WO 00/40216 PCT/US00/00132



166166



G00002

TERTIARY AMIDE TERMINATED POLYAMIDES AND USES THEREOF

TECHNICAL FIELD OF THE INVENTION

This invention generally relates to organic resins, more particularly to polyamide resins having tertiary amide termination, and to the use of these resins as gelling agents, and in particular as gellants for low polarity liquids such as hydrocarbons.

BACKGROUND OF THE INVENTION

In many commercially important compositions, the consistency of the product is critical to its commercial success. One example is personal care products, which generally contain one or more active ingredients within a carrier formulation. While the active ingredient(s) determine the ultimate performance properties of the product, the carrier formulation is equally critical to the commercial success of the product in that it largely determines the consistency of the product. The rheology of the carrier (also referred to as the "base") largely determines the flow properties of the product, and the flow properties largely determine the manner in which the consumer will apply or use the product.

For example, aluminum chlorohydrate, aluminum-zirconium tetrachlorohydrate, aluminum-zirconium polychlorohydrate complexed with glycine, and aluminum-zirconium complexed with any of trichlorohydrate, octachlorohydrate, and sesquichlorohydrate are metal salts that are commonly used as active ingredients in deodorant and antiperspirant products. Consumers have shown a preference for applying deodorant from a stick form. Thus, the carrier in a stick-form deodorant must be a relatively hard substance, and waxy fatty alcohol such as stearyl alcohol has often been used as the carrier in these products. As another example, the active ingredient in a lipstick is the colorant. A lipstick should not be as hard as a stick deodorant, but of course must maintain its shape when undisturbed at room temperature. A blend of wax and oil is known to provide a consistency that is well-suited as a carrier for a lipstick.

As a final example, shampoo desirably has a viscosity greater than water, and when the active ingredient(s) in a shampoo does not have a sufficiently high viscosity, a somewhat viscous carrier material is desirably included in the shampoo formulation.

From the above examples, it is seen that formulators of personal care products depend upon the availability of materials having various rheological properties, in order to formulate a successful personal care product. Materials which have a gel-like character, in that they maintain their shape when undisturbed but flow upon being rubbed, are often desired for personal care products.

Transparent (*i.e.*, clear) carriers are desired by formulators who develop a personal care product wherein colorant is an active ingredient, because a transparent carrier (as opposed to an opaque carrier) will minimally, if at all, interfere with the appearance of the colorant. In recent years, consumers have demonstrated an increasing preference for transparent and colorless personal care products such as deodorants and shampoos. There is thus an increasing demand for transparent materials which can provide the rheological properties needed for various personal care products, and particularly which can impart gel-like character to a formulation.

Polyamide resin prepared from polymerized fatty acid and diamine is reported to function as a gellant in formulations developed for personal care products. For example, U.S. Patent No. 3,148,125 is directed to a clear lipstick carrier composition formed from polyamide resin compounded with a lower aliphatic alcohol and a so-called "polyamide solvent." Likewise, U.S. Patent No. 5,500,209 is directed to forming a gel or stick deodorant, where the composition contains polyamide gelling agent and a solvent system including monohydric or polyhydric alcohols. Thus, the prior art recognizes to blend certain polyamides with alcohols, to thereby form a gel.

Pure hydrocarbon is desirably included in personal care formulations because it is transparent and relatively inexpensive. Pure hydrocarbons are also available in a wide variety of viscosities and grades. However, pure hydrocarbon often does not have the rheological properties that are desired in a carrier, *e.g.*, it does not naturally exhibit gel-like character. Furthermore, when hydrocarbon is present in a personal care formulation, alcohol is also typically present when a gel-like consistency

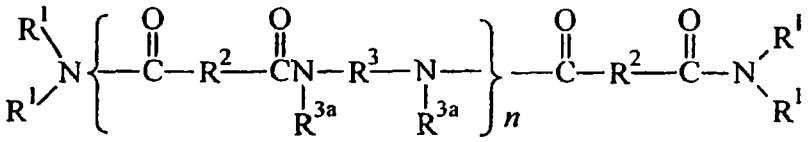
3 JUL 2003

is desired for the product. Alcohol can be irritating to skin, and accordingly, in some formulations, is desirably omitted.

Accordingly, there is a need in the art for materials which can be combined with pure hydrocarbon to afford a transparent material which has gel-like character. The present invention provides this and related advantages as described herein.

