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(54) Improved high molecular weight dispersant additives.

(57) The present invention is directed to improved oil soluble dispersant materials which comprise members selected from the group consisting of oil soluble salts, amides, imides, oxazolines, or mixtures thereof, of polyolefin-substituted mono and dicarboxylic acids or their anhydrides covered as per claim 1 wherein the polyolefin is characterized by number average molecular weight of from about 1,500 to 2,500 and a molecular weight distribution of less than about 3.0, and wherein the dispersant additive contains within its structure an average of from 0.7 to 1.3 mono- or dicarboxylic acid producing moieties (preferably acid or anhydride moieties) covered as per claim 1 per polyolefin molecule, and wherein the dispersant material contains from 0.5 to 4 equivalents of secondary amine groups per equivalent of the mono- or dicarboxylic acid producing moieties per molecule, with the proviso that the dispersant material is further characterized by a Z factor of from 4,000 to 6,000, wherein the Z factor is determined by the expression:

$$Z = \left[\frac{([N])^2}{M_n} \times (1.1\times10^6) \right] + 1.5(M_n)$$

wherein [N] is the total nitrogen content of the dispersant material expressed in wt% and M_n is the polyolefin number average molecular weight.

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IMPROVED HIGH MOLECULAR WEIGHT DISPERSANT ADDITIVES

This invention relates to improved oil soluble dispersant additives useful in fuel and lubricating compositions, and to concentrates containing said additives.

The technology of ashless dispersants has matured considerably since it was first commercialized thirty years ago. Many improvements over the original prototypes are described in the literature involving specific molecular weights of the polymer backbone, degrees of functionalization of the polymer, types of polar groups, and a variety of finishing steps and process improvements which impart certain desirable properties to candidate dispersants.

As the product technologies evolved, so, too, did the performance requirements. Gasoline and diesel engines were required to operate under more severe conditions, sludge and varnish handling specifications became more stringent, and the dispersants needed to be compatible with an increasing variety of low molecular weight additives, in concentrates which are used to formulate lubricating oils.

To meet these challenges, improved dispersant products are continually sought. However, the development of improved dispersants is greatly complicated by the tendency of any change in one property to cause undesirable effects in another. For example, increasing the concentration of polar groups attached to the polymer to enhance dispersancy in gasoline engines can result in poorer performance in diesel engines and more vigorous attack on elastomeric engine seals. Raising the polymer molecular weight to get enhanced oil solubility can cause the concentration of polar groups to dip below the minimum needed to provide efficient dispersancy for all the sludge and varnish precursors. Increasing the number of functional polymer groups to compensate for this problem can yield severe compatibility problems with high base number colloidal detergents and other conventional additives, leading to unstable viscosities and phase separation.

We herein describe a small window within the PIBSA/PAM framework which defines the dispersant compositions which could simultaneously exhibit superb The window is defined by an equation and limits which describe for the first time the required balance of polymer size and distribution, and functional group concentration and basicity which could attain the above-described goals.

SUMMARY OF THE INVENTION

The present invention is directed to improved oil soluble dispersant materials which comprise members selected from the group consisting of oil soluble salts, amides, imides, oxazolines, or mixtures thereof, of polyolefin-substituted mono and dicarboxylic acids or their anhydrides, wherein the polyolefin is characterized by a number average molecular weight of from about 1,500 to 2,500 and a molecular weight distribution of less than about 3.0, and wherein the dispersant material contains within its structure an average of from 0.7 to 1.3 mono- or dicarboxylic acid producing moieties (preferably acid or anhydride moieties) per polyolefin molecule, and wherein the dispersant material contains from 0.5 to 4 equivalents of free secondary amine groups per equivalent of the mono-or dicarboxylic acid producing moieties per molecule, with the proviso that the dispersant material is further characterized by a Z factor of from 4,000 to 6,000 (preferably from 4,200 to 5,800), wherein the Z factor is determined by the expression (I):

$$Z = \left[\frac{([N])^2}{M_n} \times (1.1 \times 10^6) \right] + 1.5(M_n)$$

wherein [N] is the total nitrogen content of the dispersant material expressed in wt% (normalized to a solution containing 50 wt% active dispersant material, viz. functionalized polymer) and M_n is the polyolefin number average molecular weight.

The materials of the invention are different from the prior art because of their effectiveness and their ability to simultaneously provide enhanced dispersancy required for modern-day gasoline and diesel performance, with minimum viscosity interactions and compatibility problems (e.g., with high base number colloids and the low molecular weight surface active agents normally present in commercial additive concentrates. In fuels, the additives serve to minimize the degree of carburetor and fuel injector fouling from deposits. In addition, the additives of this invention possess superior viscometric stability.

Therefore, the present invention is also directed to novel processes for preparing the dispersant materials of this invention.

DETAILED DESCRIPTION OF THE INVENTION

PREPARATION OF LONG CHAIN HYDROCARBYL SUBSTITUTED REACTANT

The dispersant materials of this invention are prepared by reacting at least one polyamine with a polyolefin-substituted acid, anhydride or ester material. The polymer-substituted mono- or dicarboxylic acid material, i.e., acid, anhydride or acid ester used in this invention, includes the reaction product of a long chain hydrocarbon polyolefin with a monounsaturated carboxylic reactant comprising at least one member selected from the group consisting of (i) monounsaturated C_4 to C_{10} dicarboxylic acid (preferably wherein (a) the carboxyl groups are vicinyl, (i.e. located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation); (ii) derivatives of (i) such as anhydrides or C_1 to C_5 alcohol derived mono- or di-esters of (i); (iii) monounsaturated C_3 to C_{10} monocarboxylic acids wherein the carbon-carbon double bond is conjugated to the carboxy group, i.e, of the structure

$$-C=C-\overset{\overset{\displaystyle O}{\|}}{C}-;$$

and (iv) derivatives of (iii) such as C_1 to C_5 alcohol derived monoesters of (iii). Upon reaction with the polymer, the monounsaturation of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes a polymer substituted succinic anhydride, and acrylic acid becomes a polymer substituted propionic acid.

Typically, from about 0.7 to about 2.0 (e.g., 0.8 to 1.6), preferably from about 1.0 to about 1.4, and most preferably from about 1.1 to about 1.3 moles of said monounsaturated carboxylic reactant are charged to the reactor per mole of polymer charged.

Normally, not all of the polymer reacts with the monounsaturated carboxylic reactant and the reaction mixture will contain non-acid substituted polymer. The polymer-substituted mono- or dicarboxylic acid material (also referred to herein as "functionalized" polymer or polyolefin), non-acid substituted polyolefin, and any other polymeric by-products, e.g. chlorinated polyolefin, (also referred to herein as "unfunctionalized" polymer) are collectively referred to herein as "product residue" or "product mixture". The non-acid substituted polymer is typically not removed from the reaction mixture (because such removal is difficult and would be commercially infeasible) and the product mixture, stripped of any monounsaturated carboxylic reactant is employed for further reaction with the amine or alcohol as described hereinafter to make the dispersant.

Characterization of the average number of moles of monounsaturated carboxylic reactant which have reacted per mole of polymer charged to the reaction (whether it has undergone reaction or not) is defined herein as functionality. Said functionality is based upon (i) determination of the saponification number of the resulting product mixture using potassium hydroxide; and (ii) the number average molecular weight of the polymer charged, using techniques well known in the art. Functionality is defined solely with reference to the resulting product mixture. Although the amount of said reacted polymer contained in the resulting product mixture can be subsequently modified, i.e. increased or decreased by techniques known in the art, such modifications do not alter functionality as defined above. The terms "polymer substituted monocarboxylic acid material" and "polymer substituted dicarboxylic acid material" as used herein are intended to refer to the product mixture whether it has undergone such modification or not.

To provide the improved dispersants of the present invention, the functionality of the polymer substituted mono- and dicarboxylic acid material must be from about 0.7 to 1.3, preferably from about 0.8 to 1.2, and most preferably from about 0.9 to 1.1.

Exemplary of such monounsaturated oarboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C_1 to C_4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, methyl fumarate, etc.

Preferred olefin polymers for reaction with the monounsaturated carboxylic reactants are polymers comprising a major molar amount of C_2 to C_{10}, e.g. C_2 to C_5 monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of: ethylene and propylene; butylene and isobutylene; propylene and isobutylene; etc. Mixtures of polymers prepared by polymerization of mixtures of isobutylene, butene-1 and butene-2, e.g., polyisobutylene wherein up to about 40% of the monomer units are derived from butene-1 and butene-2, is an exemplary, and preferred, olefin polymer. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C_4 to C_{18} non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene; or a copolymer of ethylene, propylene and 1,4-hexadiene; etc.

In some cases, the olefin polymer may be completely saturated, for example an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

The olefin polymers used must have number average molecular weights within the range of from about 1,500 to 2,500, preferably from about 1,600 to 2,400, more preferably between about 1,800 and about 2,300. Particularly useful olefin polymers have number average molecular weights within the range of about 1,500 and about 2,500 with approximately one terminal double bond per polymer chain. An especially useful starting material for highly potent dispersant additives useful in accordance with this invention is polyisobutylene, wherein up to about 40% of the monomer units are derived from butene-1 and/or butene-2. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information, see W. W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

The olefin polymers will generally have a molecular weight distribution (the ratio of the weight average molecular weight to number average molecular weight, i.e. $\overline{M}_w/\overline{M}_n$ of less than 3.0, preferably from about 1.4 to about 2.7, and more preferably from about 1.2 to 2.4.

The polymer can be reacted with the mono-unsaturated carboxylic reactant by a variety of methods. For example, the polymer can be first halogenated, chlorinated or brominated to about 1 to 8 wt.%, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polymer at a temperature of 20 to 160° C, preferably 60 to 140° C, e.g. 110 to 130° C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient monounsaturated carboxylic reactant at 100 to 250° C, usually about 180° to 235° C, for about 0.5 to 10, e.g. 3 to 8 hours, so the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated polymer. Processes of this general type are taught in U.S. Patents 3,087,436; 3,172,892; 3,272,746 and others. Alternatively, the polymer and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in U.S. Patents 3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and in U.K. 1,440,219.

Alternately, the polymer and the monounsaturated carboxylic reactant can be contacted at elevated temperature to cause a thermal "ene" reaction to take place. Thermal "ene" reactions have been heretofore described in U.S. Patents 3,361,673 and 3,401,118, the disclosures of which are hereby incorporated by reference in their entirety.

Preferably, the polymers used in this invention contain less than 5 wt%, more preferably less than 2 wt%, and most preferably less than 1 wt% of a polymer fraction comprising polymer molecules having a molecular weight of less than about 300, as determined by high temperature gel premeation chromatography employing the corresponding polymer calibration curve. Such preferred polymers have been found to permit the preparation of reaction products, particularly when employing maleic anhydride as the unsaturated acid reactant, with decreased sediment. In the event the polymer produced as described above contains greater than about 5 wt% of such a low molecular weight polymer fraction, the polymer can be first treated by conventional means to remove the low molecular weight fraction to the desired level prior to initiating the ene reaction, and preferably prior to contacting the polymer with the selected unsaturated carboxylic reactant(s). For example, the polymer can be heated, preferably with inert gas (e.g., nitrogen) stripping, at elevated temperature under a reduced pressure to volatilize the low molecular weight polymer components which can then be removed from the heat treatment vessel. The precise temperature, pressure and time for such heat treatment can vary widely depending on such factors as as the polymer number average molecular weight, the amount of the low molecular weight fraction to be removed, the particular monomers employed and other factors. Generally, a temperature of from about 60 to 100° C and a pressure of from about 0.1 to 0.9 atmospheres and a time of from about 0.5 to 20 hours (e.g., 2 to 8 hours) will be sufficient.

In this process, the selected polymer and monounsaturated carboxylic reactant and halogen (e.g., chlorine gas), where employed, are contacted for a time and under conditions effective to form the desired polymer substituted mono- or dicarboxylic acid material. Generally, the polymer and monounsaturated carboxylic reactant will be contacted in a unsaturated carboxylic reactant to polymer mole ratio usually from about 0.7:1 to 2:1, and preferably from about 1:1 to 1.3:1, at an elevated temperature, generally from about 120 to 260 °C, preferably from about 160 to 240 °C. The mole ratio of halogen to monounsaturated carboxylic reactant charged will also vary and will generally range from about 0.5:1 to 4:1, and more typically from about 0.7:1 to 2:1 (e.g., from about 0.9 to 1.4:1). The reaction will be generally carried out, with stirring for a time of from about 1 to 20 hours, preferably from about 2 to 6 hours.

By the use of halogen, about 65 to 95 wt. % of the polyolefin, e.g. polyisobutylene will normally react with the monounsaturated carboxylic acid reactant. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 75 wt. % of the polyisobutylene will react. Chlorination helps increase the reactivity. For convenience, the aforesaid functionality ratios of mono- or dicarboxylic acid producing units to polyolefin, e.g., 0.7 to 1.3, etc. are based upon the total amount of polyolefin, that is, the total of both the reacted and unreacted polyolefin, used to make the product.

