United States Patent Office

3,189,647
Patented June 15, 1965

3,189,647

N-ACYL-DIAMINODIPHENYL ETHERS

Ted Symon, Lombard, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

No Drawing. Original application Nov. 29, 1961, Ser. No. 155,795. Divided and this application Nov. 5, 1962, Ser. No. 235,913
4 Claims. (Cl. 260—558)

This application is a division of my copending application Serial No. 155,795, filed November 29, 1961, and relates to a novel composition of matter which is useful for the stabilization of organic substances which normally tend to deteriorate in storage, transportation or in use due to oxidation or other reactions.

The invention is particularly applicable to the stabilization of lubricants, including lubricating oils and greases. These may be either of synthetic or petroleum origin. The synthetic lubricating oils are of varied types including aliphatic esters, polyalkylene oxides, silicones, esters of phosphoric and silicic acids, highly fluorine-substituted hydrocarbons, etc. Of the aliphatic esters, di-(2-ethylhexyl) sebacate is being used on a comparatively large commercial scale. Other aliphatic esters include dialkyl azelates, dialkyl suberates, dialkyl pimelates, dialkyl adipates, dialkyl glutarates, etc. Specific examples of these esters include dihexyl azelate, di-(2-ethylhexyl) azelate, di-3,5,5-trimethylhexyl glutarate, di-3,5,5-trimethylpentyl glutarate, di-(2-ethylhexyl) pimelate, di-(2-ethylhexyl) adipate, triamyl tricarballylate, pentaerylthritol tetracaproate, pentaerythritol tetrapelargonate, dipropylene glycol dipelargonate, 1,5-pentanediol - di - (2-ethylhexanonate), etc. The polyalkylene oxides include polyisopropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diester, etc. The silicones include methyl silicone, ethylphenyl silicone, etc., and the silicates include, for example, tetraisooctyl silicate, etc. The highly fluorinated hydrocarbons include fluorinated oil, perfluorohydrocarbons, etc.

Additional synthetic lubricating oils include (1) neopentyl glycol esters, in which the ester group contains from 3 to 12 carbon atoms or more, and particularly neopentyl glycol propionate, neopentyl glycol butyrate, neopentyl glycol caproate, neopentyl glycol caprylate, neopentyl glycol pelargonate, etc., (2) trialkylol alkane esters such as the esters of trimethylol alkanes including trimethylolethane, trimethylolpropane, trimethylolbutane, trimethylolpentane, trimethylolhexane, trimethylolheptane, trimethyloloctane, trimethyloldecane, trimethylolundecane, trimethyloldodecane, etc., and particularly triesters in which the ester portions each contain from 3 to 12 carbon atoms and may be selected from those hereinbefore specifically set forth in connection with the discussion of the neopentyl glycol esters, and (3) tricresylphosphate, trioctylphosphate, trinonylphosphate, tridecylphosphate, as well as mixed aryl and alkyl phosphates, etc.

The lubricating oils of petroleum origin include those referred to as motor lubricating oil, railroad type lubricating oil, marine oil, transformer oil, turbine oil, transmission oil, differential oil, diesel lubricating oil, gear oil, cutting oil, rolling oil, cylinder oil, hydraulic oil, slushing oil, specialty products oil, etc.

The synthetic greases generally are referred to as lithium base grease, sodium base grease, calcium base grease, barium base grease, strontium base grease, aluminum base grease, etc. These greases are solid or semi-solid gels and, in general, are prepared by the addition to mineral or synthetic oils of hydrocarbon-soluble metal soaps or salts of higher fatty acids as, for example, lithium stearate, calcium stearate, aluminum naphthenate, etc. The grease may contain thickening agents such as silica, carbon black, polyacrylates, talc, etc. Another type of grease is prepared from oxidized petroleum wax, to which the saponifiable base is combined with the proper amount of the desired saponifying agent, and the resultant mixture processed to produce a grease. Other types of greases in which the features of the present invention are usable include petroleum grease, whale grease, wool grease, etc., and those made from inedible fats, tallow, butcher's waste, etc.

The present invention also is particularly applicable to the stabilization of polyolefins including polyethylene, polypropylene, polybutylene, copolymers of ethylene and propylene, copolymers of ethylene and butylene and copolymers of propylene and butylene, as well as polymers prepared from one or more higher molecular weight olefins. The polyolefins preferably are of high molecular weight, usually having a molecular weight above 1000 and extending into the hundreds of thousand range. The polyolefins may be of the high density, medium density or low density type. Polyethylene is utilized, for example, as a thermo-plastic, molding or coating agent. Because of its high dielectric strength and its resistance to water, polyethylene is particularly advantageous for use as insulators or dielectrics in condensers and other similar electronic equipment. Polyethylene plastics also are used in many applications. Polypropylene, polybutylene and copolymers of ethylene, propylene and/or butylene also are used in electronic equipment, as well as many other applications. When the polyolefin is used in outdoor exposure as, for example, in light weight outdoor furniture, cover for greenhouses, awnings, etc., it is additionally desirable that the polyolefin does not undergo discoloration. The polyolefins are subject to attack by atmospheric oxygen which impairs the desirable properties thereof.