SUMMARY OF THE INVENTION

In one aspect, the invention provides a tertiary amide terminated polyamide (ATPA) resin of the formula (1):



(1)

wherein,

n designates a number of repeating units such that terminal amide groups (*i.e.*, the amide groups to which R^1 is directly bonded) constitute from 10% to 50% of the total amide groups of the ATPA;

R^1 at each occurrence is independently selected from a C_{1-22} hydrocarbon group;

R^2 at each occurrence is independently selected from a C_{2-42} hydrocarbon group;

R^3 at each occurrence is independently selected from an organic group containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and

R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3.

In another aspect, the invention provides an ATPA resin prepared by a method that includes reacting x equivalents of carboxylic acid from diacid or a reactive equivalent thereof, y equivalents of amine from diamine, and z equivalents of a

secondary amine-containing molecule having no reactive functional groups except the secondary amine or a reactive equivalent thereof, where the secondary amine-containing molecule (*i.e.*, monoamine) is substantially the only monofunctional reactant used to form the ATPA resin, and wherein each of x, y and z is greater than 0.

In another aspect, the invention provides a composition that includes a low polarity liquid and an ATPA resin as described above.

In another aspect, the invention provides a method for preparing a gel, preferably a transparent or translucent gel, where the method includes combining a low polarity liquid with an ATPA resin as described above.

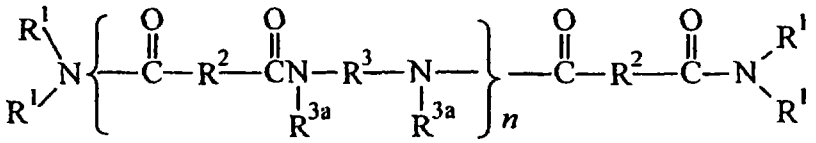
These and other aspects of the present invention will become evident upon reference to the following drawing and detailed description.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 illustrates a testing protocol for measuring the rigidity of a gelled sample.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides resins comprising short-chain polyamides of the formula (1), which will be referred to herein as tertiary amide terminated polyamides, or ATPAs.



(1)

In formula (1), *n* designates a number of repeating units such that terminal (*i e.*, R^1-containing) amide groups constitute from 10% to 50% of the total of the amide groups shown in formula (1); R^1 at each occurrence is independently selected from a C_{1-22} hydrocarbon group; R^2 at each occurrence is independently selected from a C_{2-42} hydrocarbon group with the proviso that at least 50% of the R^2 groups have 30-42 carbon atoms; R^3 at each occurrence is independently selected from an organic group

containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3, such that at least 50% of the R^{3a} groups are hydrogen.

Preferably, the resin composition further comprises diamide having formula (1) wherein n=0, such that the ratio of terminal amide groups to the sum of amide groups in the total of the molecules that comprise the resin of formula (1) is from 0.1 to 0.7. Preferably, the resin composition is at reaction equilibrium.

As may be seen from formula (1), the ATPA resins have terminal amide groups of the formula -C(=O)N(R^1)(R^1) at both ends of a series of amide groups. These terminal amide groups are formed from secondary amines (since R^1 is an organic group and is not hydrogen), and therefore the terminal amide groups in formula (1) are properly referred to as tertiary amide groups. Accordingly, the ATPA resins may be referred to as tertiary amide terminated polyamides.

The letter "n" in formula (1) designates the number of repeating units present in a molecule of ATPA, and is an integer greater than 0. According to the invention, n may be 1, in which case the ATPA contains equal numbers of terminal amide and non-terminal amide groups, *i.e.*, the terminal amide groups constitute 50% of the total of the amide groups in the ATPA molecule. The preferred ATPA resins are of relatively low molecular weight, so that n is preferably 1 to about 10, and more preferably is 1 to about 5. Because the ATPA molecules have such a low molecular weight, they could equally well be referred to as tertiary amide terminated oligoamides. In any event, viewed another way, the terminal amide groups constitute about 10% to about 50%, preferably about 15% to about 40%. and more preferably about 20% to about 35% of the total of the amide groups. A preferred ATPA resin includes a mixture of ATPA molecules of formula (1) having various n values. The ATPA resin has a weight average molecular weight of less than about 10,000, and typically less than

about 5,000, but more than 500, typically more than 1,000, when measured by gel permeation chromatography using polystyrene calibration standards.