The reaction is preferably conducted in the substantial absence of O_2 and water (to avoid competing side reactions), and to this end can be conducted in an atmosphere of dry N_2 gas or other gas inert under the reaction conditions. The reactants can be charged separately or together as a mixture to the reaction zone, and the reaction can be carried out continuously, semi-continuously or batchwise. Although not generally necessary, the reaction can be carried out in the presence of a liquid diluent or solvent, e.g., a hydrocarbon diluent such as mineral lubricating oil, toluene, xylene, dichlorobenzene and the like. The polymer substituted mono- or dicarboxylic acid material thus formed can be recovered from the liquid reaction mixture, e.g., after stripping the reaction mixture, if desired, with an inert gas such as N_2 to remove unreacted unsaturated carboxylic reactant.

If desired, a catalyst or promoter for reaction of the olefin polymer and monounsaturated carboxylic reactant (whether the olefin polymer and monounsaturated carboxylic reactant are contacted in the presence or absence of halogen (e.g., chlorine)) can be employed in the reaction zone. Such catalyst of promoters include alkoxides of Ti, Zr, V and Al, and nickel salts (e.g., Ni acetoacetonate and Ni iodide) which catalysts or promoters will be generally employed in an amount of from about 1 to 5,000 ppm by weight, based on the mass of the reaction medium.

NITROGEN-CONTAINING COMPOUNDS

As described above, the dispersant additives of the present invention are prepared by contacting a polyamine with a long chain hydrocarbyl-substituted mono-or dicarboxylic acid material. The polyamines contain at least two (e.g., from 2 to 20), preferably at least 3 (e.g. from 3 to 15), and most preferably from 3 to 8, reactive nitrogen moieties (that is, the total of the nitrogen-bonded H atoms) per molecule of the nitrogen-containing compound. The polyamines preferably comprise linked polyamines prepared by contacting a polyfunctional reactant with a nitrogen-containing compound containing at least two (e.g., from 2 to 20), preferably at least 3 (e.g. from 3 to 15), and most preferably from 3 to 8, reactive nitrogen moieties (that is, the total of the nitrogen-bonded H atoms) per molecule of the nitrogen-containing compound. The nitrogen-containing compound will generally comprise at least one member selected from the group consisting of organic primary monoamines and organic polyamines containing at least one primary amine group or at least two secondary amine groups per molecule. Generally, the organic amines will contain from about 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and about 2 to 12, preferably 3 to 12, and most preferably from 3 to 8 (e.g., 5 to 9) total nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g, hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:

$$\underset{\textbf{(I)}}{\mathrm{R{-}\underset{\substack{|\\ R''}}{N}{-}R'}}, \quad \text{and} \quad \underset{\textbf{(II)}}{\mathrm{R{-}\underset{\substack{|\\ R'}}{N}{-}(CH_2)_s{-}\left[\underset{\substack{|\\ R'''}}{N}{-}(CH_2)_s\right]_t{-}\underset{\substack{|\\ R'}}{N}{-}R}}$$

wherein R, R′, R″ and R‴ are independently selected from the group consisting of hydrogen; C_1 to C_{25}

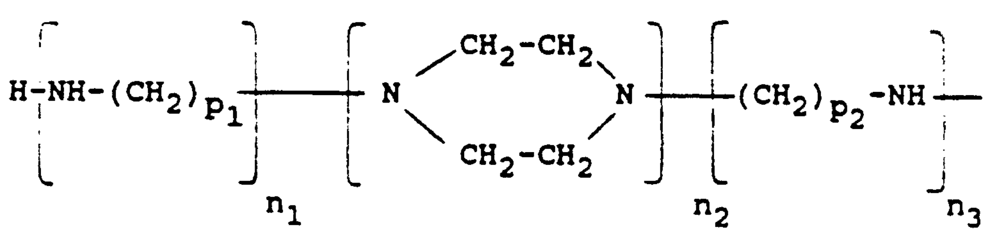
straight or branched chain alkyl radicals; C_1 to C_{12} alkoxy C_2 to C_6 alkylene radicals; C_2 to C_{12} hydroxy amino alkylene radicals; and C_1 to C_{12} alkylamino C_2 to C_6 alkylene radicals; and wherein R''' can additionally comprise a moiety of the formula:

$$-\!\!\left[(CH_2)_{s'}-\underset{\displaystyle R'}{\underset{|}{N}}\right]_{t'}\!\!-H \qquad \text{(III)}$$

wherein R' is as defined above, and wherein s and s' can be the same or a different number of from 2 to 6, preferably 2 to 4; and t and t' can be the same or different and are numbers of from 0 to 10, preferably 2 to 7, and most preferably about 3 to 7, with the proviso that the sum of t and t' is not greater than 15. To assure a facile reaction, it is preferred that R, R', R'', R''', s, s', t and t' be selected in a manner sufficient to provide the compounds of Formulas I and II with typically at least one primary or secondary amine group, preferably at least two primary or secondary amine groups. This can be achieved by selecting at least one of said R, R', R'' or R''' groups to be hydrogen or by letting t in Formula II be at least one when R''' is H or when the III moiety possesses a secondary amino group.

Non-limiting examples of suitable organic amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetra; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene)triamine; di-(1,3-propylene)triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine ; tris hydroxymethylaminomethane (THAM); diisopropanol amine; diethanol amine; triethanol amine; mono-, di-, and tri-tallow amines; amino morpholines such as N-(3-aminopropyl)-morpholine; and mixtures thereof.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula (IV):



wherein p_1 and p_2 are the same or different and are each integers of from 1 to 4, and n_1, n_2 and n_3 are the same or different and are each integers of from 1 to 3. Non-limiting examples of such amines include 2-pentadecyl imidazoline: N-(2-aminoethyl) piperazine; etc.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetra, tetraethylene pentamine and isomeric piperazines. Low cost poly(ethyleneamines) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

Useful amines also include polyoxyalkylene polyamines such as those of the formulae:

NH_2-alkylene$\left(\text{O-alkylene}\right)_m$$NH_2$ (V)

where m has a value of about 3 to 70 and preferably 10 to 35; and

R$\left(\text{alkylene}\left(\text{O-alkylene}\right)_p NH_2\right)_a$ (VI)

where "n" has a value of about 1 to 40 with the provision that the sum of all the n's is from about 3 to about 70 and preferably from about 6 to about 35, and R is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms wherein the number of substituents on the R group is represented by the value of "p", which is a number of from 3 to 6. The alkylene groups in either formula (V) or (VI) may be straight or branched chains containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

The polyoxyalkylene polyamines of formulas (V) or (VI) above, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from about 200 to about 4000 and preferably from about 400 to about 2000. The preferred polyoxyalkylene polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from about 200 to 2000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc.

Additional amines useful in the present invention are described in U.S. Patent 3,445,441, the disclosure of which is hereby incorporated by reference in its entirety.

Most preferred as the nitrogen-containing compound are members selected from the group consisting of organic diprimary amines having from 2 to 12 carbon atoms and from 2 to 8 nitrogen atoms per molecule. Examples of such preferred organic diprimary amines are ethylene diamine, propylene diamine, diethylene triamine, dipropylene triamine, triethylene tetraamine, tripropylene tetraamine, tetraethylene pentaamine, tetrapropylene pentaamine, polyhexamethylene diamine, phenyl diamine.

POLYFUNCTIONAL REACTANT

Polyfunctional reactants useful in this invention comprise compounds containing at least 2 (e.g., from 2 to 4) functional groups per molecule which are reactive with -NH- groups under the selected reaction conditions, and which when reacted with the selected nitrogen-containing compound serves to link two or more such N-compounds, to form a linked polyamine containing within its structure, on average, (i) at least two unreacted primary or secondary amine groups, and preferably also (ii) at least two nitrogen-containing moieties derived from said nitrogen-containing compound per moiety of said polyfunctional reactant

The linked polyamine can be illustrated by the generalized structure:

$A' - \text{Link} - (A'')_{t_1}$

wherein A, and A″ are each the same or different and are nitrogen-containing moieties corresponding to the nitrogen-containing compound, "Link" is the reacted polyfunctional reactant, and "t_1 is an integer of at least 1 (e.g., from 1 to 3). Preferably, A′ and A″ each contain at least one unreacted primary amine group, and preferably t_1 is 1 or 2. It will be understood that the reaction mixtures containing the linked polyamine will also generally contain as by-products other addition adducts, such as adducts of the structure:

$A' - \text{Link} - A'' - (\text{Link} - A'')_{t_2}$

wherein A′, "Link" and A″ are as defined above, and "t_2 is an integer of at least 1. Similarly, when a trifunctional reactant is employed, by-product adducts of the following structure can be present:

$$\begin{array}{l} A' - \text{Link} - A'' - \text{Link} - A'' \\ \qquad\quad \diagdown \qquad\qquad\qquad \diagdown \\ \qquad\quad\; A''\ ) - \qquad\qquad\;\; A''\ ) - \end{array}$$

and the like. Polyfunctional reactants useful in this invention include compounds having the formula (VII):

$$X - \overset{\overset{\displaystyle W^1}{\|}}{C} - (T)_a - [(\overset{\overset{\displaystyle W^2}{\|}}{C})_b - Y]_c$$

wherein W^1 and W^2 are the same or different and are O or S, X and Y are the same or different and are preferably each groups which are reactive with a -NH- group (i.e., with primary or secondary amine groups), T is a substituted or unsubstituted hydrocarbon moiety, "a" is 0 or 1, "b" is 0 or 1, and "c" is an integer of at least 1, with the provisos that c = 1 when a = 0 and that b = 1 when a = 1.

The X and Y functional groups are the same or different and include reactive groups selected from the group consisting of: halide, $-OR^4$, $-SR^4$, $-N(R^4)(R^5)$, $-Z^1C(O)OR^4$, $-C(O)R^4$, $-(R^3)C=C(R^1)(R^2)$, $-Z^1$-epoxy, $-Z^1$-nitrile, $-Z^1$-cyano, $-Z^1$-thiocyano, $-Z^1$-isothiocyano, and $-Z^1$-isocyano, wherein R^1, R^2, R^3, R^4 and R^5 are the same or different and are H or substituted or unsubstituted hydrocarbyl and wherein Z^1 is C_1 to C_{20} (preferably C^1 to C^{10}) bivalent hydrocarbylene (preferably alkylene or arylene). If a = b = 1, and T contains at least one >C=C< group, X and Y can together further comprise -O- or -S-, to provide as reactants a class of ethylenically unsaturated and aromatic anhydrides and sulfo-anhydrides. wherein R^1, R^2, R^3, R^4 and

R^5 are the same or different and are H or substituted or unsubstituted hydrocarbyl. If a = b = 1, and T contains at least one >C=C< group, X and Y can together further comprise -O-, to provide as reactants a class of ethylenically unsaturated and aromatic anhydrides.

When R^1, R^2, R^3, R^4 or R^5 are hydrocarbyl, these groups can comprise alkyl, cycloalkyl, aryl, alkaryl, aralkyl or heterocyclic, which can be substituted with groups which are substantially inert to any component of the reaction mixture under conditions selected for preparation of the amido-amine. Such substituent groups include hydroxy, halide (e.g., Cl, Fl, I, Br), -SH and alkylthio. When one or more of R^1 through R^5 are alkyl, such alkyl groups can be straight or branched chain, and will generally contain from 1 to 20, more usually from 1 to 10, and preferably from 1 to 4, carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, hexadecyl, octadecyl and the like. When one or more of R^1 through R^5 are aryl, the aryl group will generally contain from 6 to 10 carbon atoms (e.g., phenyl, naphthyl).

When one or more of R^1 through R^5 are alkaryl, the alkaryl group will generally contain from about 7 to 20 carbon atoms, and preferably from 7 to 12 carbon atoms. Illustrative of such alkaryl groups are tolyl, m-ethylphenyl, o-ethyltolyl, and m-hexyltolyl. When one or more of R^1 through R^5 are aralkyl, the aryl component generally consists of phenyl or (C_1 to C_6) alkyl-substituted phenol and the alkyl component generally contains from 1 to 12 carbon atoms, and preferably from 1 to 6 carbon atoms. Examples of such aralkyl groups are benzyl, o-ethylbenzyl, and 4-isobutylbenzyl. When one or more of R^1 and R^5 are cycloalkyl, the cycloalkyl group will generally contain from 3 to 12 carbon atoms, and preferably from 3 to 6 carbon atoms. Illustrative of such cycloalkyl groups are cyclopropyl, cyclobutyl, cyclohexyl, cyclooctyl, and cyclododecyl. When one or more of R^1 through R^5 are heterocyclic, the heterocyclic group generally consists of a compound having at least one ring of 6 to 12 members in which on one more ring carbon atoms is replaced by oxygen or nitrogen. Examples of such heterocyclic groups are furyl, pyranyl, pyridyl, piperidyl, dioxanyl, tetrahydrofuryl, pyrazinyl and 1,4-oxazinyl.

T is a polyvalent organic radical whose valence is equal to c + 1, wherein "c" is an integer of at least 1, preferably 1 to 3. Ordinarily T will not contain more than 20 carbon atoms and preferably not more than 10 carbon atoms. T can therefore include divalent groups such as as saturated and unsaturated hydrocarbylene (e.g., alkylene, alkenylene, arylene, and the like). When T is substituted, it can contain 1 or more substituents selected from the class consisting of halo, lower alkoxy, lower alkyl mercapto, nitro, lower alkyl and oxo. It also may contain interrupting groups such as -O-, -S-, -S(O)-, $-S(O)_2-$, -NH-, -C(O) and the like.