The present invention also is applicable to the stabilization of fatty materials including the stabilization of edible fats and oils, which may be of animal, vegetable or mineral origin and which tend to become rancid, especially during long periods of storage prior to use. Typical representatives of edible fats and oils include linseed oil, menhaden oil, cod liver oil, castor oil, olive oil, rapeseed oil, coconut oil, palm oil, corn oil, sesame oil, peanut oil, butter, fat, lard, beef, tallow, etc. It is understood that other oils and fats may be treated within the scope of the present invention, including oil and fats which previously have been subjected to various treatments, such as blowing with air, heat treatment, hydrogenation, etc.

In another embodiment the present invention may be applied to the treatment of crops by dusting or spraying in order to preserve food accessory factors such as carotene, vitamins, various fatty acids, alcohols, etc.

Other organic substances which deteriorate in storage, during treatment and/or in use, include hydrocarbons, and particularly motor fuels such as saturated and particularly unsaturated gasoline, blends of unsaturated and saturated gasolines, including cracked gasoline, straight run gasoline, polymer gasoline, coker gasoline, alkylate, etc., as well as jet fuel, diesel oil, mineral oil, fuel oil, residual oil, drying oil, waxes, resins, etc. These substances are adversely affected by oxygen, with the resultant formation of undesirable gum, discoloration and/or other deleterious reaction products.

In one embodiment the present invention relates to a method of stabilizing an organic substance normally subject to oxidative deterioration which comprises incorporating therein a stabilizing concentration of an N-acyl-diaminodiphenyl ether.

In a specific embodiment the present invention relates to a method of stabilizing polyethylene against oxidative deterioration which comprises incorporating therein a stabilizing concentration of 2-(N-benzoyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether.

In another specific embodiment the present invention relates to a method of stabilizing lubricating oil against oxidative deterioration which comprises incorporating therein a stabilizing concentration of 2-(N-acetyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether.

In still another specific embodiment the present invention relates to a method of stabilizing grease which comprises incorporating therein a stabilizing concentration of 2-(N-benzoyl-N-isopropylamino) - 4′ - diisopropylaminodiphenyl ether.

In another embodiment the present invention relates to an organic substance, particularly polyolefin, lubricating oil and grease, containing a stabilizing concentration of an inhibitor as set forth herein.

The novel inhibitor of the present invention is an N-acyl-diaminodiphenyl ether. Although many diaminodiphenyl compounds have been suggested heretofore as additives to organic substances, difficulty has been experienced with such compounds because of deposit formation during use at elevated temperatures. For example, lubricating oil for use in jet planes is subjected to high temperature, high altitude, long period of service during long distance flights, etc., and, under these conditions, sludging of the lubricating oil has been experienced. The deposit formation in the lubricating oil is a serious disadvantage because it may result in poor lubrication and in clogging the moving parts of the engine. The present applicant has found that diaminodiphenyl ethers containing an acyl group attached to a nitrogen atom reduces the sludging properties of the lubricating oil and avoids the disadvantages hereinbefore set forth. The acyl substituted diaminodiphenyl ether also is an effective antioxidant in polyolefins and, in addition, avoids excessive discoloration of the polyolefin during high temperature oxidation.

Any suitable N-acyl-diaminodiphenyl ether may be used in accordance with the present invention. In a preferred embodiment, the inhibitor is a monoacyl diaminodiphenyl ether. Particularly preferred acyl radicals are acetyl and benzoyl. Other acyl radicals include formyl, propionyl, butyryl, valeryl (pentanoyl), caproyl (hexanoyl), heptanoyl, octanoyl, nonanoyl, deconoyl, undecanoyl, dodecanoyl, etc., benzoyl, toloyl, xyloyl, etc.

Illustrative inhibitors of the present invention include

2-formylamino-4′-aminodiphenyl ether,
2-acetylamino-4′-aminodiphenyl ether,
2-propionylamino-4′-aminodiphenyl ether,
2-butyrylamino-4′-aminodiphenyl ether,
2-valerylamino-4′-aminodiphenyl ether,
2-capropylamino-4′-aminodiphenyl ether,
2-heptanoylamino-4′-aminodiphenyl ether,
2-octanoylamino-4′-aminodiphenyl ether, etc.,
2-amino-4′-formylaminodiphenyl ether,
2-amino-4′-acetylaminodiphenyl ether,
2-amino-4′-propionylaminodiphenyl ether,
2-amino-4′-butrylaminodiphenyl ether,
2-amino-4′-valerylaminodihpenyl ether,
2-amino-4′-capropylaminodiphenyl ether,
2-amino-4′-heptanoylaminodiphenyl ether,
2-amino-4′-octanoylaminodiphenyl ether, etc.,
4-formylamino-4′-aminodiphenyl ether,
4-acetylamino-4′-aminodiphenyl ether,
4-propionylamino-4′-aminodiphenyl ether,
4-butyrylamino-4′-aminodiphenyl ether,
4-valerylamino-4′-aminodiphenyl ether,
4-caproylamino-4′-aminodiphenyl ether,
4-heptanoylamino-4′-aminodiphenyl ether,
4-octanoylamino-4′-aminodiphenyl ether, etc.