The R^1 group in formula (1) is a hydrocarbon group, and preferably is an alkyl or alkenyl group which contains at least 1, typically at least 4, and preferably more than 4 carbon atoms, *e.g.*, 8, 10, 12, 14, 16, 18, 20, or 22 carbon atoms. Alkyl groups are preferred, however alkenyl groups having 1-3, and preferably 1 site of unsaturation are also suitable. The upper range for the number of carbon atoms in the R^1 group is not particularly critical, however preferably the R^1 group has less than or equal to about 22 carbon atoms. R^1 groups having about 16-22 carbon atoms are highly preferred. The identity of R^1 at any occurrence is independent of the identity of R^1 at any other occurrence.

Suitable R^1 groups are readily introduced into a molecule of formula (1) when secondary monoamine(s) is used as a co-reactant in preparing the ATPA resin. The secondary monoamine has the formula $HN(R^1)(R^1)$, wherein R^1 is defined above. Suitable secondary monoamines are commercially available from a variety of sources, including Witco Corporation (Greenwich, CT; http://www.witco.com); Akzo Nobel Chemicals, Surface Chemistry (Chicago, IL; http://www.akzonobelusa.com); and Aldrich (Milwaukee, WI; http://www.aldrich.sial.com). Ditallow amine is a preferred secondary monoamine.

The R^2 group in formula (1) is suitably a hydrocarbon containing 2 to 42 carbon atoms, and preferably contains 4 to 42 carbon atoms. A more preferred R^2 group contains 30-42 carbon atoms (*i.e.*, is a C_{30-42} group), and at least 50% of the R^2 groups in an ATPA resin preferably have 30-42 carbon atoms. Such R^2 groups are readily introduced into an ATPA when the resin is prepared from polymerized fatty acid, also known as dimer acid. Polymerized fatty acid is typically a mixture of structures, where individual dimer acids may be saturated, unsaturated, cyclic, acyclic, etc. Thus, a detailed characterization of the structure of the R^2 groups is not readily available. However, good discussions of fatty acid polymerization may be found in, for example, U.S. Patent No. 3,157,681 and *Naval Stores - Production, Chemistry and Utilization*, D.F. Zinkel and J. Russel (eds.), Pulp. Chem. Assoc. Inc., 1989, Chapter

23. Dimer acid is available commercially as, for example, UNIDYME™ dimer acid from Union Camp Corporation (Wayne, NJ), EMPOL™ dimer acid from Henkel Corporation, Emery Oleochemicals Division (Cincinnati, OH); PRIPOL™ dimer acid from Unichema North America (Chicago, IL), and SYLVADYM™ dimer acid from Arizona Chemical, division of International Paper, (Panama City, FL).

While the preferred ATPA resins contain at least 50% C_{30-42} groups as the R^2 group, more preferably the total of the R^2 groups consist of at least 75% C_{30-42} groups, and still more preferably consist of at least 90% C_{30-42} groups. ATPA resins of formula (1) wherein R^2 is entirely C_{30-42} are preferred gelling agents of the invention.

However, ATPA resins may also contain R^2 groups having less than 30 carbon atoms. For example, an ATPA resin may contain one or more R^2 groups having about 4 to 19, preferably about 4 to 12, and more preferably about 4 to 8 carbon atoms. The carbon atoms may be arranged in a linear, branched or cyclic fashion, and unsaturation may be present between any two carbon atoms. Thus, R^2 may be aliphatic or aromatic. When present, these lower carbon-number R^2 groups are preferably formed entirely of carbon and hydrogen, *i.e.*, are hydrocarbyl groups. Such lower carbon-number R^2 groups preferably constitute less than 50% of the R^2 groups; however, when present, constitute about 1% to about 50%, and preferably about 5% to about 35% of the total of the R^2 groups. The identity of R^2 at each occurrence is independent of the identity of R^2 at any other occurrence. Suitable co-diacids are available from, for example, Aldrich (Milwaukee, WI).