Examples of polyfunctional reactants of formula VII wherein X is $(R^1)(R^2)C=C(R^3)-$, a = b = 0 and c = 1 are difunctional reactants comprising alpha, beta-ethylenically unsaturated compounds selected from the group consisting of compounds of the formula:

$$R^1-\overset{\displaystyle R^2}{\overset{|}{C}}=\overset{\displaystyle R^3}{\overset{|}{C}}-\overset{\displaystyle W^1}{\overset{\|}{C}}-Y \qquad \text{(VIII)}$$

wherein W^1 is sulfur or oxygen, Y is as defined above, and is preferably $-OR^4$, $-SR^4$, or $-NR^4(R^5)$, wherein R^1, R^2, R^3, R^4 and R^5 are as defined above.

The alpha, beta-ethylenically unsaturated carboxylate compounds employed herein have the following formula:

$$R^1-\overset{\displaystyle R^2}{\overset{|}{C}}=\overset{\displaystyle R^3}{\overset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OR^4 \qquad \text{(IX)}$$

wherein R^1, R^2, R^3, and R^4 are the same of different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of such alpha, beta-ethylenically unsaturated carboxylate compounds of formula IX are acrylic acid, methacrylic acid, the methyl, ethyl, isopropyl, n-butyl, and isobutyl esters of acrylic and methacrylic acids, 2-butenoic acid, 2-hexenoic acid, 2-decenoic acid, 3-methyl-2-heptenoic acid, 3-methyl-2-butenoic acids 3-phenyl-2-propenoic acid, 3-cyclohexyl-2-butenoic acid, 2-methyl-2-butenoic acid, 2-propyl-2-propenoic acid, 2-isopropyl-2-hexenoic acid, 2,3-dimethyl-2-butenoic acid, 3-cyclohexyl-2-methyl-2-pentenoic acid, 2-propenoic acid, methyl 2-propenoate, methyl 2-methyl 2-propenoate, methyl 2-butenoate, ethyl 2-hexenoate, isopropyl 2-decenoate, phenyl 2-pentenoate, tertiary butyl 2-propenoate, octadecyl 2-propenoate, dodecyl 2-decenoate, cyclopropyl 2,3-dimethyl-2-butenoate, methyl 3-phenyl-2-propenoate, and the like.

The alpha, beta-ethylenically unsaturated reactants of formula IX wherein $-OR^4$ is instead $-R^4$ are aldehydes and ketones of the formula:

$$R^1-\overset{\displaystyle R^2}{\underset{}{C}}=\overset{\displaystyle R^3}{\underset{}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-R^4 \qquad \text{(IXa)}$$

wherein R^1, R^2, R^3, and R^4 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of such alpha, beta-ethylenically unsaturated aldehydes and ketones of formula IXa are:

$H_2C=CH-C(O)-CH_3$
$H_2C=CH-C(O)-C_2H_5$
$H_2C=CH-C(O)-C_3H_7$
$H_2C=CH-C(O)-C(CH_3)_3$
$H_2C=CH-C(O)-C_5H_{11}$
$H_2C=C(CH_3)-C(O)-CH(CH_3)_2$
$H_2C=C(CH_3)-C(O)-C_2H_5$
$H(CH_3)C=CH-C(O)-CH_3$
$H(CH_3)C=CH-C(O)-CH(CH_3)_2$
$H(CH_3)C=CH-C(O)-C_2H_5$
$H(CH_3)C=CH-C(O)-C_3H_7$
$H(C_2H_5)C=CH-C(O)-C(CH_3)_3$
$H(CH_3)C=CH-C(O)-C_5H_{11}$
$(CH_3)(C_2H_5)C=C(CH_3)-C(O)-CH_3$
$H(CH_3)C=C(CH_3)-C(O)-C_2H_5$

The alpha, beta-ethylenically unsaturated carboxylate thioester compounds employed herein have the following formula:

$$R^1-\overset{\displaystyle R^2}{\underset{}{C}}=\overset{\displaystyle R^3}{\underset{}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-SR^4 \qquad \text{(X)}$$

wherein R^1, R^2, R^3, and R^4 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of such alpha, beta-ethylenically unsaturated carboxylate thioesters of formula X are methylmercapto 2-butenoate, ethylmercapto 2-hexenoate, isopropylmercapto 2-decenoate, phenylmercapto 2-pentenoate, tertiary butylmercapto 2-propenoate, octa decylmercapto 2-propenoate, dodecylmercapto 2-decenoate, cyclopropylmercapto 2,3-dimethyl-2-butenoate, methylmercapto 3-phenyl-2-propenoate, methylmercapto 2-propenoate, methylmercapto 2-methyl-2-propenoate, and the like.

The alpha, beta-ethylenically unsaturated carboxyamide compounds employed herein have the following formula:

$$R^1-\overset{\displaystyle R^2}{\underset{}{C}}=\overset{\displaystyle R^3}{\underset{}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-NR^4(R^5) \qquad \text{(XI)}$$

wherein R^1, R^2, R^3, R^4 and R^5 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of alpha, beta-ethylenically unsaturated carboxyamides of formula XI are 2-butenamide, 2-hexenamide, 2-decenamide, 3-methyl-2-heptenamide, 3-methyl-2-butenamide, 3-phenyl-2-propenamide, 3-cyclohexyl-2-butenamide, 2-methyl-2-butenamide, 2-propyl-2-propenamide, 2-isopropyl-2-hexenamide, 2,3-dimethyl-2-butenamide, 3-cyclohexyl-2-methyl-2-pentenamide, N-methyl 2-butenamide, N,N-diethyl 2-hexenamide, N-isopropyl 2-decenamide, N-phenyl 2-pentenamide, N-tertiary butyl 2-propenamide, N-octadecyl 2-propenamide, N,N-didodecyl 2-decenamide, N-cyclopropyl 2,3-dimethyl-2-butenamide, N-methyl 3-phenyl-2-propenamide, 2-propenamide, 2-methyl-2-propenamide, 2-ethyl-2-propenamide and the like.

The alpha, beta-ethylenically unsaturated thiocarboxylate compounds employed herein have the following formula:

$$R^1-\overset{R^2}{\overset{|}{C}}=\overset{R^3}{\overset{|}{C}}-\overset{S}{\overset{\|}{C}}-OR^4 \qquad (XII)$$

wherein R^1, R^2, R^3 and R^4 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of alpha, beta-ethylenically unsaturated thiocarboxylate compounds of formula XII are 2-butenthioic acid, 2-hexenthioic acid, 2-decenthioic acid, 3-methyl-2-heptenthioic acid, 3-methyl-2-butenthioic acid, 3-phenyl-2-propenthioic acid, 3-cyclohexyl-2-butenthioic acid, 2-methyl-2-butenthioic acid, 2-propyl-2-propenthioic acid, 2-isopropyl-2-hexenthioic acid, 2,3-dimethyl-2-butenthioic acid, 3-cyclohexyl-2-methyl-2-pententhioic acid, 2-propenthioic acid, methyl 2-propenthioate, methyl 2-methyl 2-propenthioate, methyl 2-butenthioate, ethyl 2-hexenthioate, isopropyl 2-decenthioate, phenyl 2-pententhioate, tertiary butyl 2-propenthioate, octadecyl 2-propenthioate, dodecyl 2-decenthioate, cyclopropyl 2,3-dimethyl-2-butenthioate, methyl 3-phenyl-2-propenthioate, and the like.

The alpha, beta-ethylenically unsaturated dithioic acid and acid ester compounds employed herein have the following formula:

$$R^1-\overset{R^2}{\overset{|}{C}}=\overset{R^3}{\overset{|}{C}}-\overset{S}{\overset{\|}{C}}-SR^4 \qquad (XIII)$$

wherein R^1, R^2, R^3, and R^4 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of alpha, beta-ethylenically unsaturated dithioic acids and acid esters of formula XIII are 2-butendithioic acid, 2-hexendithioic acid, 2-decendithioic acid, 3-methyl-2-heptendithioic acid, 3-methyl-2-butendithioic acid, 3-phenyl-2-propendithioic acid, 3-cyclohexyl-2-butendithioic acid, 2-methyl-2-butendithioic acid, 2-propyl-2-propendithioic acid, 2-isopropyl-2-hexendithioic acid, 2,3-dimethyl-2-butendithioic acid, 3-cyclohexyl-2-methyl-2-pentendithioic acid, 2-propendithioic acid, methyl 2-propendithioate, methyl 2-methyl 2-propendithioate, methyl 2-butendithioate, ethyl 2-hexendithioate, isopropyl 2-decendithioate, phenyl 2-pentendithioate, tertiary butyl 2-propendithioate, octadecyl-2-propendithioate, dodecyl 2-decendithioate, cyclopropyl-2,3-dimethyl-2-butendithioate, methyl 3-phenyl-2-propendithioate, and the like.

The alpha, beta-ethylenically unsaturated thiocarboxyamide compounds employed herein have the following formula:

$$R^1-\overset{R^2}{\overset{|}{C}}=\overset{R^3}{\overset{|}{C}}-\overset{S}{\overset{\|}{C}}-NR^4(R^5) \qquad (XIV)$$

wherein R^1, R^2, R^3, R^4 and R^5 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above. Examples of alpha, beta-ethylenically unsaturated thiocarboxyamides of formula XIV are 2-butenthioamide, 2-hexenthioamide, 2-decenthioamide, 3-methyl-2-heptenthioamide, 3-methyl-2-butenthioamide, 3-phenyl-2-propenthioamide, 3-cyclohexyl-2-butenthioamide, 2-methyl-2-butenthioamide, 2-propyl-2-propenthioamide, 2-isopropyl-2-hexenthioamide, 2,3-dimethyl-2-butenthioamide, 3-cyclohexyl-2-methyl-2-pententhioamide, N-methyl 2-butenthioamide, N,N-diethyl 2-hexenthioamide, N-isopropyl 2-decenthioamide, N-phenyl 2-pententhioamide, N-tertiary butyl 2-propenthioamide, N-octadecyl 2-propenthioamide, N,N-didodecyl 2-decenthioamide, N-cyclopropyl 2,3-dimethyl-2-butenthioamide, N-methyl 3-phenyl-2-propenthioamide, 2-propenthioamide, 2-methyl-2-propenthioamide, 2-ethyl-2-propenthioamide and the like.

Exemplary of polyfunctional reactants of formula VII wherein a = c = 1 are compounds of the formula (XV):

$$X - \overset{\overset{W^1}{\|}}{C} - T - \overset{\overset{W^2}{\|}}{C} - Y$$

wherein W^1, W^2, X, Y and T are as defined above.

Preferred members of this class of reactants are compounds of the formula (XVI):

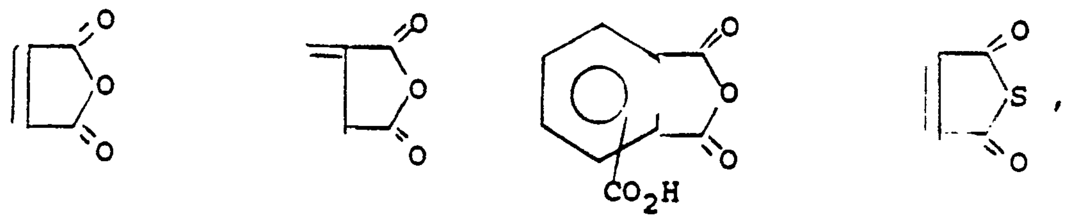
$$X - \overset{\overset{O}{\|}}{C} - T' - \overset{\overset{O}{\|}}{C} - Y$$

wherein X and Y are as defined above and wherein T′ is substituted or unsubstituted divalent C_1 to C_{20} - (preferably, C_1 to C_{10}) alkylene or alkenylene, e.g $-C_2H_5-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CH=CH-$, $-C(CH_2)-CH_2-$, and the like, or C_6 to C_{20} (preferably, C_6 to C_{14}) divalent substituted or unsubstituted arylene such as phenylene, naphthylene, bisphenylene, -phenyl-O-phenyl- and the like. Illustrative of difunctional reactants of formula XVI are:

$H_2C=CH-C(O)-CH-C(O)-OCH_3$
$H_2C=CH-C(O)-C_2H_4-C(O)-OCH_3$
$H_2C=CH-C(O)-CH-C(O)-CH=CH_2$
$H_2C=CH-C(O)-C_2H_4-C(O)-CH=CH_2$
$H_2C=CH-C(O)-C_2H_4-C(O)-OC_2H_5$
$H_2C=CH-C(O)-C_3H_6-C(O)-Cl$
$H_2C=CH-C(O)-C_2H_4-C(O)-SH$
$H_2C=CH-C(O)-C_5H_{10}-C(O)-SCH_3$
$H_2C=C(CH_3)-C(O)-C_2H_4-C(O)-OCH_3$
$H_2C=C(CH_3)-C(O)-C_2H_4-C(O)-OC_2H_5$
$H_2C=CH-C(O)-CH-C(O)-CH_3$
$H_2C=CH-C(O)-C_2H_4-C(O)-CH_3$
$H_2C=CH-C(O)-C_2H_4-C(O)-C_2H_5$
$H(CH_3)C=CH-C(O)-CH_2-C(O)-OCH_3$
$H(CH_3)C=CH-C(O)-C_2H_4-C(O)-OCH_3$
$H(CH_3)C=CH-C(O)-CH_2-C(O)-CH=CH_2$
$H(CH_3)C=CH-C(O)-C_2H_4-C(O)-CH=CH_2$
$H(CH_3)C=CH-C(O)-C_2H_4-C(O)-OC_2H_5$
$H(CH_3)C=CH-C(O)-C_3H_6-C(O)-Cl$
$H(C_2H_5)C=CH-C(O)-C_2H_4-C(O)-SH$
$H(CH_3)C=CH-C(O)-C_5H_{10}-C(O)-SCH_3$
$(CH_3)(C_2H_5)C=C(CH_3)-C(O)-C_2H_4-C(O)-OCH_3$
$H(CH_3)C=C(CH_3)-C(O)-C_2H_4-C(O)-OC_2H_5$
$H(CH_3)C=CH-C(O)-CH_2-C(O)-CH_3$
$H(CH_3)C=CH-C(O)-C_2H_4-C(O)-CH_3$
$H(CH_3)C=CH-C(O)-C_2H_4-C(O)-C_2H_5$
$Cl-C(O)-CH_2-C(O)-OCH_3$
$Cl-C(O)-C_2H_4-C(O)-OCH_3$
$CH_3O-C(O)-CH_2-C(O)-OCH_3$
$CH_3O-C(O)-C_2H_4-C(O)-OCH_3$
$CH_3S-C(O)-CH_2-C(O)-SCH_3$
$CH_3S-C(O)-C_2H_4-C(O)-SCH_3$
$CH_3O-C(O)-CH_2-C(O)-SCH_3$
$CH_3S-C(O)-C_2H_4-C(O)-SC_2H_5$
$Cl-C(O)-C_2H_4-C(O)-OC_2H_5$
$Cl-C(O)-C_3H_6-C(O)-OH$
$Cl-C(O)-C_2H_4-C(O)-SH$
$Cl-C(O)-C_5H_{10}-C(O)-SCH_3$
$Cl-C(O)-C_2H_4-C(O)-OCH_3$
$Cl-C(O)-C_2H_4-C(O)-OC_2H_5$
$Cl-C(O)-CH_2-C(O)-CH_3$
$Cl-C(O)-C_2H_4-C(O)-CH_3$
$Cl-C(O)-C_2H_4-C(O)-C_2H_5$
$CH_3O-C(O)-CH_2-C(O)-OH$

CH_3O-C(O)-C_2H_4-C(O)-OH
CH_3O-C(O)-C_2H_4-C(O)-SH
CH_3O-C(O)-C_3H_6-C(O)-Cl
C_2H_5O-C(O)-C_2H_4-C(O)-SH
CH_3O-C(O)-C_5H_{10}-C(O)-SCH_3
CH_3S-C(O)-CH_2-C(O)-OCH_3
CH_3-C(O)-CH_2-C(O)-OH
CH_3-C(O)-C_2H_4-C(O)-OH
CH_3-C(O)-C_2H_4-C(O)-SH

Exemplary of reactants of formula VII wherein a = b = c = 1, W' and W^2 are O, T contains a >C=C< group and wherein X and Y together comprise -O- or -S- are:



chloromaleic anhydride, and the like.

Exemplary of polyfunctional reactants of formula VII wherein a = b = 1 and c > 1 are compounds of the formula (XVII):

$$X - \overset{W^1}{\overset{\|}{C}} - T - [(\overset{W^2}{\overset{\|}{C}}) - Y]_c$$

wherein W', W^2, X, Y, T and "c" are as defined above.
Illustrative of compounds of formula XVII above are:
H_2C=CH-C(O)-CH_2-[C(O)-$OCH_3]_2$
H_2C=CH-C(O)-C_2H_3-[C(O)-$OCH_3]_2$
H_2C=CH-C(O)-ARYL-[C(O)-$OCH_3]_2$
H_2C=CH-C(O)-ARYL-[C(O)-$OCH_3]_2$
H_2C=CH-C(O)-C_2H_3-[C(O)-$OC_2H_5]_2$
C_2C=CH-C(O)-NAPTHYL-[C(O)-$OCH_3]_2$
C_2C=CH-C(O)-NAPHTHYL-[C(O)-$OCH_3]_2$
H_2C=CH-C(O)-C_2H_3-[C(O)-$OC_2H_5]_2$
H_2C=CH-C(O)-C_3H_5-[C(O)-Cl$]_2$
H_2C=CH-[C(O)-C_2H_3-[C(O)-SH$]_2$
H_2C=CH-C(O)-C_5H_9-[C(O)-$SCH_3]_2$
H_2C=C(CH_3)-C(O)-C_2H_3-[C(O)-$OCH_3]_2$
H_2C=C(CH_3)-C(O)-C_2H_3-[C(O)-$OC_2H_5]_2$
H_2C=CH-C(O)-CH_2-[C(O)-$CH_3]_2$
H_2C=CH-C(O)-C_2H_3-[C(O)-$CH_3]_2$
H_2C=CH-C(O)-ARYL-[C(O)-$CH_3]_2$
H(CH_3)C=CH-C(O)-CH-[C(O)-$OCH_3]_2$
H(CH_3)C=CH-C(O)-C_2H_3-[C(O)-$OCH_3]_2$
H(CH_3)C=CH-C(O)-C_2H_3-[C(O)-$OC_2H_5]_2$
H(CH_3)C=CH-C(O)-C_3H_5-[C(O)-Cl$]_2$
H(C_2H_5)C=CH-C(O)-C_2H_3-[C(O)-SH$]_2$
H(CH_3)C=CH-C(O)-C_5H_9-[C(O)-$SCH_3]_2$
(CH_3)(C_2H_5)C=C(CH_3)-C(O)-C_2H_3-[C(O)-$OCH_3]_2$
H(CH_3)C=C(CH_3)-C(O)-C_2H_3-[C(O)-$OC_2H_5]_2$
H(CH_3)C=CH-C(O)-CH-[C(O)-$CH_3]_2$
H(CH_3)C=CH-C(O)-C_2H_3-[C(O)-$CH_3]_2$

$H(CH_3)C=CH\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}C_2H_5]_2$
$Cl\text{-}C(O)\text{-}CH\text{-}[C(O)\text{-}OCH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OCH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OC_2H_5]_2$
$Cl\text{-}C(O)\text{-}C_3H_5\text{-}[C(O)\text{-}OH]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}SH]_2$
$Cl\text{-}C(O)\text{-}C_5H_9\text{-}[C(O)\text{-}SCH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OCH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OC_2H_5]_2$
$Cl\text{-}C(O)\text{-}CH\text{-}[C(O)\text{-}CH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}CH_3]_2$
$Cl\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}C_2H_5]_2$
$CH_3O\text{-}C(O)\text{-}CH\text{-}[C(O)\text{-}OH]_2$
$CH_3O\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OH]_2$
$CH_3O\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}SH]_2$
$CH_3O\text{-}C(O)\text{-}C_3H_5\text{-}[C(O)\text{-}Cl]_2$
$C_2H_5O\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}SH]_2$
$CH_3O\text{-}C(O)\text{-}C_5H_9\text{-}[C(O)\text{-}SCH_3]_2$
$CH_3S\text{-}C(O)\text{-}CH\text{-}[C(O)\text{-}OCH_3]_2$
$CH_3\text{-}C(O)\text{-}CH\text{-}[C(O)\text{-}OH]_2$
$CH_3\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}OH]_2$
$CH_3\text{-}C(O)\text{-}C_2H_3\text{-}[C(O)\text{-}SH]_2$

Exemplary of the polyfunctional reactants of formula VII wherein a = 0 and b = c = 1 are bisfunctional compounds of the formula (XIX):

$$X-\overset{\overset{W^1}{\|}}{C}-\overset{\overset{W^2}{\|}}{C}-Y$$

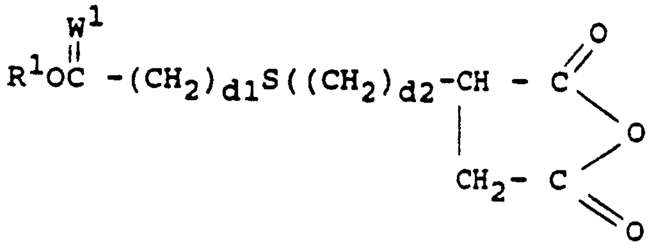
wherein W^1, W^2, X and Y are as defined above.

Illustrative of compounds of formula XIX above are:

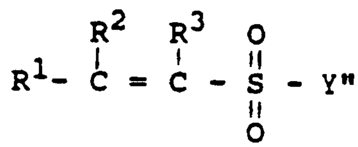
$C_2C=CH\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$C_2C=CH\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$H_2C=CH\text{-}C(O)\text{-}C(O)\text{-}OC_2H_5$
$H_2C=CH\text{-}C(O)\text{-}C(O)\text{-}Cl$
$H_2C=CH\text{-}C(O)\text{-}C(O)\text{-}SH$
$H_2C=CH\text{-}C(O)\text{-}C(O)\text{-}SCH_3$
$H_2C=C(CH_3)\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$H_2C=C(CH_3)\text{-}C(O)\text{-}C(O)\text{-}OC_2H_5$
$C_2C=CH\text{-}C(O)\text{-}C(O)\text{-}CH_3$
$C_2C=CH\text{-}C(O)\text{-}C(O)\text{-}CH_3$
$H_2C=CH\text{-}C(O)\text{-}C(O)\text{-}C_2H_5$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}OC_2H_5$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}Cl$
$H(C_2H_5)C=CH\text{-}C(O)\text{-}C(O)\text{-}SH$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}SCH_3$
$(CH_3)(C_2H_5)C=C(CH_3)\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$H(CH_3)C=C(CH_3)\text{-}C(O)\text{-}C(O)\text{-}OC_2H_5$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}CH_3$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}CH_3$
$H(CH_3)C=CH\text{-}C(O)\text{-}C(O)\text{-}C_2H_5$
$Cl\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$Cl\text{-}C(O)\text{-}C(O)\text{-}OCH_3$
$Cl\text{-}C(O)\text{-}C(O)\text{-}OC_2H_5$
$Cl\text{-}C(O)\text{-}C(O)\text{-}OH$

Cl-C(O)-C(O)-SH
Cl-C(O)-C(O)-SCH$_3$
Cl-C(O)-C(O)-OCH$_3$
Cl-C(O)-C(O)-OC$_2$H$_5$
Cl-C(O)-C(O)-CH$_3$
Cl-C(O)-C(O)-CH$_3$
Cl-C(O)-C(O)-C$_2$H$_5$
CH$_3$O-C(O)-C(O)-OH
C$_2$H$_5$-C(O)-C(O)-OH
CH$_3$O-C(O)-C(O)-SH
CH$_3$O-C(O)-C(O)-Cl
C$_2$H$_5$O-C(O)-C(O)-SH
CH$_3$O-C(O)-C(O)-SCH$_3$
CH$_3$O-C(O)-C(O)-OCH$_3$
CH$_3$-C(O)-C(O)-OH
C$_2$H$_5$-C(O)-C(O)-OH
CH$_3$O-C(O)-C(O)-SH

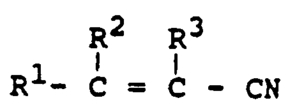
Also useful as polyfunctional reactants in the present invention are compounds of the formula (XX):



wherein R^1 and W^1 are as defined above, and wherein "d1" and "d2" are each integers of from 1 to 10; compounds of the formula (XXI):



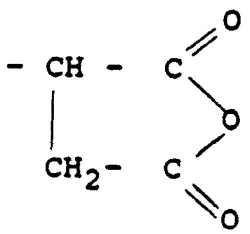
wherein R^1, R^2, and R^3 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above, and wherein Y$''$ comprises a reactive functional group selected from the group consisting of: halide, -OR^4, -SR^4, -N(R^4)(R^5), -Z^{1}C(O)OR^4 and -(R^3)C=C(R^1)(R^2), wherein R^4 is H or substituted or unsubstituted hydrocarbyl as defined above, and
compounds of the formula (XXIa):



wherein R^1, R^2, and R^3 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above.