In another embodiment it is preferred that one or both of the nitrogen atoms also is substituted with a hydrocarbon group. Alkyl and cycloalkyl groups are especially preferred, although the hydrocarbon substituent may be selected from alkaryl, aryl, aralkyl, etc. It is understood that the hydrocarbon substituent also may contain non-hydrocarbon groups attached thereto and, particularly, those containing oxygen, nitrogen, sulfur, etc.

Illustrative preferred compounds containing one or more alkyl substituents attached to one or both nitrogen atoms include

2-acetylamino-4′-isopropylaminodiphenyl ether,
2-acetylamino-4′-sec-butylaminodiphenyl ether,
2-acetylamino-4′-sec-amylaminodiphenyl ether,
2-acetylamino-4′-sec-hexylaminodiphenyl ether,
2-acetylamino-4′-sec-heptylaminodiphenyl ether,
2-acetylamino-4′-sec-octylaminodiphenyl ether, etc.,
2-isopropylamino-4′-acetylaminodiphenyl ether,
2-sec-butylamino-4′-acetylaminodiphenyl ether,
2-sec-amylamino-4′-acetylaminodiphenyl ether,
2-sec-hexylamino-4′-acetylaminodiphenyl ether,
2-sec-heptylamino-4′-acetylaminodiphenyl ether,
2-sec-octylamino-4′-acetylaminodiphenyl ether, etc.,
4-acetylamino-4′-isopropylaminodiphenyl ether,
4-acetylamino-4′-sec-butylaminodiphenyl ether,
4-acetylamino-4′-sec-amylaminodiphenyl ether,
4-acetylamino-4′-sec-hexylaminodiphenyl ether,
4-acetylamino-4′-sec-heptylaminodiphenyl ether,
4-acetylamino-4′-sec-octylaminodiphenyl ether, etc.,
2-(N-acetyl-N-isopropylamino)-4′-aminodiphenyl ether,
2-(N-acetyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether,
2-(N-acetyl-N-sec-butylamino)-4′-sec-butylaminodiphenyl ether,
2-(N-acetyl-N-hexylamino)-4′-sec-hexylaminodiphenyl phenyl ether,
2-(N-acetyl-N-hexylamino)-4′-sec-hexylaminodiphenyl ether,
2-(N-acetyl-N-sec-heptylamino)-4′-sec-heptylamino)-4′-sec-heptylaminodiphenyl ether,
2-(N-acetyl-N-sec-octylamino)-4′-sec-octylaminodiphenyl ether, etc.,
2-amino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
2-isopropylamino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
2-sec-butylamino-4′-(N-acetyl-N-sec-butylamino)-diphenyl ether,
2-sec-amylamino-4′-(N-acetyl-N-sec-amylamino)-diphenyl ether,
2-sec-hexylamino-4′-(N-acetyl-N-sec-hexylamino)-diphenyl ether,
2-sec-heptylamino-4′-(N-acetyl-N-sec-heptylamino)-diphenyl ether,
2-sec-octylamino-4′-(N-sec-octylamino)-diphenyl ether, etc.,
4-amino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
4-isopropylamino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
4-sec-butylamino-4′-(N-acetyl-N-sec-butylamino)-diphenyl ether,
4-sec-amylamino-4′-(N-acetyl-N-sec-amylamino)-diphenyl ether,
4-sec-hexylamino-4′-(N-acetyl-N-sec-hexylamino)-diphenyl ether,
4-sec-heptylamino-4′-(N-acetyl-N-sec-heptylamino)-diphenyl ether,
4-sec-octylamino-4′-(N-acetyl-N-sec-octylamino)-diphenyl ether, etc.,
2-acetylamino-4′-diisopropylaminodiphenyl ether,
2-acetylamino-4′-disec-butylaminodiphenyl ether,
2-acetylamino-4′-disec-amylaminodiphenyl ether.
2-acetylamino-4′-disec-hexylaminodiphenyl ether,
2-acetylamino-4′-disec-heptylaminodiphenyl ether,
2-acetylamino-4′-disec-octylaminodiphenyl ether, etc.,
2-diisopropylamino-4′-acetylaminodiphenyl ether,
2-disec-butylamino-4′-acetylaminodiphenyl ether,
2-disec-amylamino-4′-acetylaminodiphenyl ether,
2-disec-hexylamino-4′-acetylaminodiphenyl ether,

2-disec-heptylamino-4′-acetylaminodiphenyl ether,
2-disec-octylamino-4′-acetylaminodiphenyl ether, etc.,
4-acetylamino-4′-diisopropylaminodiphenyl ether,
4-acetylamino-4′-disec-butylaminodiphenyl ether,
4-acetylamino-4′-disec-amylaminodiphenyl ether,
4-acetylamino-4′-disec-hexylaminodiphenyl ether,
4-acetylamino-4′-disec-heptylaminodiphenyl ether,
4-acetylamino-4′-disec-octylaminodiphenyl ether, etc.,
2-(N-acetyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether,
2-(N-acetyl-N-sec-butylamino)-4′-disec-butylaminodiphenyl ether,
2-(N-acetyl-N-sec-amylamino)-4′-disec-amylaminodiphenyl ether,
2-(N-acetyl-N-sec-hexylamino)-4′-disec-hexylaminodiphenyl ether,
2-(N-acetyl-N-sec-heptylamino)-4′-disec-heptylaminodiphenyl ether,
2-(N-acetyl-N-sec-octylamino)-4′-disec-octylaminodiphenyl ether, etc.