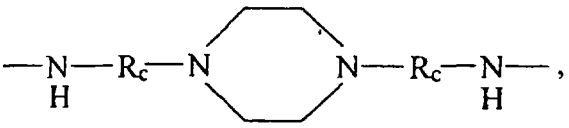
The $-N(R^{3a})-R^3-N(R^{3a})-$ group in formula (1) links two carbonyl (C=O) groups. In a preferred embodiment of the invention, all of the R^{3a} groups in an ATPA resin are hydrogen, so that R^3 alone joins the two nitrogen atoms shown in the formula $-N(R^{3a})-R^3-N(R^{3a})-$. In this case, the R^3 group contains at least two carbon atoms, and optionally oxygen and/or nitrogen atoms, in addition to any hydrogen atoms that are necessary to complete otherwise unfilled valencies of the carbon, oxygen and nitrogen atoms. In one embodiment, R^3 is a hydrocarbon group, having 2 to about 36 carbon atoms, preferably having 2 to about 12 carbon atoms, and more preferably having 2 to about 8 carbon atoms. These carbon atoms may be arranged in a linear, branched or

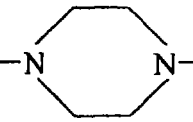
cyclic fashion, and unsaturation may be present between any two of the carbon atoms. Thus, R^3 may contain aliphatic or aromatic structures. The identities of R^3 and R^{3a} at each occurrence are independent of their identities at any other occurrence.

The R^3 groups may contain oxygen and/or nitrogen in addition to carbon and hydrogen atoms. A typical oxygen atom-containing R^3 group is a polyalkylene oxide, *i.e.*, a group having alternating alkylene groups and oxygen atoms. Indeed, the oxygenation in a R^3 group is preferably present as an ether group. Representative polyalkylene oxides include, without limitation, polyethylene oxide, polypropylene oxide and copolymers (either random, alternating or block) of ethylene oxide and propylene oxide. Such oxygenated R^3 groups are readily introduced into an ATPA resin through use of JEFFAMINE™ diamines (Huntsman Chemical, Inc., Houston, TX). These materials are available in a wide range of molecular weights, where any molecular weight diamine may be used in the preparation of the resins of the invention. While some of the R^3 groups may contain oxygen (at least about 1%), preferably a minor number (less than 50%) of the R^3 groups contain oxygen, and more preferably less than about 20% of the R^3 groups contain oxygen. The presence of oxygen-containing R^3 groups tends to lower the softening point of the ATPA resin.

When present, the nitrogen atoms in an R^3 group are preferably present as secondary or tertiary amines. A typical nitrogen-containing R^3 group having secondary amine groups is a polyalkylene amine, *i.e.*, a group containing alternating alkylene groups and amine groups, which is sometimes referred to as a polyalkylene polyamine. The alkylene group is preferably a lower alkylene group, *e.g.*, methylene, ethylene, (*i.e.*, $-CH_2CH_2-$), propylene, etc. A typical polyalkylene amine may be represented by the formula $-NH-(CH_2CH_2NH)_mCH_2CH_2-NH-$ wherein *m* is an integer from 1 to about 5.

However, the nitrogen atoms in the nitrogen-containing R^3 group may alternatively (or additionally) be present as tertiary nitrogen atoms, *e.g.*, they may be

present in a heterocycle of the formula: , wherein R_c is a C_{1-3} alkylene group.

In the above-described nitrogen-containing R^3 groups, R^{3a} was hydrogen. However, R^{3a} is not limited to hydrogen. In fact, R^{3a} may be a C_{1-10}alkyl group, preferably a C_{1-5}alkyl group, and more preferably a C_{1-3}alkyl group. In addition, R^3 and R^{3a}, or two R^{3a} groups, may together form a heterocyclic structure, *e.g.*, a piperazine structure such as . In this case, the two R^{3a} groups may be seen as joining together to form an ethylene bridge between the two nitrogen atoms, while R^3 is also an ethylene bridge. Additional suitable diamines are available from, for example, Aldrich (Milwaukee, WI).

The ATPA resin typically includes a mixture of ATPA molecules of formula (1) in addition to, for example, by-products that are formed during the ATPA-forming reaction. While the ATPA molecules of formula (1) may be purified from such by-products using, for example, chromatography or distillation, the by-products are typically either minimal in amount or impart desirable properties to the resin when the resin functions as a gelling agent, and thus need not be separated from the molecules of formula (1) in order for a suitable ATPA resin to be formed.

As described herein, amines and carboxylic acids are preferred starting materials to form the ATPA resins of the invention. These starting materials are preferably reacted together with a stoichiometry, and under reaction conditions, such that the acid number of the resulting ATPA resin is less than 25, preferably less than 15, and more preferably less than 10, while the amine number is preferably less than 10, more preferably less than 5, and still more preferably less than 1. The softening point of the ATPA resin is preferably greater than room temperature, more preferably is about 50°C to about 150°C, and still more preferably is about 80°C to about 130°C.