Examples of such compounds of formula XX are:
CH$_3$OC(O)C$_2$H$_4$SCH$_2$-ANHY
CH$_3$OC(O)CH$_2$SCH$_2$-ANHY
CH$_3$OC(O)C$_3$H$_6$SCH$_2$-ANHY
CH$_3$OC(O)C(CH$_3$)$_2$SCH$_2$-ANHY
CH$_3$OC(O)CH(CH$_3$)SCH$_2$-ANHY
C$_2$H$_5$OC(O)C$_2$H$_4$SCH$_2$-ANHY
C$_2$H$_5$OC(O)CH$_2$SCH$_2$-ANHY

$C_2H_5OC(O)C_3H_6SCH_2$-ANHY
$C_2H_5OC(O)C(CH_3)_2SCH_2$-ANHY
$C_2H_5OC(O)CH(CH_3)SCH_2$-ANHY
wherein ANHY is the moiety:

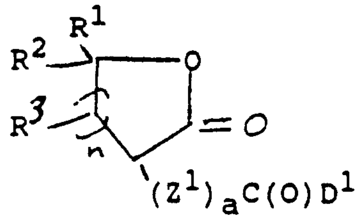


Examples of such compounds of formula XXI are:
$H_2C=CH\text{-}S(O)_2\text{-}OCH_3$
$H_2C=CH\text{-}S(O)_2\text{-}OCH_3$
$H_2C=CH\text{-}S(O)_2\text{-}OC_2H_5$
$H_2C=CH\text{-}S(O)_2\text{-}Cl$
$H_2C=CH\text{-}S(O)_2\text{-}SH$
$H_2C=CH\text{-}S(O)_2\text{-}SCH_3$
$H_2C=C(CH_3)\text{-}S(O)_2\text{-}OCH_3$
$H_2C=C(CH_3)\text{-}S(O)_2\text{-}OC_2H_5$
$H_2C=CH\text{-}S(O)_2\text{-}OCH(CH_3)_2$
$H(CH_3)C=CH\text{-}S(O)_2\text{-}OCH_3$
$H(CH_3)C=CH\text{-}S(O)_2\text{-}OCH_3$
$H(CH_3)C=CH\text{-}S(O)_2\text{-}OC_2H_5$
$H(CH_3)C=CH\text{-}S(O)_2\text{-}Cl$
$H(C_2H_5)C=CH\text{-}S(O)_2\text{-}SH$
$H(CH_3)C=CH\text{-}S(O)_2\text{-}SCH_3$
$(CH_3)(C_2H_5)C=C(CH_3)\text{-}S(O)_2\text{-}OCH_3$
$H(CH_3)C=C(CH_3)\text{-}S(O)_2\text{-}OC_2H_5$

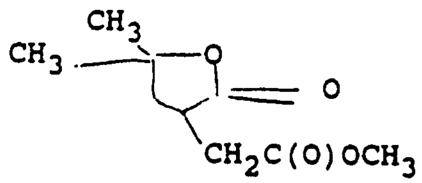
Examples of such compounds of formula XXIa are:
$H_2C=CH\text{-}CN$
$H_2C=C(CH_3)\text{-}CN$
$H(CH_3)C=CH\text{-}CN$
$H(C_2H_5)C=CH\text{-}CN$
$H(CH_3)C=C(CH_3)\text{-}CN$
$(CH_3)(C_2H_5)C=C(CH_3)\text{-}CN$

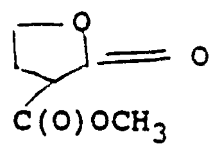
Also useful as polyfunctional reactants in the present invention are compounds containing two or more epoxy groups and compounds containing two or more anhydride groups, such as compounds of the structures:
EPOXY - $(CH_2)_x$ - EPOXY
ANHY - $(CH_2)_x$ - ANHY
EPOXY - Ar - EPOXY
ANHY - Ar - ANHY
wherein EPOXY is the oxirane group - CH $\underset{O}{-}$ CH_2,
ANHY is an anhydride groups "x'" is an integerof from 1 to 20 (preferalbly from 2 to 10), and "Ar" is bivalent arylene which may be substituted or unsubstituted (e.g., alkyl-substituted).

Also useful as polyfunctional reactants in the practice of the present invention are compounds of the formula (XXIb):



R^1, R^2, R^3, "a" and Z^1 are as defined above, "n′" is an integer of from 1 to 3, and wherein D^1 is H, hydrocarbyl (e.g., C_1 to C_{10} alkyl) or hydrocarboxyl (e.g., C_1 to C_{10} alkoxy). Illustrative of compounds of formula XXIb wherein D^1 is C_1 to C_{10} alkoxy are:





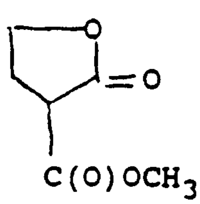
and the like. Such lactone esters form linked polyamines by ring-opening of the lactone to form an amide linkage with one -NH- group of a first amine molecule, and by elimination of the corresponding alcohol (e.g. CH_3OH) to form a second amide linkage with -NH- group of a second amine molecules Illustrative of linked polyamine products are:

Alkamine-NH-C(O)CHCH$_2$C(O)-NH-Alkamine,
 | CH$_2$C(CH$_3$)$_2$-OH

Alkamine-NH-C(O)CHC(O)-NH-Alkamine
 | CH$_2$CH$_2$OH

and the like.

When D^1 in formula XXIb is H or hydrocarbyl, the corresponding lactone aldehyde and ketones form linked polyamines by ring opening of the lactone to form an amide linkage with one -NH- group of a first amine molecule, and by forming an enamine group (-C=N-) by reaction of the second carbonyl group with a primary amine group of a second amine molecule. Such linking reactions are illustrated by the following:



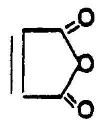
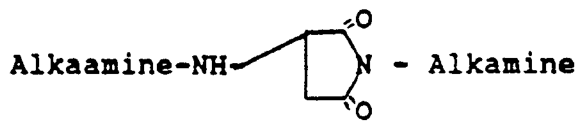
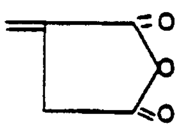
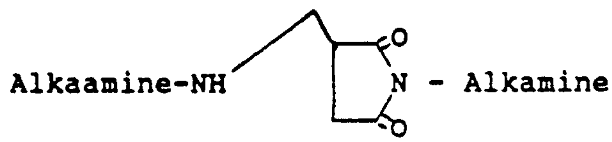
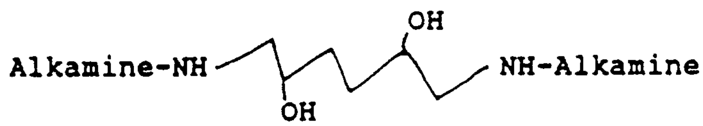
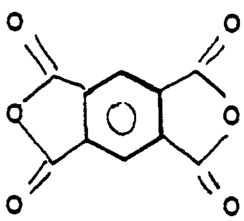
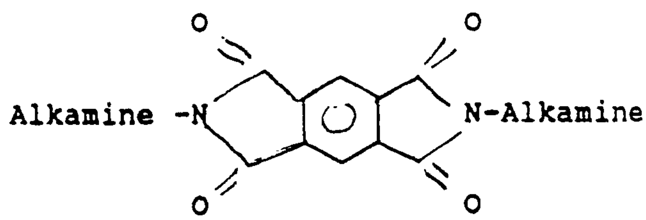
+ 2 NH$_2$-Alkamine ⟶

Alkamine-NH-C(O)-CH-C(CH$_3$)=N-Alkamine
 | CH$_2$CH$_2$OH

The use of exemplary polyfunctional reactants with a nitrogen-compound is illustrated in the following Table wherein the nitrogen-compound comprises:

$NH_2(C_2H_4NH)_xC_2H_4NH_2$

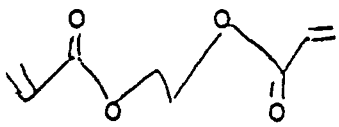
wherein x is an integer of from 0 to 8, and wherein "Alkamine-"is the moiety $-C_2H_4(NHC_2H_4)_xNH_2$, and wherein the reactants are contacted in a 2:1 molar ratio of nitrogen-compound to polyfunctional reactant.

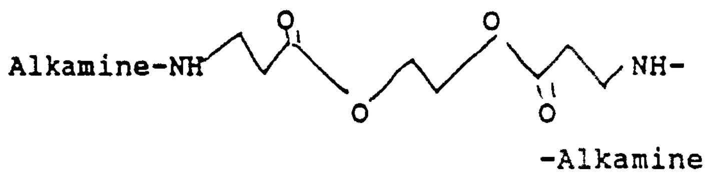
Polyfunctional Reactant	Linked Polyamine Product
	
	
	
	
$CH_3OC(O)Cl$	Alkamine-NHC(O)NH-Alkamine
$CH_3OC(O)OCH_3$	Alkamine-NHC(O)NH-Alkamine

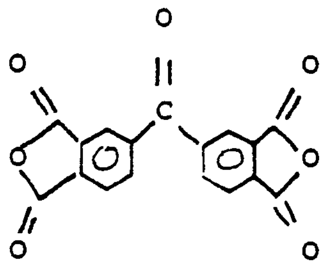
$C_2H_5OC(O)OC_2H_5$ Alkamine-NHC(O)NH-Alkamine

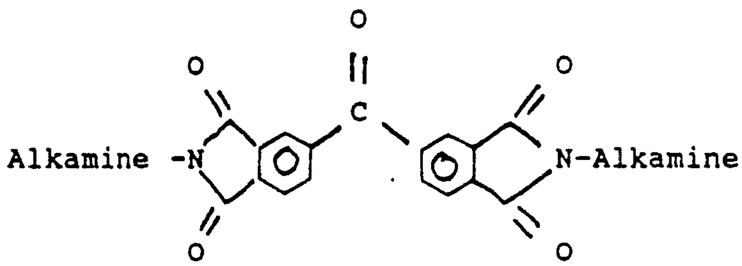
$CH_3OC(S)OCH_3$ Alkamine-NHC(S)NH-Alkamine

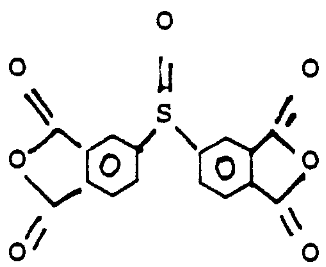
$NH_2C(O)NH_2$ Alkamine-NHC(O)NH-Alkamine

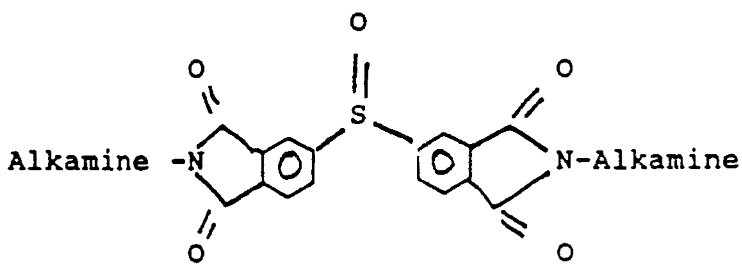










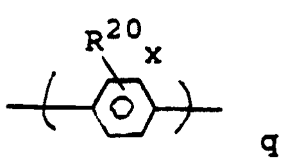


Also useful as polyfunctional reactants herein are mixtures of an aldehyde and at least one of hydroxy-substituted aromatic compounds, SH-substituted aromatic compounds, mercaptans, and bis-secondary amine terminated compounds, which can be admixed with nitrogen-containing compounds for linking of the latter by Mannich Base condensation. Such Mannich condensation products generally are prepared by condensing about 1 mole of an optionally hydrocarbyl-substituted, hydroxy aromatic compound with about 1 to 2.5 moles of an aldehyde such as formaldehyde or paraformaldehyde and about 0.5 to 2 moles of the nitrogen-containing compound, using the condensation conditions as disclosed, e.g., in U.S. Patents 3,442,808; 3,649,229; and 3,798,165 (the disclosures which are hereby incorporated by reference in their entirety).

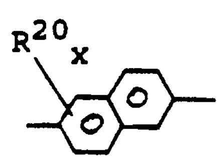
The optionally substituted hydroxy aromatic compounds used in the preparation of the Mannich base products include those compounds having the formula

$R^{2'}{}_y$ - Ar - $(OH)_z$

wherein Ar represents



or



,

wherein q is 1 or 2, $R^{2'}$ is a hydrocarbon, R^{20} is a hydrocarbon or substituted hydrocarbon radical having from 1 to about 3 carbon atoms or a halogen radical such as the bromide or chloride radical, y is an integer from 0 to 2, x is an integer from 0 to 2, and z is an integer from 1 to 2.

Illustrative of such Ar groups are phenylene, biphenylene, naphthylene and the like.

The hydrocarbon R^{21} substituents are C_1-C_{20} hydrocarbyl, e.g., alkyl.

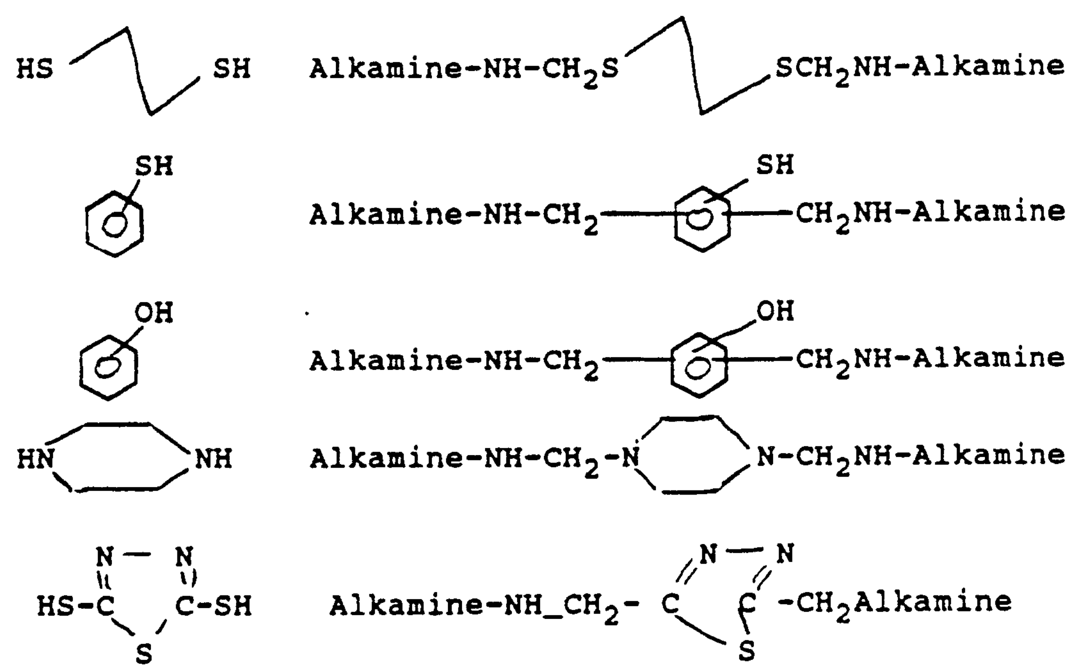
Representative hydrocarbyl substituted hydroxy aromatic compounds contemplated for use in the present invention include, but are not limited to, 2-propyl phenol, 3-propyl phenol, 4-propyl phenol, 2-butyl phenol, 3-isobutyl phenol, 4-isobutyl phenol, 4-isobutyl-2-chlorophenol, 4-isobutyl-2-methylphenol, and the like.