The specific compounds set forth above are preferred. It is understood that the specified alkyl groups may be replaced by or supplemented with alkyl groups containing 1, 2, 9 or more carbon atoms each. Generally, the number of carbon atoms in each alkyl group will not exceed about 20 although, in some cases, the alkyl group may contain more than 20 carbon atoms and up to about 40 carbon atoms. Also, it is understood that the acetyl group may be replaced by or supplemented with other acyl groups including formyl, propionyl, butyryl, valeryl, caproyl, etc.

Illustrative compounds in which the hydrocarbon substituent is a cyclic radical include the following. Preferred compounds comprise

2-benzoylamino-4′-isopropylaminodiphenyl ether,
2-benzoylamino-4′-sec-butylaminodiphenyl ether, etc.,
2-isopropylamino-4′-benzoylaminodiphenyl ether,
2-sec-butylamino-4′-benzoylaminodiphenyl ether, etc.,
4-benzoylamino-4′-isopropylaminodiphenyl ether,
4-benzoylamino-4′-sec-butylaminodiphenyl ether, etc.,
2-(N-benzoyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether,
2-(N-benzoyl-N-sec-butylamino)-4′-sec-butylaminodiphenyl ether, etc.,
2-(N-benzoyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether,
2-(N-benzoyl-N-isopropylamino)-4′-disec-butylaminodiphenyl ether, etc.,
2-isopropylamino-4′-(N-benzoyl-N-isopropylamino)-diphenyl ether,
2-sec-butylamino-4′-(N-benzoyl-N-sec-butylamino)-diphenyl ether, etc.,
2-diisopropylamino-4′-(N-benzoyl-N-isopropylamino) diphenyl ether,
2-disec-butylamino-4′-(N-benzoyl-N-sec-butylamino)-diphenyl ether, etc.

As set forth above, these specific compounds are preferred. Other useful compounds comprise those in which the benzoyl group is replaced by toloyl, xyoyl, etc., and/or those in which the alkyl group contains 1, 2, or 5 to 20 or more carbon atoms per group. In another embodiment, the hydrocarbon substituent is a cycloalkyl radical including cyclopropyl, cyclohexyl, etc. Illustrative compounds in this embodiment include

2-acetylamino-4′-cyclohexylaminodiphenyl ether,
2-(N-acetyl-N-cyclohexylamino)-4′-aminodiphenyl ether,
2-(N-acetyl-N-cyclohexylamino)-4′-cyclohexylaminodiphenyl ether, etc.,
2-benzoylamino-4′-cyclohexylaminodiphenyl ether,
2-(N-benzoyl-N-cyclohexylamino)-4′-aminodiphenyl ether,
2-(N-benzoyl-N-cyclohexylamino)-4′-cyclohexylaminodiphenyl ether, etc.,
2-acetylamino-4′-dicyclohexylaminodiphenyl ether,
2-acetylamino-4′-(N-acetyl-N-cyclohexyamino)-diphenyl ether,
2-cyclohexylamino-4′-(N-acetyl-N-cyclohexylamino)-diphenyl ether, etc.,
2-benzoylamino-4′-dicyclohexylaminodiphenyl ether,
2-benzoylamino-4′-(N-benzoyl-N-cyclohexylamino)-diphenyl ether,
2-cyclohexylamino-4′-(N-benzoyl-N-cyclohexylamino)-diphenyl ether, etc.,
4-acetylamino-4′-cyclohexylaminodiphenyl ether,
4-(N-acetyl-N-cyclohexylamino)-4′-aminodiphenyl ether,
4-(N-acetyl-N-cyclohexylamino)-4′-cyclohexylaminodiphenyl ether, etc.,
4-benzoylamino-4′-cyclohexylaminodiphenyl ether,
4-(N-benzoyl-N-cyclohexylamino)-4′-aminodiphenyl ether,
4-(N-benzoyl-N-cyclohexylamino)-4′-cyclohexylaminodiphenyl ether, etc.

Here again, these are illustrative preferred compounds, it being understood that other cycloalkyl and/or other acyl groups may be used.

The specific compounds hereinbefore set forth are monoacylated diaminodiphenyl ethers. In another embodiment of the invention, di, tri and tetra acylated diaminodiphenyl ethers may be employed. Illustrative examples in this embodiment include