It is important to control the stoichiometry of the reactants in order to prepare an ATPA resin according to the invention. In the following discussion

regarding reactant stoichiometry, the terms "equivalent(s)" and "equivalent percent" will be used, and are intended to have their standard meanings as employed in the art. However, for additional clarity, it is noted that equivalents refer to the number of reactive groups present in a molar quantity of a molecule, such that a mole of a dicarboxylic acid (*e.g.*, sebacic acid) has two equivalents of carboxylic acid, while a mole of monoamine has one equivalent of amine. Furthermore, it is emphasized that in preparing an ATPA resin, the diacid has only two reactive groups (both carboxylic acids), the monoamine has only one reactive group (a secondary amine group) and the diamine has only two reactive groups (preferably both primary amines), and these are preferably, although not necessarily, the only reactive materials present in the reaction mixture.

When co-diacid is employed to prepare an ATPA resin, the co-diacid preferably contributes no more than about 50% of the equivalents of carboxylic acid present in the reaction mixture. Stated another way, the co-diacid contributes from 0-50 equivalent percent of the acid equivalents in the reaction mixture. Preferably, the co-diacid contributes 0-30 equivalent percent, and more preferably contributes 0-10 equivalent percent of the acid equivalents in the reaction mixture.

The stoichiometry of the reactants will have a significant impact on the composition of the ATPA resin. For example, ATPA resins made with increasing amounts of secondary monoamine will tend to have lower (number and weight) average molecular weights. In other words, as more monofunctional reactant is used, the number of amide pairs in an average molecule of formula (1) will decrease. On the other hand, as less monoamine is used, the average molecular weight of the molecules in the ATPA resin will increase. In general, increasing the average molecular weight of the ATPA will tend to increase the melting point and melt viscosity of the resin. When a high melting point ATPA is combined with a solvent to thereby form a gel, the gel will tend to have a firmer consistency than does a gel formed from an ATPA with a low melting point.

In order to prepare an ATPA resin, the above-described reactants (diacid, monoamine and diamine, or reactive equivalents thereof) may be combined in any

order. Preferably, the reactants are simply mixed together and heated for a time and at a temperature sufficient to achieve essentially complete reaction, to thereby form the ATPA resin. During formation of the ATPA resin, the diacid and diamine groups will alternate to form what may be termed an alternating copolymer. The ATPA is not a block copolymer. The terms "complete reaction" and "reaction equilibrium" as used herein have essentially the same meaning, which is that further heating of the product gelling agent does not result in any appreciable change in the acid or amine numbers of the resin.

Thus, the ATPA resin may be formed in a one-step procedure, wherein all of the diacid (including co-diacid), secondary monoamine, and diamine are combined and then heated to about 180-250°C for a few hours, typically 2-8 hours. When lower temperatures are used, a longer reaction time is typically needed to achieve complete reaction. When the reaction temperature is too high, the reactants and/or products may undergo undesirable thermally-induced decomposition. Since one or more of the reactants may be a solid at room temperature, it may be convenient to combine each of the ingredients at a slightly elevated temperature, and then form a homogeneous mixture prior to heating the reaction mixture to a temperature sufficient to cause reaction between the diacid, monoamine and diamine. Alternatively, although less preferably, two of the reactants may be combined and reacted together, and then the third reactant is added followed by further heating until the desired product is obtained. Reaction progress may be conveniently monitored by periodically measuring the acid and/or amine number of the product mixture.

As one example, dimer acid may be reacted with diamine so as to form polyamide, and then this intermediate polyamide may be reacted with monoamine to form a tertiary amide terminated dimer acid-based polyamide. Or, dimer acid may be reacted with the monoamine to thereby form diamide, and this diamide may be reacted with diamine to thereby form tertiary amide terminated dimer acid-based polyamide. Because the components of the ATPA resin are preferably in reaction equilibrium (due to transamidation), the order in which the reactants are combined typically does not impact on the properties of the gelling agent.

Any catalyst that may accelerate amide formation between carboxylic acid and amine groups may be present in the reaction mixture described above. Thus, mineral acid such as phosphoric acid, or tin salts such as dibutyltin oxide, may be present during the reaction. In addition, it is preferred to remove water from the reaction mixture as it is formed upon amide formation. This is preferably accomplished by maintaining a vacuum on the reacting mixture, or by passing a gentle stream of an inert gas (*e.g.*, nitrogen) across the top of the reaction mixture.

