacted in a proportion of 3 moles thereof with 1 mole of boric acid by heating and refluxing in the presence of benzene solvent. Following completion of the reaction, the borated product is recovered as a solution in benzene.

Example X

As hereinbefore set forth, the compound of the present invention is useful as a weathering agent in plastics. The plastic of this example is solid polypropylene. The solid polypropylene without inhibitor is stated to have properties substantially as follows:

TABLE I

Specific gravity	0.910-0.920
Refractive index, n_D^{25}	1.510
Heat distortion temperature	
at 66 p.s.i. load	116° C.
at 264 p.s.i. load	66° C.
Tensile yield strength, p.s.i. (ASTM D-638-58T) (0.2" per min.)	4700
Total elongation, percent	300-400
Stiffness Flexural (ASTM D747-50) 10 ⁶ p.s.i.	1.8
Shore Hardness (ASTM D676-55T)	74D

The polypropylene was milled in a two-roll heated mill of conventional commercial design and the additive, when employed, was incorporated in the sample during the milling. The samples were pressed into sheets of about 17 mil. thickness and cut into plaques of about 1 3/8" x 1 1/2". The plaques were inserted into plastic holders, affixed onto a rotating drum and exposed to carbon arc rays at about 52° C. in a Weather-Ometer. The samples were examined periodically by infrared analysis to determine the carbonyl band at 1715 cm.⁻¹ which is reported as the "carbonyl number." The higher intensity of the carbonyl band indicates a higher carbonyl concentration (expressed as carbonyl number) and accordingly increased deterioration.

A sample of the polypropylene without inhibitor developed a carbonyl number of greater than 1000 within 120 hours of exposure in the Weather-Ometer. Another sample of the same polypropylene containing 0.15% by weight of 2,6-ditertiarybutyl-4-methylphenol developed a carbonyl number over 1000 within 360 hours of exposure in the Weather-Ometer.

Another sample of the solid polypropylene containing 1% by weight of the borated compound of Example I and 0.15% by weight of 2,6-ditertiarybutyl-4-methylphenol was evaluated in the Weather-Ometer in the same manner. After 1100 hours of exposure in the Weather-Ometer, the carbonyl number of this sample was 240. As another important advantage of the additive of the present invention, the sample of polypropylene containing this additive, even after exposure in the Weather-Ometer for

this long period of time, still remained clear and did not undergo discoloration.

Example XI

The solid polypropylene plastic of Example I also was evaluated for physical properties after exposure in the Weather-Ometer. Dumbbell specimens (1" wide, 4¾" long and 0.020" thick with the neck being 1" long and ¼" wide) were exposed in the Weather-Ometer in the same manner described in Example X and then the physical properties were evaluated in an Instron Universal tester. In general, the Instron Universal tester is a machine in which the dumbbell specimen is gripped firmly at the top and bottom. A constant pull of two inches per minute is exerted downwardly and the following data are obtained: (1) the percent elongation until rupture occurs, (2) the tensile strength which is the pounds per square inch of force at which rupture occurs, (3) the pull strength which is the pounds per square inch of elongation between the yield point and the tensile strength and (4) the elastic modulus which also is reported in pounds per square inch. The data in the following table report the results of such evaluations for (1) a sample of the polypropylene without additive and (2) a sample of the polypropylene containing 1% by weight of the additive of Example I and 0.15% by weight of 2,6-ditertiarybutyl-4-methylphenol. In each case, these data were obtained prior to exposure in the Weather-Ometer and after 480 hours. The sample containing the additive also was evaluated after 720 hours of exposure in the Weather-Ometer.

TABLE II

Additive	Elongation, percent			Tensile Strength, p.s.i.			Pull Strength, p.s.i.			Elastic Modulus p.s.i.×10 ⁴		
	0	480	720	0	480	720	0	480	720	0	480	720
None	555			4,785			2,400			5.14		
Composition of Example X	503	426	380	4,110	3,390	3,315	2,500	2,620	2,725	5.14	5.27	4.82

From the data in the above table, it will be seen that the control sample (not containing an additive) lost all of its desirable physical properties after exposure in the Weather-Ometer for 480 hours. In contrast, the sample containing the additive composition of Example X still retained a considerable portion of these desired physical properties even after exposure in the Weather-Ometer for 720 hours.

Example XII

The plastic of this example is solid polyethylene of the high density type. An inhibited product of this polyethylene is marketed commercially under the trade name of Fortiflex by the Celanese Corporation of America. A batch of this polyethylene free of inhibitor is obtained and is cut into plaques in the same manner described in Example X and evaluated in the Weather-Ometter. A sample of this polyethylene without inhibitor, when evaluated in the Weather-Ometer, increases from a carbonyl number of 28 to a carbonyl number of 855 within 624 hours. In contrast, another sample of the polyethylene containing 1% by weight of the borated compound of Example II does not develop a carbonyl number of above 800 for a considerably longer period of time.

Example XIII

The additive of Example III is incorporated in a concentration of 1% by weight in polystyrene and serves to inhibit deterioration of the polystyrene upon exposure to weathering.

Example XIV

The compound of Example I is used in a concentration of 0.3% by weight as an additive in gasoline and serves to improve the combustion characteristics of the gasoline, as well as serving as an anti-static agent therein.

I claim as my invention:

1. Borate of

(a) N-hydroxyalkyl-mononitrogen - heterocyclic compound free of unsaturation in the heterocyclic ring and selected from the group consisting of piperidine, pyrrolidine, hydrogenated indole, hydrogenated carbazole, hydrogenated quinoline, and hydrogenated acridine; or

(b) N-hydroxyalkyl - N' - hydrocarbyl-polynitrogen-heterocyclic compound, the hydrocarbyl being alkyl or cycloalkyl containing from 4 to 12 carbon atoms in the ring, and the heterocyclic compound being free of unsaturation in the heterocyclic ring and being selected from the group consisting of piperazine, hexahydropyrimidine, hexahydropyridazine, imidazolidine, pyrazolidine, hydrogenated triazole, and hydrogenated phenazine; at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

2. Borate of N - hydroxyalkyl-N' - alkyl-piperazine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

3. Borate of N-hydroxyethyl - N'-sec-octyl-piperazine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyethyl group.

4. Borate of N - hydroxyalkyl-N'-cycloalkyl-piperazine, the cycloalkyl containing from 4 to 12 carbon atoms in the ring and at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

5. Borate of N - hydroxyethyl-N'-cyclohexyl-piperazine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyethyl group.

6. Borate of N - hydroxyalkyl-N'-alkyl-hexahydro-pyrimidine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

7. Borate of N-hydroxyalkyl - N'-cycloalkyl-hexahydropyrimidine, the cycloalkyl containing from 4 to 12 carbon atoms in the ring and at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

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8. Borate of N-hydroxyalkyl - N'-alkyl-hexahydropyridazine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

9. Borate of N - hydroxyethyl-N'-sec-alkyl-hexa-hydropyridazine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyethyl group.

10. Borate of N - hydroxyalkyl-N'-sec-alkyl-imidazolidine, at least one valence of the boron atom being satisfied by a bond between the boron and the oxygen of said hydroxyalkyl group.

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