2-acetylamino-4′-acetylaminodiphenyl ether,
2-(N-acetyl-N-isopropylamino)-4′-acetylaminodiphenyl ether,
2-(N-acetyl-N-sec-butylamino)-4′-acetylaminodiphenyl ether, etc.,
2-(N-acetyl-N-isopropylamino)-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
2-(N-acetyl-N-secbutylamino)-4′-acetyl-N-sec-butylamino)diphenyl ether, etc.
2-benzoylamino-4′-benzoylaminodiphenyl ether,
2-(N-benzoyl-N-isopropylamino)-4′-benzoylaminodiphenyl ether,
2-(N-benzoyl-N-sec-butylamino)-4′-benzoylaminodiphenyl ether, etc.,
2-(N-benzoyl-N-isopropylamino)-4′-(N-benzoyl-N-isopropylamino)-diphenyl ether,
2-(N-benzoyl-N-sec-butylamino)-4′-(N-benzoyl-N-sec-butylamino)-diphenyl ether, etc.,
2-acetylamino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
2-acetylamino-4′-(N-acetyl-N-sec-butylamino)-diphenyl ether, etc.,
2-benzoylamino-4′-(N-benzoyl-N-isopropylamino)-diphenyl ether,
2-benzoylamino-4′-(N-benzoyl-N-sec-butylamino)-diphenyl ether, etc.,
4-acetylamino-4′-acetylamino-diphenyl ether,
4-acetylamino-4′-(N-acetyl-N-isopropylamino)-diphenyl ether,
4-acetylamino-4′-(N-acetyl-N-sec-butylamino)diphenyl ether, etc.,
4-benzoylamino-4′-(N-benzoyl-N-isopropylamino)-diphenyl ether,
4-benzoylamino-4′-benzoyl-N-sec-butylamino)-diphenyl ether, etc.,
2-acetylamino-4′-benzoylaminodiphenyl ether,
2-benzoylamino-4′-acetylamino-diphenyl ether, etc.,
4-(N-acetyl-N-isopropylamino)-4′-benzoylaminodiphenyl ether,
4-(N-acetyl-N-sec-butylamino)-4′-benzoylaminodiphenyl ether,
4-(N-acetyl-N-isopropylamino)-4′-N-benzoyl-N-isopropylamino)-dihepnyl ether,
4-(N-acetyl-N-sec-butylamino)-4′-(N-benzoyl-N-sec-butylamino)-diphenyl ether, etc.

Here again, it is understood that the specific compounds recited above are illustrative of typical compounds for use in the present invention, and that corresponding compounds substituted with other hydrocarbon groups and/or other acyl groups are used in accordance with the present invention.

From the description hereinbefore set forth, it will be seen that a number of different compounds may be used in accordance with the present invention. However, it is understood that all of these compounds are not necessarily equivalent in their activity in a particular organic substance. However, all of these compounds containing the acyl and diaminodiphenyl ether composition will be effective in retarding oxidation of organic substances. Also, it is understood that a mixture of the acylated diaminodiphenyl ethers may be used.

The inhibitors of the present invention are new compositions of matter and, accordingly, are being so claimed in the present application. These inhibitors may be prepared in any suitable manner. The preparations of a number of these inhibitors are set forth in the examples appended to the present specifications. It is understood that other acylated diaminodiphenyl ethers may be prepared by the same general methods.

In general, the inhibitor of the present invention will be used in the organic substance in a concentration of from about 0.0001% to about 5% by weight of the organic substance, although in some cases higher or lower concentrations may be employed. The exact concentration to be used will depend upon the particular organic substance being treated. In most cases, concentrations of from about 0.01% to about 2% by weight generally will be employed.

It is understood that the inhibitor of the present invention may be used along with other additives incorporated in the organic substance. For example, in grease the inhibitor may be used along with higher alcohols, esters, organic amines, polybutene, sulfurized fatty materials, sulfur chlorine compounds, molybdenum disulfide, dyes, perfumed materials, fillers, etc. In lubricating oil, the inhibitor may be used along with one or more of the above additives and/ or viscosity index improver, pourpoint depressor, anti-foaming agent, detergent, lubricity or extreme pressure additive, etc. In polymers, such as polyolefins, the inhibitor is used along with dyes and/or pigments, anti-static agents, plasticizers, ultraviolet light stabilizers, etc. In some cases, it may be of advantage to also include a metal deactivator as, for example, disalicylal diamino propane, ethylene diamine tetraacetic acid tetrasodium salt, etc., or to include other additives such as tricresyl phosphate, trialkyl phenols including 2,6-di-tert-butyl-4-methylphenol, 2,4-dimethyl-6-tert-butylphenol, alkylated diphenyl amines, phenyl naphthyl amines, dialkyl phenylene diamines, phenothiazine, organic selenium compounds, etc. When desired, the inhibitor of the present invention may be prepared as a mixture with one or more of these other additives and incorporated in this manner in the organic substance.

Also, it is understood that the inhibitor of the present invention may be prepared as a solution in a suitable solvent including hydrocarbons, alcohols, ketones, etc. In some cases, the same solvent used for the inhibitor of the present invention may be used for one or more of the other additives to be incorporated in the organic substance. In another method, the inhibitor of the present invention may be prepared as a stock solution in a small quantity of the organic substance and the stock solution then is incorporated into the major quantity of the organic substances.

The inhibitor of the present invention may be incorporated in the organic substance in any suitable manner and at any suitable stage of preparation. For example, in an organic substance which comprises a mixture of several components as, for example, grease, the inhibitor may be added to one or more of the components of the grease prior to compositing and processing thereof, or it may be added to the mix at any time, preferably before final processing in order to obtain intimate mixing and dissolving of the inhibitor in the grease.