The ATPA resins of the invention may be used to thicken and/or gel a solvent (where the term "a solvent" includes a mixture of solvents). As used herein, the term solvent includes any substance which is a liquid at a temperature between 10-60°C, and which forms a gel upon being combined with an ATPA resin. As used herein, the term solvent will be used to encompass oils and other fluids which may be gelled by ATPA, and is not otherwise limited.

The combination of ATPA resin and solvent has a gel-like consistency. In general, materials which have a gel-like character will maintain their shape when undisturbed but flow upon being rubbed. Gels prepared with ATPA may be anywhere from soft to hard, where a "hard" gel has a rigid structure and is very resistant to deformation, while a "soft" gel exhibits some, but not too much, resistance to deformation. An illustration of "soft" gel may be seen in the preparation of Jell-O® dessert, which is a well known food product from Kraft Foods Inc. (division of Philip Morris Companies Inc., Northfield, IL). When prepared according to the package instructions, Jell-O® dessert is mixed with water to form a relatively soft gel.

The solvent may be a liquid or solid at room temperature, but is preferably a liquid. Examples of solvents that are solid at room temperature include fatty acids and fatty alcohols, such as myristic acid (flash point > 159°C) and myristyl alcohol (flash point > 143°C). A preferred solvent has a low polarity, where exemplary low polarity solvents include hydrocarbons and organic esters. The solvent may include minor amounts of co-solvents, such as alcohol (*e.g.*, propylene glycol).

A preferred solvent is a hydrocarbon, where the hydrocarbon may be aliphatic or aromatic. A preferred hydrocarbon solvent is an oil, where mineral oil is a

preferred oil. Mineral oils useful in the invention include, but are not limited to, transformer oil, spindle oil, cable insulating oil and machine oil. In one embodiment, the mineral oil is food grade mineral oil. Examples of suitable, commercially available mineral oils include SONNEBORN™ and CARNATION™ white oils from Witco Corp. (Greenwich, CT); ISOPAR™ K and ISOPAR™ H from Exxon Corp. (Houston, TX); and DRAKEOL™ and PENETECK™ white mineral oils from Penreco (Karns City, PA).

Other hydrocarbon solvents that may be used in the invention include relatively lower molecular weight hydrocarbons including linear saturated hydrocarbons such a tetradecane, hexadecane, octadecane, etc. Cyclic hydrocarbons such as decahydronaphthalene (DECALIN™), fuel grade hydrocarbons, branched chain hydrocarbons such as PERMETHYL™ from Permethyl Corp. and ISOPAR™ from Exxon Corp. (Houston, TX); and hydrocarbon mixtures such as product PD-23™ from Witco Corp. (Greenwich, CT) may also be used in preparing gels of the invention. Such hydrocarbons, particularly saturated hydrocarbon oils, are a preferred solvent for preparing a gel of the invention. Aromatic hydrocarbons, *e.g.*, toluene or xylene, may also function as the solvent in a gel of the invention.

Another class of suitable solvents is esters. An ester will include the structural formula -C(=O)-O-, and preferably includes the structural formula -C(=O)-O-R^5 where R^5 is selected from C_1-C_{22} hydrocarbyl groups. As used herein, a hydrocarbyl group is formed exclusively from carbon and hydrogen. Such esters may be monofunctional esters (*i.e.*, have a single ester moiety) or may be polyfunctional (*i.e.*, have more than one ester group). Suitable esters include, but are not limited to, the reaction products of C_{1-24} monoalcohols with C_{1-22} monocarboxylic acids, where the carbon atoms may be arranged in a linear, branched and/or cyclic fashion, and unsaturation may optionally be present between carbon atoms. Preferably, the ester has at least about 18 carbon atoms. Examples include, but are not limited to, fatty acid esters such as isopropyl isostearate, *n*-propyl myristate, isopropyl myristate, *n*-propyl palmitate, isopropyl palmitate, hexacosanyl palmitate, octacosanyl palmitate, triacontanyl palmitate, dotriacontanyl palmitate, tetratriacontanyl palmitate,

hexacosanyl stearate, octacosanyl stearate, and triacontanyl stearate. Other suitable esters include glycerol and propylene glycol esters of fatty acids, including the so-called polyglycerol fatty acid esters and triglycerides.