Suitable hydrocarbyl-substitued polyhydroxy aromatic compounds include catechols, resorcinols, and hydroquinones, e.g., 4-isobutyl-1,2-dihydroxybenzene, 3-propyl-1,2-dihydroxybenzene, 5-isobutyl-1,3-dihydroxybenzene, 4-amyl-1,3-dihydroxybenzene, and the like.

Suitable hydrocarbyl-substituted naphthols include 1-isobutyl-5-hydroxynaphthalene, 1-propyl-3-hydroxynaphthalene and the like.

The use of exemplary Mannich Base condensations to link nitrogen-containing compounds can be illustrated as follows, wherein "alkamine-" is as defined above and wherein the Mannich Base reactants are charged in the ratio of 2 moles of the amine: NH_2-Alkamine-NH_2, 2 moles of CH_2O, and 1 mole of linking reactant:

Linking Reactant	Linked Polyamine Product



Also useful as polyfunctional reactants are mercaptan compounds of the formula:

$$X - \overset{\overset{\textstyle W^1}{\|}}{C} - T - SH \qquad \text{(XXIc)}$$

wherein X, W', and T are as defined above, wherein the X group is thermally reactive with a -NH- group of a nitrogen-containing compound and -SH can be reacted with an aldehyde and the nitrogen-containing compound in a Mannich Base condensation as described above. Exemplary of polyfunctional reactants of formula XXIc are:

$H_2C=CH-C(O)-CH_2SH$

$H_2C=CH-C(O)-CH2^{H}4^{-SH}$

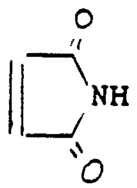
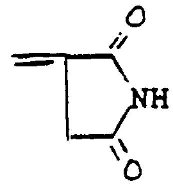
$H_2C=CH-C(O)-C_3H_6-SH$

$H_2C=CH-C(O)-C_5H_{10}-SH$

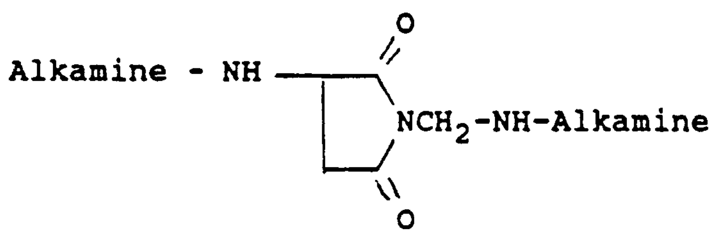
$H(CH_3)C=CH-C(O)-CH_2-SH$

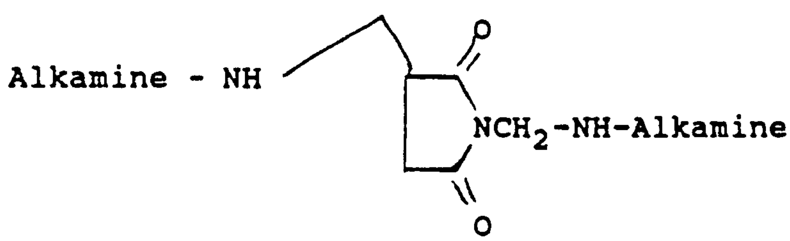
$H(CH_3)C=CH-C(O)-C_2H_4-SH$
$H(CH_3)C=CH-C(O)-C_3H_6-SH$
$H(CH_3)C=CH-C(O)-C_5H_{10}-SH$
$Cl-C(O)-CH_2-SH$
$Cl-C(O)-C_2H_4-SH$
$Cl-C(O)-C_3H_6-SH$
$Cl-C(O)-C_5H_{10}-SH$
$CH_3O-C(O)-CH_2-SH$
$CH_3O-C(O)-C_2H_4-SH$
$CH_3O-C(O)-C_3H_6-SH$
$CH_3O-C(O)-C_5H_{10}-SH$
$CH_3S-C(O)-CH_2-C(O)-SH$
$HS-C(O)-CH_2-C(O)-SH$

Also useful as polyfunctional reactants are monoethylenically unsaturated imides, such as

 , 

and the like,
which can undergo linking of one -NH- group through a Michael condensation of the >C=C< bond, and a Mannich condensation of the imide N, aldehyde and a second -NH-group, of the nitrogen-containing compound. Examples of such linked products are:





and the like.

Preferred compounds for reaction with the nit rogen-containing compound in accordance with this invention are lower alkyl esters of acrylic and lower alkyl alpha-substituted acrylic acid. Illustrative of such preferred compounds are compounds of the formula:

$$CH_2 = \overset{R^3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}}OR^4 \qquad (XXII)$$

where R^3 is hydrogen or a C_1 to C_4 alkyl group, such as methyl, and R^4 is hydrogen or a C_1 to C_4 alkyl group, capable of being removed so as to form an amido group, for example, methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, aryl, hexyl, etc. e.g., propyl acrylate and propyl methacrylate. In the most preferred embodiments these compounds are acrylic and methacrylic esters such as methyl or ethyl acrylate, methyl or ethyl methacrylate.

The polyfunctional reactants useful in this invention are known materials and can be prepared by conventional methods known to those skilled in the art, which need not be decribed herein.

PREPARATION OF THE LINKED POLYAMINE

The selected nitrogen-containing compound and polyfunctional reactant are contacted in a first reaction mixture in an amount and under conditions sufficient to react at least a portion of the functional groups of the latter with at least a portion of the reactive nitrogen moieties in the first nitrogen-containing compound to form a linked polyamine characterized by having at least two, (e.g., 2 to 20), preferably at least 3 (e.g., 3 to 18), nitrogen-containing moieties derived from the nitrogen-containing compound per linking moiety derived from the polyfunctional reactant and (ii) at least two (e.g., 2 to 6; preferably 2 to 4) unreacted primary or secondary amine groups per molecule.

In preparing the linked polyamine, it is preferred that the moles of the polyfunctional reactant be employed in an amount of from about 0.1 to 1.0, preferably from about 0.1 to 0.5, moles per equivalent of the reactive nitrogen moieties in the nitrogen-containing compound (that is, the sum of the nitrogen-bonded H atoms in the first nitrogen-containing compound).

The polyfunctional reactant and nitrogen compound can be contacted in any order but are preferably admixed by introducing the polyfunctional reactant into the liquid reaction mixture containing the nitrogen compound.

The conditions of the temperature and pressure employed for employed for contacting of the first nitrogen-containing compound and the polyfunctional reactant can vary widely. Lower temperatures (e.g., 25° C) can be used, although longer reaction times may be required. Temperatures up to the decomposition points of reactants and products can be employed. In practice, one generally carries out the reaction by heating the reactants below 100° C, such as 80-90° C, for a suitable period of time, such as a few hours. Where the first adduct was formed using an acrylic-type ester is employed, the progress of the reaction can be judged by the removal of the alcohol in forming the amide. During the early part of the reaction alcohol is removed quite readily below 100° C in the case of low boiling alcohols such as methanol or ethanol. As the reaction slows, the temperature is raised to push the reaction to completion and the temperature may be raised to 150° C toward the end of the reaction. Removal of alcohol is a convenient method of judging the progress and completion of the reaction which is generally continued until no more alcohol is evolved. Based on removal of alcohol, the yields are generally stoichiometric. In more difficult reactions, yields of at least 95% are generally obtained.

Similarly, it will be understood that the reaction of a polyamine with a first adduct prepared using an ethylenically unsaturated carboxylate thioester of formula IX liberates the corresponding HSR^4 compound (e.g., H_2S when R^4 is hydrogen) as a by-product, and the reaction of a polyamine with a first adduct prepared using an ethylenically unsaturated carboxyamide of formula X liberates the corresponding HNR^4-(R^5) compound (e.g., ammonia when R^4 and R^5 are each hydrogen) as by-product in forming the second adduct.

The reaction time involved can vary widely depending on a wide variety of factors. For example, there is a relationship between time and temperature. In general, lower temperature demands longer times. Usually, reaction times of from about 2 to 30 hours, such as 5 to 25 hours, and preferably 3 to 10 hours will be employed.

Although one can employ a solvent, the reaction can be run without the use of any solvent. It is preferred to avoid the use of an aqueous solvent such as water. However, taking into consideration the effect of solvent on the reaction, where desired, any suitable solvent can be employed, whether organic or inorganic, polar or non-polar. Suitable solvents include alkanols (e.g., C_1 to C_6 alkanols such as methanol, isopropanol, ethanol and the like), ethers, xylene, benzene, toluene, tretrahydrofuran, methlyene chloride, chloroform, chlorobenzene, and the like.

The resulting product mixture is then preferably treated, as by stripping or sparging (with, e.g, nitrogen gas) (e.g., from about 20 to about 100° C) optionally under vacuum to remove any volatile reaction by-products and unreacted reactants.

When the selected polyfunctional reactant comprises an alpha, beta-unsaturated compound of formula VII wherein W^1 is oxygen, the resulting first adduct reaction product contains at least one amido linkage (-C-

(O)N<) and such materials are herein termed "amido-amines." Similarly, when the selected alpha, beta-unsaturated compound of formula VII comprises a compound wherein W is sulfur, the resulting reaction product with the polyamine contains thioamide linkage (-C(S)N<) and these materials are herein termed "thioamido-amines." For convenience, the following discussion is directed to the preparation and use of amido-amines, although it will be understood that such discussion is also applicable to the thioamido-amines.

Th ese amido-amine adducts so formed are characterized by both amido and amino groups. In their simplest embodiments they may be represented by units of the following idealized formula:

$$-\overset{R}{\overset{|}{N}}\left(A-\overset{R}{\overset{|}{N}}\right)_{n}CH_2-\overset{R}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-$$

wherein the R's, which may be the same or different, are hydrogen or a substituted group, such as a hydrocarbon group, for example, alkyl, alkenyl, alkynyl, aryl, etc., and A is a moiety of the polyamine which, for example, may be aryl, cycloalkyl, alkyl, etc., and n is an integer such as 1-10 or greater. The amido-amine adducts preferably contain an average of from 1 to 3 amido groups per molecule of the amido-amine adduct.

Preferably, however, the amido-amines of this invention are not cross-linked to any substantial degree, and more preferably are substantially linear.

The reaction of the polyfunctional reactants of formula VII with a nitrogen-containing compound can be illustrated as follows:

(Eq. 1)

$$2\ H_2NC_2H_4NH_2 + H_2C{=}CH-\overset{O}{\overset{\|}{C}}-OCH_3 \rightarrow$$

$$H_2NC_2H_4N-C_2H_4\overset{O}{\overset{\|}{C}}-HNC_2H_4NH_2 + 2\ CH_3OH$$

(Eq. 2)

$$2\ H_2N(C_2H_4NH)_4C_2H_4NH_2 + H_2C{=}CH-\overset{O}{\overset{\|}{C}}-OCH_3 \rightarrow$$

$$H_2N[C_2H_4NH]_4C_2H_4NC_2H_4\overset{O}{\overset{\|}{C}}-N[C_2H_4NH]_4C_2H_4NH_2$$

It will be recognized from the above that the selective reaction of the nitrogen-containing compound with an alpha, beta-ethylenically unsaturated compound of formula VII results in the addition of a portion of the reactive nitrogen equivalents across the double bond of these polyfunctional reactants, and by addition of a second reactive nitrogen equivalent to form an amide linkage, with elimination of the -Y group.

PREPARATION OF THE DISPERSANT

The selected polyamine is readily reacted with the selected polymer substituted mono- or dicarboxylic acid material, e.g. polyisobutylene-substituted succinic anhydride, by heating an oil solution containing 5 to 95 wt. % of the polymer substituted mono- or dicarboxylic acid material to about 100 to 175 °C., preferably 125 to 160 °C., generally for 1 to 10, e.g. 2 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides and/or amides, rather than salts. Generally from 1 to 5, preferably from about 1.5 to 3 moles of mono- or dicarboxylic acid moiety content (e.g., grafted maleic anhydride or grafted acrylic acid content) is used per reactive nitrogen equivalent of the second adduct.

Preferably, the polymer substituted mono- or dicarboxylic acid producing material and amido-amine will be contacted for a time and under conditions sufficient to react substantially all of the primary nitrogens in the second adduct reactant. The progress of this reaction can be followed by infra-red analysis.

The dispersant-forming reaction can be conducted in a polar or non-polar solvent (e.g., xylene, toluene, benzene and the like), and is preferably conducted in the presence of a mineral or synthetic lubricating oil.

The weight percent secondary amine in the dispersant material can be readily determined. For example, a dispersant material sample can be titrated with 2,4-pentanedione to determine its primary amine content, and a separate sample can be titrated with phenyl isocyanate to form thiourea groups with all primary and secondary amines in the second sample, which can then be acidified with HCl to form salts with the tertiary amine groups, thereby identifying the tertiary amine groups in the dispersant. After determining the total nitrogen content of the the dispersant, the sum of the wt% primary and tertiary nitrogens can be subtracted from the total nitrogen content, to provide the desired wt% secondary nitrogen information.