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

2-amino-4'-acetylaminodiphenyl ether was prepared as follows: p-aminophenol was acetylated by refluxing 400 g. of p-aminophenol, 400 g. of acetic acid and 200 cc. of xylene solvent for six hours. The water formed during the reaction was continuously removed as an azeotrope with excess acetic acid. After completion of the reaction, the product were cooled, filtered, and washed with dilute HCl. The product was recovered by recrystallization from water.

The acetylated aminophenol prepared in the above manner then was reacted with o-chloronitrobenzene as follows: 152 g. of p-acetylaminophenol, 471 g. of o-chloronitrobenzene and 65 g. of 85% potassium hydroxide dissolved in 300 cc. of methanol were heated to 155° C. for four hours. Methanol solvent and water of reaction were removed continuously. The reaction mixture then was steam distilled to remove excess chloronitrobenzene, and the remaining product was filtered, dried and recrystallized from methanol. The product was 2-nitro-4'-acetylaminodiphenyl ether, having a melting point of 141.5–142.5° C. Calculated: 61.76% carbon and 4.44% hydrogen. Found: 61.56% carbon and 4.56% hydrogen.

The 2-nitro-4'-acetylaminodiphenyl ether prepared in the above manner was reduced by dissolving 208 g. thereof in 600 cc. of ethyl acetate and reacting with 100 atmospheres of hydrogen at 75° C. in the presence of 15 g. of nickel catalyst. The product was separated from the catalyst by filtering, the ethyl acetate solvent removed, and the product was recrystallized from benzene. The product is 2-amino-4'-acetylaminodiphenyl ether having a melting point of 118–120° C. Calculated: 69.40% carbon and 5.82% hydrogen. Found: 69.54% carbon and 5.89% hydrogen.

EXAMPLE II

2-isopropylamino-4'-acetylaminodiphenyl ether was prepared as follows: 170 g. of 2-amino-4'-acetylaminodiphenyl ether, prepared as described in Example I, were dissolved in one liter of acetone and reductively alkylated at 160° C. under 100 atmospheres of hydrogen in the presence of an alumina-platinum catalyst. The liquid reaction product was filtered out to separate the catalyst, the solvent was evaporated, and the product purified by recrystallization from benzene. The 2-isopropylamino-4'-acetylaminodiphenyl ether was recovered as a solid, having a melting point of 148–149° C. Calculated: 71.80% carbon and 7.09% hydrogen. Found: 71.85% carbon and 7.00% hydrogen.

EXAMPLE III

4-acetylamino-4'-aminodiphenyl ether was prepared as follows: 253 g. of p-acetylaminophenol, prepared in the manner described in Example I, 780 g. of p-chloronitrobenzene and 108 g. of 85% potassium hydroxide were dissolved in 400 cc. of methanol and heated at 155° C. for four hours under a nitrogen atmosphere. Methanol solvent and water of reaction were removed continuously. The product was steam distilled to remove excess chloronitrobenzene, then cooled, filtered and recrystallized from benzene. 4-acetylamino-4'-nitrodiphenyl ether was recovered as a solid having a melting point of 150–151° C. Calculated: 61.76% carbon and 4.44% hydrogen. Found: 61.54% carbon and 4.41% hydrogen.

285 g. of the 4-acetylamino-4'-nitrodiphenyl ether, prepared in the above manner, dissolved in 700 cc. of ethyl acetate was reacted with hydrogen at 75° C. in the presence of nickel catalyst. The hydrogen pressure was 100

atmospheres. Catalyst was filtered off, the product heated to remove solvent and then recrystallized from benzene. 4-acetylamino-4'-aminodiphenyl ether was recovered as a solid, having a melting point of 131–133° C. Calculated: 69.40% carbon and 5.82% hydrogen. Found: 69.53% carbon and 5.65% hydrogen.

EXAMPLE IV

4-acetylamino-4'-sec-butylaminodiphenyl ether was prepared as follows: 175 g. of 4-acetylamino-4'-aminodiphenyl ether, prepared as described in Example III, were dissolved in one liter of methyl ethyl ketone and reductively alkylated at 160° C. under 100 atmospheres of hydrogen in the presence of an alumina-platinum catalyst. The reaction product were filtered to remove the catalyst and then heated to evaporate the solvent. 4-acetylamino-4'-sec-butylaminodiphenyl ether was recovered as a light amber viscous liquid.

EXAMPLE V

2-(N-acetyl-N-isopropylamino)-4'-diisopropylaminodiphenyl ether was prepared as follows: 2,4'-diaminodiphenyl ether was reductively alkylated with acetone at 160° C. under 100 atmospheres of hydrogen in the presence of an alumina-platinum catalyst. The reductive alkylation was carried out in a series of four different reactions with separation of water between steps. The final reaction product was distilled to remove water and ketone. The remaining liquid consisted of a mixture of 2,4-diisopropylaminodiphenyl ether and 2-isopropylamino-4'-diisopropylaminodiphenyl ether. The above mixture then was acetylated in benzene solvent by reaction with acetic anhydride and heated on a steam bath for two hours. After cooling, the excess acetic anhydride and acetic acid were extracted with 10% sodium hydroxide solution and the 2-(N-acetyl-N-isopropylamino)-4'-diisopropylaminodiphenyl ether was separated from diacetylated material by extraction with 5% hydrochloric acid solution, followed by neutralization with 10% sodium hydroxide and extraction with benzene. The benzene was evaporated and the product was distilled. 2-(N-acetyl-N-isopropylamino)-4'-diisopropylaminodiphenyl ether was recovered as a solid, having a melting point of 71–75° C.