Preferably, the solvent is a low-polarity liquid as described above, and more preferably the solvent is a liquid hydrocarbon. The liquid may contain more than one component, *e.g.*, hydrocarbon as well as ester-containing material. In the mixture, the gellant (ATPA) typically contributes 10-95%, and the solvent typically contributes 5-90%, of the combined weight of the gellant and the solvent. Preferably, the gellant is combined with the solvent such that the weight percent of gellant in the gellant + solvent mixture is about 5-50%, and preferably is about 10-45%. Such gels may be transparent, translucent or opaque, depending on the precise identities of the gellant and solvent, as well as the concentration of gellant in the mixture.

In order to prepare a gel from a solvent and ATPA resin, the two components are mixed together and heated until homogeneous. A temperature within the range of about 80-150°C is typically sufficient to allow the ATPA to completely dissolve in the solvent. A lower temperature may be used if a solution can be prepared at the lower temperature. Upon cooling, the mixture forms the gelled composition of the invention. Optional components may be added to the molten composition, and are dispersed and/or dissolved to provide a homogeneous composition prior to cooling of the molten composition.

In one embodiment of the invention, the ATPA resin in combination with one or more solvents forms a rigid gel. As used herein, the term "rigidity" refers to the amount of deflection which a gel displays when responding to a force. More specifically, rigidity may be measured by holding a cylinder (or similar shape) of gel material in a horizontal direction. The extent to which the cylinder bends toward the earth under the force of gravity is used as a measure of the rigidity of the gel. A very rigid gel will not bend to any noticeable degree, while a gel that exhibits little or no rigidity will display considerable bend.

In order to impart quantitative meaning to the term "rigid", the test described below has been devised, which provides a measure of rigidity in terms of a

"deflection value". The deflection values may range from a minimum of zero to a maximum of 90, where completely rigid material does not show any deflection and thus has a deflection value of zero, while a very flexible/limp material will show the maximum deflection and be described by a deflection value of 90.

The testing protocol is illustrated in Figure 1. A gel sample having dimensions 57 x 10 x 3 mm is placed on a flat horizontal surface, such that 10 mm of the sample is on the surface and the remainder of the sample extends over the side of the surface and is unsupported. The degree to which the unsupported portion of the sample bends downward provides the deflection value. Thus, if the sample does not bend downward at all, it is assigned a deflection value of 0, because the unsupported portion is directed at an angle of 0° different from the supported portion of the sample. However, if the unsupported portion of the sample bends straight downward as soon as it is unsupported, then this sample has a deflection value of 90 because the unsupported and supported portions form a 90° angle with respect to each other. A material with a lower deflection value corresponds to a material with higher rigidity.

The present invention provides ATPA-containing gels having deflection values of less than or equal to 70, more preferably less than or equal to 60, still more preferably less than or equal to 50, yet more preferably less than or equal to 40, and still more preferably less than or equal to 30, yet still more preferably less than or equal to 20, further still more preferably less than or equal to 10, and further still more preferably less than or equal to 5, and most preferably equal to or essentially equal to zero.

In another embodiment, the ATPA gels of the present invention may be formulated such that they are transparent. There are various degrees of transparency, ranging from crystal clear to hazy, which may be achieved with gels of the invention. In order to provide some measure of the absolute transparency of a gel, the following test has been devised. A white light is shined through a gel sample of a given thickness at room temperature, and the diffuse transmittance and the total transmittance of the light are determined. The percent haze for a sample is determined by the equation: %haze = (diffuse transmittance/total transmittance) x 100. Samples are prepared by

melting the gel (or product made therefrom) and pouring the melt into 50 mm diameter molds. The samples may be prepared at two thicknesses, *e.g.*, 5.5 ± 0.4 mm and 2.3 ± 0.2 mm.

Clarity measurements are made on a Hunter Lab Ultrascan Sphere Spectrocolorimeter using the following settings: specular included, UV off, large area of view, illuminate D65, and observer 10°. Using this protocol with a 2.3 mm thickness sample, an ATPA gel of the present invention may have a %haze value of less than 75, while paraffin wax has a %haze value of over 90. The %haze value for a gel of the present invention can be increased if desired, by appropriate selection of solvent and gellant. Thus, the present invention provides gels (and articles made therefrom) having a transparency (measured by %haze) of less than 75, preferably less than 50, more preferably less than 25, still more preferably less than 10, and yet still more preferably of 5 or less.