The nitrogen-containing dispersant materials of the instant invention as described above can be post-treated by contacting said nitrogen-containing dispersant materials with one or more post-treating reagents selected from the group consisting of carbon disulfide, sulfur, sulfur chlorides, alkenyl cyanides, aldehydes, ketones, urea, thio-urea, guanidine, dicyanodiamide, hydrocarbyl phosphates, hydrocarbyl phosphites, hydrocarbyl thiophosphates, hydrocarbyl thiophosphites, phosphorus sulfides, phosphorus oxides, phosphoric acid, hydrocarbyl thiocyanates, hydrocarbyl isocyanates, hydrocarbyl isothiocyantes, epoxides, episulfides, formaldehyde or formaldehyde-producing compounds plus phenols, and sulfur plus phenols, and C_1 to C_{30} hydrocarbyl substituted succinic acids and anhydrides (e.g., succinic anhydride, dodecyl succinic anhydride and the like), fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C_1 to C_4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, methyl fumarate, and the like.

Since post-treating processes involving the use of these post-treating reagents is known insofar as application to high molecular weight nitrogen containing dispersants of the prior art, further descriptions of these processes herein is unnecessary. In order to apply the prior art processes to the compositions of this invention, all that is necessary is that reaction conditions, ratio of reactants, and the like as described in the prior art, be applied to the novel compositions of this invention. The following U.S. patents are expressly incorporated herein by reference for their disclosure of post-treating processes and post-treating reagents applicable to the compositions of this invention: U.S. Pat. Nos. 3,087,936; 3,200,107; 3,254,025; 3,256,185; 3,278,550; 3,281,428; 3,282,955; 3,284,410; 3,338,832, 3,344,069; 3,366,569; 3,373,111; 3,367,943; 3,403,102; 3,428,561; 3,502,677; 3,513,093; 3,533,945; 3,541,012; 3,639,242; 3,708,522; 3,859,318; 3,865,813; 3,470,098; 3,369,021; 3,184,411; 3,185,645; 3,245,908; 3.245,909; 3,245,910; 3,573,205; 3,692,681; 3,749,695; 3,865,740; 3,954,639; 3,458,530; 3,390,086; 3,367,943; 3,185,704, 3,551,466; 3,415,750; 3,312,619; 3,280,034; 3,718,663; 3,652,616; UK Pat. No. 1,085,903; UK Pat. No. 1,162,436; U.S. Pat. No. 3,558,743.

The nitrogen containing dispersant materials of this invention can also be treated with polymerizable lactones (such as epsilon-caprolactone) to form dispersant adducts having the moiety $-[C(O)(CH_2)_zO]_mH$, wherein z is a number of from 4 to 8 (e.g., 5 to 7) and m has an average value of from about 0 to 100 (e.g., 0.2 to 20). The dispersants of this invention can be post-treated with a C_5 to C_9 lactone, (e.g., C_6 to C_9 lactone, such as epsilon-caprolactone) by heating a mixture of the dispersant material and lactone in a reaction vessel in the absence of a solvent at a temperature of about 50°C to about 200°C, more preferably from about 75°C to about 180°C, and most preferably from about 90°C to about 160°C, for a sufficient period of time to effect reaction. Optionally, a solvent for the lactone, dispersant material and/or the resulting adduct may be employed to control viscosity and/or the reaction rates.

In one preferred embodiment, the C_5 to C_9 lactone, e.g., epsilon-caprolactone, is reacted with a dispersant material in a 1:1 mole ratio of lactone to dispersant material. In practice, the ratio of lactone to dispersant material may vary considerably as a means of controlling the length of the sequence of the lactone units in the adduct. For examples the mole ratio of the lactone to the dispersant material may vary from about 10:1 to about 0.1:1, more preferably from about 5:1 to about 0.2:1, and most preferably from about 2:1 to about 0.4:1. It is preferable to maintain the average degree of polymerization of the lactone monomer below about 100, with a degree of polymerization on the order of from about 0.2 to about 50 being preferred, and from about 0.2 to about 20 being more preferred. For optimum dispersant performance, sequences of from about 1 to about 5 lactone units in a row are preferred.

Catalysts useful in the promotion of the lactone-dispersant material reactions are selected from the group consisting of stannous octanoate, stannous hexanoate, tetrabutyl titanate, a variety of organic based acid catalysts and amine catalysts, as described on page 266, and forward, in a book chapter authored by R.D. Lundberg and E. F. Cox, entitled "Kinetics and Mechanisms of Polymerization: Ring Opening Polymerization", edited by Frisch and Reegen, published by Marcel Dekker in 1969, wherein stannous octanoate is an especially preferred catalyst. The catalyst is added to the reaction mixture at a concentration level of about 50 to about 10,000 parts per weight of catalyst per one million parts of the total reaction mixture.

The reactions of such lactones with dispersant materials containing nitrogen or ester groups is more completely described in GB-A-2197312, EP-A-0263703, EP-A-0263704, GB-A-2211849, GB-A-2201678, EP-A-0263706, EP-A-0263702 and EP-A-0336664.

The nitrogen-containing dispersant materials of this invention can also be post-treated by reaction with an alkyl acetoacetate or alkyl thioacetate of the formula:

$$R^a - \underset{\underset{O}{\parallel}}{C} - CH_2 - \underset{\underset{O}{\parallel}}{C} - X^a - R^b$$

wherein X^a is O or S, R^b is H or R^a, and R^a is in each instance in which it appears independently selected from the group consisting of substituted and unsubstituted alkyl or aryl (preferably alkyl of 1 to 6 carbon atoms, e.g., methyl, ethyl, etc.) to form an amino compound N-substituted by at least one tautomeric substituent of the formula:

$$-\underset{\underset{O}{\parallel}}{C} - CH_2 - \underset{\underset{O}{\parallel}}{C} - R^a \longleftrightarrow -\underset{\underset{O}{\parallel}}{C} - CH = \underset{\underset{OH}{|}}{C} - R^a$$

wherein R^9 is as defined above.

The reaction is preferably effected at a temperature sufficiently high so as to substantially minimize the production of the enaminone and produce, instead, the keto-enol tautomer. Temperatures of at least about 150°C are preferred to meet this goal although proper choice of temperature depends on many factors, including reactants, concentration, reaction solvent choice, etc. Temperatures of from about 120°C to 220°C, preferably from about 150°C to 180°C will generally be used. The reaction of the nitrogen-containing dispersant material and the alkyl acetonate and the alkyl thioacetate will liberate the corresponding HOR^b and HSR^b by-products, respectively. Preferably, such by-products are substantially removed, as by distilltion or stripping with an inert gas (such as N_2), prior to use of the thus prepared dispersant adduct. Such distillation and stripping steps are conveniently performed at elevated temperature, e.g., at the selected reaction temperature (for example, at 150°C or higher). A neutral diluent such as mineral oil may be used for the reaction.

The amount of alkyl aceto-acetate and or alkyl thioacetate reactants used can vary widely, and is preferably selected so as to avoid substantial excesses of these reactants. Generally, these reactants are used in a reactant:amine nitrogen-equivalent molar ratio of from about 0.1 to 1:1, and preferably from about 0.5 to 1:1, wherein the moles of amine nitrogen-equivalent is the moles of secondary nitrogens plus twice the moles of primary nitrogens in the nitrogen-containing dispersant material (e.g., polyisobutenyl succinimide) which is thus contacted with the alkylacetonate or alkyl thioacetate. The reaction should also be conducted in the substantial absence of strong acids (e.g., mineral acids, such as HCl, HB_2, H_2SO_4, H_3PO_3 and the like, and sulfonic acids, such as para-toluene sulfonic acids) to avoid the undesired side-reactions and decrease in yield to the adducts of this invention.

The reactions of such alkyl acetoacetates and thioacetoacetates with nitrogen-containing dispersant materials is more completely described in EP-A-0295789.

Further aspects of the present invention reside in the formation of metal complexes of the novel dispersant additives prepared in accordance with this invention. Suitable metal complexes may be formed in accordance with known techniques of employing a reactive metal ion species during or after the formation of the present dispersant materials. Complex forming metal reactants include the metal nitrates, thiocyanates, halides, carboxylates, phosphates, thio-phosphates, sulfates, and borates of transition metals such as iron, cobalt, nickel, copper, chromium, manganese, molybdenum, tungsten, ruthenium, palladium, platinum, cadmium, lead, silver, mercury, antimony and the like. Prior art disclosures of these complexing reactions may be also found in U.S. Patents 3,306,908 and Re. 26,433, the disclosures of which are hereby incorporated by reference in their entirety.

The processes of these incorporated patents, as applied to the compositions of this invention, and the post-treated compositions thus produced constitute a further aspect of this invention.

The dispersant-forming reaction can be conducted in a polar or non-polar solvent (e.g., xylene, toluene, benzene and the like), and is preferably conducted in the presence of a mineral or synthetic lubricating oil.

The nitrogen containing dispersants can be further treated by boration as generally taught in U.S. Patent Nos. 3,087,936 and 3,254,025 (incorporated herein by reference thereto). This is readily accomplished by treating the selected acyl nitrogen dispersant with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition. Usefully the dispersants of the inventive combination contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of said borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(HBO_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of said diimide.

Treating is readily carried out by adding from about 0.05 to 4, e.g. 1 to 3 wt. % (based on the weight of said acyl nitrogen compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said acyl nitrogen compound and heating with stirring at from about 135° C. to 190, e.g. 140-170° C., for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges. Or, the boron treatment can be carried out by adding boric acid to the hot reaction mixture of the monocarboxylic acid material and amine while removing water.

The ashless dispersants of this invention can be used alone or in admixture with other dispersants such as esters derived from the aforesaid long chain hydrocarbon substituted dicarboxylic acid material and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols, etc. The polyhydric alcohols are the most preferred hydroxy compound and preferably contain from 2 to about 10 hydroxy radicals, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to about 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof.

The ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the esters of this invention comprise the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene or amino-arylene oxy-arylene radicals. They are exemplified by Cellosolve, Carbitol, N,N,N′,N′-tetrahydroxy-trimethylene di-amine, and ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to about 8 carbon atoms.

The ester dispersant may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids; as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxyl radicals. Mixtures of the above illustrated esters likewise are contemplated within the scope of this invention.

The ester dispersant may be prepared by one of several known methods as illustrated for example in U.S. Patent 3,381,022. The ester dispersants may also be borated, similar to the nitrogen containing dispersants, as described above.

Hydroxyamines which can be reacted with the aforesaid long chain hydrocarbon substituted dicarboxylic acid materials to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1, 3-propane-diol, 2-amino-2-ethyl-1, 3-propanediol, N-(beta-hydroxy-propyl)-N′-(beta-aminoethyl)-piperazine, tris(hydroxymethyl) amino-methane (also known as trismethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)ethylamine, and the like. Mixtures of these or similar amines can also be employed. The above description of nucleophilic reactants suitable for reaction with the hydrocarbyl substituted dicarboxylic acid or anhydride includes amines, alcohols, and compounds of mixed amine and hydroxy containing reactive functional groups, i.e., amino-alcohols.

The tris(hydroxymethyl) amino methane (THAM) can be reacted with the aforesaid acid material to form amides, imides or ester type additives as taught by U.K. 984,409, or to form oxazoline compounds and borated oxazoline compounds as described, for example, in U.S. 4,102,798; 4,116,876 and 4,113,639.

Other dispersants which can be employed in admixture with the novel dispersants of this invention are those derived from the aforesaid long chain hydrocarbyl substituted dicarboxylic acid material and the aforesaid amines, such as polyalkylene polyamines, e.g., long chain hydrocarbyl substituted succinimides.

Exemplary of such other dispersants are those described in EP-A-0307132.

A preferred group of ashless dispersants are those derived from polyisobutylene substituted with succinic anhydride groups and reacted with linked polyamines containing on average at least 6 (e.g., from 6 to 30), reactive nitrogen moieties and from 2 to 4 primary amine groups per molecule, formed by reacting polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxypropylene amines, e.g., polyoxypropylene diamine, trismethylolaminomethane and pentaerythritol, and combinations thereof, with a branched first adduct prepared by reacting ammonia or a diprimary amine having from 2 to 4 total nitrogen atoms and from 2 to 12 carbon atoms per molecule with an acrylate-type compound of formula (IX) above, and most preferably with an acrylate-type reactant selected from the group consisting of lower alkyl alky-acrylates (e.g., methyl, ethyl, iso-propyl, propyl, iso-butyl, n-butyl, tert-butyl, etc., esters of methacrylic acid, acrylic acid, and the like).

The dispersants of the present invention can be incorporated into a lubricating oil (or a fuel in any convenient way. Thus, these mixtures can be added directly to the lubricating oil (or fuel) by dispersing or dissolving the same in the lubricating oil (or fuel) at the desired level of concentration of the dispersant. Such blending into the additional lubricating oil (or fuel) can occur at room temperature or elevated temperatures. Alternatively, the dispersants can be blended with a suitable oil-soluble solvent diluent (such as benzene, xylene, toluene, lubricating base oils and petroleum distillates, including the various normally liquid fuels described in detail below) to form a concentrate, and then blending the concentrate with a lubricating oil (or fuel) to obtain the final formulation. Such dispersant concentrates will typically contain (on an active ingredient (A.I.) basis) from about 3 to about 45 wt.%, and preferably from about 10 to about 35 wt.%, dispersant additive, and typically from about 30 to 90 wt. %, preferably from about 40 to 60 wt.%, base oil, based on the concentrate weight.