EXAMPLE VI

2-(N-benzoyl-N-isopropylamino)-4'-diisopropylaminodiphenyl ether was prepared in substantially the same manner as described in Example V, except that benzoyl chloride was used in place of acetic anhydride. 2-(N-benzoyl-N-isopropylamine)-4'-diisopropylaminodiphenyl ether was recovered as a solid, having a melting point of 81–83° C. Calculated: 78.10% carbon and 7.96% hydrogen. Found: 78.27% carbon and 7.98% hydrogen.

EXAMPLE VII

The inhibitor of this example is 2,4'-bis-(N-acetyl-N-isopropylamino)-diphenyl ether and was prepared by reductively alkylating 2,4'-diaminodiphenyl ether with acetone until no primary amine remained. The reductive alkylation was effected in substantially the same manner as hereinbefore set forth. The product then was dissolved in benzene, 2.1 equivalents of acetic anhydride was added, and the mixture was heated on a steam bath for two hours, after the initial exothermic reaction subsided. The reaction mixture was cooled, extracted with 10% sodium hydroxide solution to remove unreacted acetic acid, and then extracted with 5% hydrochloric acid solution to remove any non-acetylated and tertiary amines which may be present. The solvent was evaporated and the product was recrystallized from methanol. 2,4'-bis-(N-acetyl-N-isopropylamino)-diphenyl ether was recovered as a solid, having a melting point of 131–132° C.

EXAMPLE VIII

4,4'-bis(N-acetyl-N-isopropylamino)-diphenyl ether was prepared in the same manner as descibed in Example VII, except that 4,4'-diaminophenyl ether was used in place of 2,4'-diaminodiphenyl ether. 4,4'-bis-(N-acetyl-N-isopropylamino)-diphenyl ether was recovered as a solid, having a melting point of 127–129° C. Calculated: 71.71% carbon and 7.66% hydrogen. Found: 71.59% carbon and 7.57% hydrogen.

EXAMPLE IX

A number of the N-acyl-diaminodiphenyl ethers were evaluated in various substrates. This example reports the results of evaluations of two of the inhibitors of the present invention in a synthetic lubricating oil consisting of mixed esters of trimethylolpropane. The lubricating oil is available commercially under the trade name of "Cellutherm." Typical properties of this lubricating oil are set forth below:

Specific gravity, 60/60° F.	0.965
Acidity, mg./KOH/g.	0.03
Color, ASTM	2
Fire point, COC, ° F.	520
Flash point, COC, ° F.	460
Hydrolysis number	0.27
Viscosity—	
At −65° cs.	14,900
At 100° F., SSU	76.93
At 210° F., SSU	37.77

The lubricating oil was evaluated in accordance with a standard Oxygen Stability Test, in which a 100 cc. sample of the lubricating oil is placed in a bath maintained at 400° F. and air is blown therethrough at a rate of 5 liters of air per hour. The sample of lubricating oil is examined periodically and the time to reach an acid number of 5 is reported. It is apparent that the longer the time required to reach an acid number of 5, the more stable is the sample of lubricating oil. In other words, it takes longer for the more stable oil to deteriorate.

In addition, the samples of lubricating oil after treatment in the above manner were extracted with iso-octane to determine the percent insolubles which, in turn, determine the percent of heavier materials formed during such treatment. Also, the samples of lubricating oil were analyzed for viscosity in order to determine the percent viscosity change caused by such treatment. The tube used to contain the lubricating oil during such treatment is examined visually to determine whether it is clean or contains sludge. This last evaluation is very important because the deposition of sludge is of serious consequence in that it may result in plugging of the filters or moving parts of the engine.

Inhibitor A is 2-(N-acetyl-N-isopropylamino)-4'-diisopropylaminodiphenyl ether and is the compound of Example V which describes the preparation thereof in detail.

Inhibitor B is 2-(N-acetyl-N-isopropylamino)-4'-isopropylaminodiphenyl ether and was prepared as follows: 2-(N-acetyl-N-isopropylamino)-4'-aminodiphenyl ether was dissolved in acetone and was reductively alkylated with acetone at 120° C. under 100 atmospheres of hydrogen in the presence of an alumina-platinum catalyst. The catalyst was filtered off, the solvent evaporated, and the product recrystallized fom methanol. The product had a melting point of 118–119° C. Calculated: 73.59% carbon and 8.03% hydrogen. Found: 73.58% carbon and 7.95% hydrogen.

The following table reports the results of evaluations made with samples of the "Cellutherm" lubricating oil with and without the inhibitors. The inhibitors were used in a concentration of 0.0033 mole per 100 cc. of lubricating oil. This is approximately 0.8% by weight thereof.

Table I

Run No.	Inhibitor	Hours to Acid No. of 5	Percent Insolubles in Iso-octane	Percent of Viscosity Change	Tube Condition
1	None	9			
2	A	91	0.4	4.1	Clean.
3	B	89	0.43	4.0	Clean.

As mentioned above, Inhibitor A is 2-(N-acetyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether and Inhibitor B is 2-(N-acetyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether.

It has been established that the lubricating oil must have an Induction Period (hours to acid number of 5) of at least 48 hours. Accordingly, it will be noted that the inhibitors of the present invention served to more than meet this requirement in effecting Induction Periods of 91 and 89. Also, it will be noted that the percent of insolubles in iso-octane was very low and that the percent viscosity change also was low. The percent viscosity change reported in the table is that found after 48 hours.

As hereinbefore set forth, the condition of the tube is a very important criterion. It will be noted that the tube was clean in the above runs. This means that the tubes did not contain any sludge and, therefore, that the lubricating oil containing these inhibitors will not clog the filters or the moving parts of jet engines.

EXAMPLE X

Inhibitor A of Examples V and IX also was evaluated in dioctyl sebacate marketed under the trade name of "Plexol 201." This synthetic lubricating oil is being used commercially on a comparatively large scale.

The evaluation was made in the same manner as described in Example IX, again using the inhibitor in the same concentration as described therein. The results of this run, as well as the results of a sample of the lubricating oil without inhibitor are reported in the following table:

Table II

Run No.	Inhibitor	Hours to Acid Number of 5
4	None	9
5	4-(N-acetyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether.	51

Here again, it will be noted that inhibitor was effective in stabilizing the lubricating oil.

EXAMPLE XI

This example reports the results of using an inhibitor of the present invention in grease. The inhibitor of this example is 2-(N-benzoyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether and was prepared as described in Example VI. The grease is a lithium grease and is prepared by mixing 91% by weight of highly refined lubricating oil with 8% by weight of lithium stearate. The mixture is heated at about 232° C. while agitating the same. Subsequently, the grease is cooled while agitating to 160° C. and, at this temperature, 0.5% by weight of 2-(N-benzoyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether is added. Agitation is continued, and the mixture is allowed to cool to about 120° C. and the grease then is further cooled slowly to room temperature.

The stability of the grease is tested according to a modified Norma Hoffman method, in which a sample of the grease is placed in a bomb and oxygen is charged thereto. The bomb then is heated to 100° C. and the time required for a drop of 5 pounds pressure is taken as the Induction Period.

When evaluated in the above manner, a sample of the grease without added inhibitor developed a pressure drop of 5 pounds in nine hours. In contrast, a sample of the grease containing 0.3% by weight of 2-(N-benzoyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether did not develop a 5 pound pressure drop until 20 hours.

EXAMPLE XII

A number of the acetylated aminodiphenyl ethers of the present invention also were evaluated as antioxidants in a polyethylene. The polyethylene used in this example is of high density and marketed under the trade name of "Fortiflex" by the Celanese Corporation of America. In the samples containing inhibitor, the inhibitor was used in a concentration of 0.075% by weight of the polyethylene and was incorporated therein by milling. The different samples of polyethylene were evaluated in a method similar to that described by Hawkins, Hansen, Matreyek and Winslow in Rubber Chemistry and Technology, October-November 1959, pages 1164–1170, except that an electrically heated aluminum block rather than an oven was used to maintain the desired temperature. The oxygen absorption of the sample was determined manometrically rather than volumetrically. In this method, samples of the polyethylene weighing about 0.5 g. are placed in separate 8 mm. glass tubes and the tubes then are inserted into horizontal rows of openings located concentrically around the heater. The temperature is maintained at about 140° C. The glass tubing also is packed with glass wool and molecular sieves to absorb the gases. Each of the glass tubes is connected to individual manometers containing mercury and the differential pressure is periodically determined. The Induction Period is taken as the number of hours required to reach a pressure differential of 20 cm. Hg.

The following table reports the results of a sample of the polyethylene without inhibitor and two samples containing the inhibitors as indicated below.

Table III

Run No.	Inhibitor	Induction Period Hours to ΔP of 20 cm. Hg	Color
6	None	7.5	White.
7	2-(N-benzoyl-N-isopropyl-amino)-4′-diisopropyl-aminodiphenyl ether.	190	White to light tan.
8	4-acetylamino-4′-sec-butyl-amino-diphenyl ether.	155	Do.

From the data in the above table, it will be seen that the inhibitors of the present invention are effective in extending the Induction Period of the samples of polyethylene. Also, it will be noted that there was very little discoloration in the stabilized polyethylene.

I claim as my invention:

1. 2-(N-acetyl-N-isopropylamino)-4′-isopropylaminodiphenyl ether.

2. 2-(N-acetyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether.

3. 4-acetylamino-4′-sec-butylaminodiphenyl ether.

4. 2-(N-benzoyl-N-isopropylamino)-4′-diisopropylaminodiphenyl ether.

References Cited by the Examiner

UNITED STATES PATENTS

1,900,442	3/33	Grether	260—562

OTHER REFERENCES

Finar et al.: J. Chem. Soc. (London), pages 483–486 (1960).

IRVING MARCUS, *Primary Examiner.*

NICHOLAS S. RIZZO, WALTER A. MODANCE, *Examiners.*