OLEAGINOUS COMPOSITIONS

The additive mixtures of the present invention possess very good dispersant properties as measured herein in a wide variety of environments. Accordingly, the additive mixtures are used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additive mixtures of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from about 65° to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from about 0.001 to about 0.5, and preferably 0.005 to about 0.15 weight percent, based on the total weight of the composition, will usually be employed. The properties of such fuels are well known as illustrated, for example, by ASTM Specifications D #396-73 (Fuel Oils) and D #439-73 (Gasolines) available from the American Society for Testing Materials ("ASTM"), 1916 Race Street, Philadelphia, Pennsylvania 19103.

The fuel compositions of this invention can contain, in addition to the products of this invention, other additives which are well known to those of skill in the art. These can include anti-knock agents such as tetraalkyl lead compounds, lead scavengers such as haloalkanes, deposit preventers or modifiers such as triaryl phosphates, dyes, cetane improvers, anitoxidants such as 2,6-ditertiary-butyl-4-methylphenol, rust inhibitors, bacteriostatic agents, gum inhibitors, metal deactivators, upper cylinder lubricants and the like.

The additive mixtures of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives re dissolved or dispersed. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the present invention in base oils conventionally employed in and or adapted for use as power transmitting fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additive mixtures of the present invention.

These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, friction modifiers, etc. as described in U. S. Patent 4,797,219, the disclosure of which is hereby incorporated by reference in its entirety. Some of these numerous additives can provide a multiplicity of effects, e.g. a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 80 wt. %, e.g., 20 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40 parts by weight of lubricating oil, per part by weight of the additive package, in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, a dispersant would be usually employed in the form of a 40 to 50 wt. % concentrate, for example, in a lubricating oil fraction.

The ashless dispersants of the present invention will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

Natural oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) ; and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters and C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexa-(4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

Compositions when containing these conventional additives are typically blended into the base oil in amounts effective to provide their normal attendant function. Representative effective amounts of such additives (as the respective active ingredients) in the fully formulated oil are illustrated as follows:

Compositions	Wt.% A.I. (Preferred)	Wt.% A.I. (Broad)
Viscosity Modifier	.01-4	0.01-12
Detergents	0.01-3	0.01-20
Corrosion Inhibitor	0.01-1.5	.01-5
Oxidation Inhibitor	0.01-1.5	.01-5
Dispersant	0.1-8	.1-20
Pour Point Depressant	0.01-1.5	.01-5
Anti-Foaming Agents	0.001-0.15	.001-3
Anti-Wear Agents	0.001-1.5	.001-5
Friction Modifiers	0.01-1.5	.01-5
Mineral Oil Base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the novel dispersants of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the dispersants of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from about 2.5 to about 90%, and preferably from about 15 to about 75%, and most preferably from about 25 to about 60% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

All of said weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. An improved lubricating oil nitrogen-containing dispersant additive which comprises oil soluble salts, amides, imides, oxazolines, or mixtures thereof, of polyolefin-substituted mono and dicarboxylic acids or their anhydrides prepared by the reaction of at least one polyamine and long chain hydrocarbon substituted mono- or dicarboxylic acid producing material formed by reacting a polyolefin and at least one monounsaturated carboxylic reactant comprising members selected from the group consisting of (i) monounsaturated C_4 to C_{10} dicarboxylic acid; (ii) anhydride derivatives of (i) or C_1 to C_5 alcohol derived mono- or di-esters of (i) ; (iii) monounsaturated C_3 to C_{10} monocarboxylic acids wherein the carbon-carbon double bond is conjugated to the carboxy group; and (iv) C_1 to C_5 alcohol derived monoesters of (iii), wherein the polyolefin has a number average molecular weight of from 1,500 to 2,500 and a ratio of the weight average molecular weight to number average molecular weight of the polyolefin of less than 3, and wherein the dispersant material contains within its structure an average of from 0.7 to 1.3 mono- or dicarboxylic acid producing moieties derived from said monounsaturated carboxylic reactant per polyolefin molecule, and wherein the dispersant material contains from 0.5 to 4 equivalents of secondary amine groups per equivalent of said mono- or dicarboxylic acid producing moieties per molecule, with the proviso that the

dispersant material is further characterized by a Z factor of from 4,000 to 6,000, wherein the Z factor is determined by the expression:

$$Z = \left[\frac{([N])^2}{M_n} \times (1.1\times10^6) \right] + 1.5(M_n)$$

wherein [N] is the total nitrogen content of the dispersant material expressed in wt% (as a 50wt% active ingredient solution of said dispersant material) and M_n is the polyolefin number average molecular weight.

2. The dispersant additive according to claim 1 wherein said nitrogen-containing dispersant comprises an amide, imide or mixtures thereof derived from the reaction of said polyolefin-substituted mono- or polycarboxylic acid material and a linked polyamine.

3. The dispersant additive according to claim 2 wherein said linked polyamine contains at least one primary amine group per molecule and comprises an adduct of at least one nitrogen-containing compound and an amine linking reactant.

4. The dispersant additive according to claim 3 wherein said linked polyamine is prepared by contacting a nitrogen-containing compound having at least two reactive nitrogen moieties with a polyfunctional reactant having within its structure at least two functional groups reactive with a -NH- group in an amount and under conditions sufficient to react said functional groups in said polyfunctional reactant with said reactive nitrogen moieties to form a high nitrogen linked polyamine characterized by having within its structure on average at least two unreacted primary or secondary amine groups.

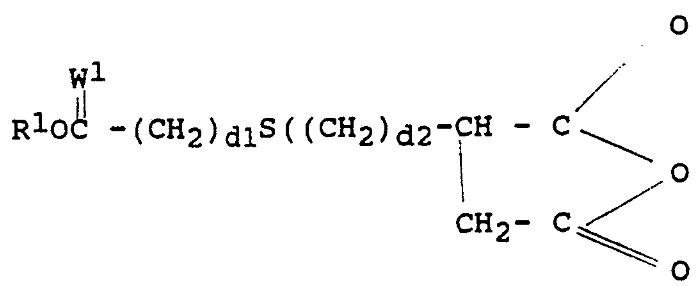
5. The dispersant additive according to claim 4 wherein said polyfunctional reactant comprises at least one of:

(i) compounds having the formula:

$$X - \overset{W^1}{\overset{\|}{C}} - (T)_a - [(\overset{W^2}{\overset{\|}{C}})_b - Y]_c$$

wherein W^1 and W^2 are the same or different and are O or S, X and Y are the same or different and comprise members selected from the group consisting of: halide, $-OR^4$, $-SR^4$, $-N(R^4)(R^5)$, $-Z^1C(O)OR^4$, $-C(O)R^4$, $-(R^3)C=C(R^1)(R^2)$, $-Z^1$-nitrile, $-Z^1$-epoxy, $-Z^1$-cyano, $-Z^1$-thiocyano, $-Z^1$-isothiocyano, and $-Z^1$-isocyano, wherein R^1, R^2, R^3, R^4 and R^5 are the same or different and are H or substituted or unsubstituted hydrocarbyl and wherein Z^1 is C_1 to C_{20} bivalent hydrocarbylene, T is a substituted or unsubstituted hydrocarbon moiety, "a" is 0 or 1, "b" is 0 or 1, and "c" is an integer of at least 1, and wherein X and Y can together comprise -O- or -S- when "a" is 1 and T contains a $>C=C<$ group, wherein at least two of X, Y and T are groups reactive with a -NH- group, with the provisos that $c = 1$ when $a = 0$ and $b = 1$ when $a = 1$;

(ii) compounds of the formula:



wherein W^1 is as defined above, and wherein R^1 is H or substituted or unsubstituted hydrocarbyl, and "d1" and "d2" are each integers of from 1 to 10;

(iii) compounds of the formula:

$$R^1-\overset{\overset{\displaystyle R^2}{|}}{C}=\overset{\overset{\displaystyle R^3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-Y''$$

wherein R^1, R^2, and R^3 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above, and wherein Y'' comprises a reactive functional group selected from the group consisting of: halide, $-OR^4$, $-SR^4$, $-N(R^4)(R^5)$, $-Z'C(O)OR^4$, and $-(R^3)C=C(R^1)(R^2)$, wherein R^4 is as defined above; and

(iv) compounds of the formula:

$$R^1-\overset{\overset{\displaystyle R^2}{|}}{C}=\overset{\overset{\displaystyle R^3}{|}}{C}-CN$$

wherein R^1, R^2, and R^3 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl as defined above.

6. The disperant additive according to claim 4 wherein said polyfunctional reactant comprises at least one alpha, beta-unsaturated compound of the formula:

$$R^1-\overset{\overset{\displaystyle R^2}{|}}{C}=\overset{\overset{\displaystyle R^3}{|}}{C}-\overset{\displaystyle X}{C}-Y$$

wherein X is sulfur or oxygen, Y is $-OR^4$, $-SR^4$, or $-NR^4$ (R^5), and R^1, R^2, R^3, R^4 and R^5 are the same or different and are hydrogen or substituted or unsubstituted hydrocarbyl.

7. The dispersant additive according to claim 6 wherein said alpha, beta-unsaturated compound comprises at least one member selected from the group consisting of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate.

8. The dispersant additive according to any of claims 3 to 7, wherein said nitrogen-containing compound contains from 2 to 60 carbon atoms and from 2 to 12 nitrogen atoms per molecule.

9. The dispersant additive according to claim 8, wherein said nitrogen-containing compound comprises a polyalkylenepolyamine wherein each said alkylene group contains from 2 to 6 carbons and said polyalkylenepolyamine contains from 5 to 9 nitrogen atoms per molecule.

10. The dispersant additive according to claim 9 wherein said nitrogen-containing compound comprises polyethylenepolyamine or polypropyleneamine.

11. The dispersant additive according to any of claims 3 to 10 wherein said nitrogen-containing compound comprises a polyamine which contains at least 2 primary nitrogen atoms per molecule.

12. The dispersant additive according to any of claims 1 to 11 wherein said monounsaturated acid material comprises maleic anhydride.

13. The dispersant additive according to any of claims 1 to 12 wherein said olefin polymer comprises polyisobutylene.

14. The dispersant additive according to claim 13, wherein said acid hydrocarbyl substituted C_4 to C_{10} monounsaturated dicarboxylic acid producing material which comprises polyisobutylene of from 1,500 to 2,500 number average molecular weight substituted with succinic anhydride moieties.

15. The dispersant additive according to any of claims 1 to 12 wherein said olefin polymer comprises ethylene-propylene copolymer.

16. The dispersant additive according to any of claims 1 to 15 wherein the ratio of acid producing moieties per molecule of olefin polymer in said dispersant additive is from 1.05 to 1.8.

17. The dispersant additive of any of claims 1 to 16, wherein said number average molecular weight of said olefin polymer is from 1600 to 2400.

18. The dispersant additive according to any of claims 1 to 17 wherein said Z factor is from 4,200 to 5,800.

19. The dispersant additive according to any of claims 1 to 18 wherein said dispersant additive is borated to provide from 0.05 to 2.0 weight percent boron in said borated dispersant additive.

20. A process for producing a dispersant additive as claimed in any of claims 1 to 19 which comprises:

(a) providing a linked polyamine containing at least two primary or secondary amine groups per molecule;

(b) providing a long chain hydrocarbyl substituted mono- or dicarboxylic acid producing material formed by reacting an olefin polymer of C_2 to C_{10} monoolefin having a number average molecular weight of 1,500 to 2,500 and at least one of a C_4 to C_{10} monounsaturated dicarboxylic acid material and a C_3 to C_{10} monounsaturated moncarboxylic acid material, said acid producing material having an average of from 0.7 to 1.3 mono- or dicarboxylic acid producing moieties, per molecule of said olefin polymer present in the reaction mixture used to form said acid producing material; and said olefin polymer having a ratio of the weight average molecular weight to number average molecular weight of less than 3.0; and

(c) contacting the said acid producing material with said branched nitrogen-containing adduct under conditions sufficient to form a nitrogen-containing dispersant material which contains from 0.5 to 4 equivalents of secondary amine groups per equivalent of said mono- or dicarboxylic acid producing moieties per molecule, with the proviso that the dispersant material is further characterized by a Z factor of from 4,000 to 6,000, wherein the Z factor is determined by the expression:

$$Z = \left[\frac{([N])^2}{M_n} \times (1.1 \times 10^6)\right] + 1.5(M_n)$$

wherein [N] is the total nitrogen content of the dispersant material expressed in wt% (as a 50wt% active ingredient solution of said dispersant material) and M_n is the polyolefin number average molecular weight.

21. The dispersant additive according to claim 20 wherein 1 to 5 moles of said acid producing material per primary nitrogen equivalent of said second adduct are present in said step (c) liquid reaction mixture.

22. A lubricating oil composition containing from 0.001 to 0.5 wt. % of the dispersant additive of any of claims 1 to 19.

23. A lubricating oil composition containing from 0.1 to 20 wt. % of the dispersant additive of any of claims 1 to 19.

24. A lubricating oil composition containing from 0.1 to 8 wt. % of the dispersant additive of any of claims 1 to 19.