In one embodiment, the ATPA gels of the invention are also stable, in that they do not display syneresis. As defined in the McGraw-Hill Dictionary of Scientific and Technical Terms (3rd Edition), syneresis is the spontaneous separation of a liquid from a gel or colloidal suspension due to contraction of the gel. Typically, syneresis is observed as the separation of liquid from a gel, and is sometimes referred to as "bleeding", in that wetness is seen along the surfaces of a gel that displays syneresis. From a commercial point of view, syneresis is typically an undesirable property, and the gels of the present invention desirably, and surprisingly do not exhibit syneresis. In one embodiment, the gels of the invention, and articles prepared therefrom, may be stable in the sense that they do not exhibit syneresis. Thus, they do not have an oily feeling when handled.

The ATPA gels of the invention may be (although need not be) essentially transparent. When transparent, the gels may be combined with colorants (as well as other ingredients) to form lipstick or other cosmetic products, without the gel interfering with or tainting the appearance of the colorant. The ATPA gels may be combined with aluminum zirconium salts, as well as other ingredients, to form colorless underarm deodorant/antiperspirant, which is currently quite popular. The gels of the

invention are also useful in other personal care products, *e.g.*, cosmetics such as eye make-up, lipstick, foundation make-up, costume make-up, as well as baby oil, make-up removers, bath oil, skin moisturizers, sun care products, lip balm, waterless hand cleaner, medicated ointments, ethnic hair care products, perfume, cologne, and suppositories.

In addition, the ATPA gels may be used in household products such as automobile wax/polish, candles, furniture polish, metal cleaners/polishes, household cleaners, paint strippers and insecticide carriers.

The ATPA gels may also be used in industrial products such as fuels (sterno, lighters), toilet bowl rings, lubricants/greases, wire rope lubricant, joint and cable fillers, soldering flux, buffing compounds, crayons and markers, modeling clay, rust preventatives, printing inks, paints, protective/removable coatings, and jet inks. For example, hydrocarbon gelled with an ATPA resin of the invention may be used as a heat source in, *e.g.*, a cooking apparatus used in camping and hiking. Such a composition will not flow if tilted, and thus may be safer and neater than similar products made from flowing materials.

Formulations to prepare such materials are well known in the art. For example, U.S. Patent Nos. 3,615,289 and 3,645,705 describe the formulation of candles. U.S. Patent Nos. 3,148,125 and 5,538,718 describe the formulation of lipstick and other cosmetic sticks. U.S. Patent Nos. 4,275,054, 4,937,069, 5,069,897, 5,102,656 and 5,500,209 each describe the formulation of deodorant and/or antiperspirant.

The ATPA resin of the invention may be incorporated into commercial products such as those listed above by blending the ATPA resin with the other components of the product. In these commercial products, the ATPA resin will typically be present at a concentration of about 1% to about 50% of the composition, based on the total weight of the composition. It is a routine matter to optimize the amount of ATPA resin in a composition, and indeed the amount will vary depending on the actual product and the desired consistency of the product. In general, as more ATPA resin is used in a formulation, the product will display a more pronounced gel character, and will form a more rigid, or hard, gel.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLES

In the following Examples, softening point was measured using a Model FP83HT Dropping Point Cell from Mettler Instruments, Mettler-Toledo International, Inc. (CH-8606 Greifensee, Switzerland; http://www.mt.com), with a heating rate of 1.5°C/min. Techniques to measure acid and amine numbers are well known in the art and need not be described here. *See, e.g.*, ASTM D-465 (1982) from American Society for Testing and Materials (West Conshohocken, PA; http://www.astm.org).

EXAMPLE 1

TERTIARY AMIDE TERMINATED POLYAMIDES (ATPA)

Several ATPA's (labeled ATPA A, B, and C) were made from the reactants, and relative amounts thereof, as set forth in Table 1. In Table 1, "DTA" is an abbreviation for ditallow amine, "EDA" is an abbreviation for ethylene diamine, "SA" is an abbreviation for stearyl amine, and PD-23™ is a petroleum distillate, all available from Witco Corporation (Greenwich, CT; http://www.witco.com). Selected properties for the ATPAs are also set forth in Table 1, including acid number, amine number, softening point ("S.P.") and the appearance when combined at 20 wt% solids in PD-23™ petroleum distillate ("Appearance").

In preparing ATPAs, a 60/40 EDA/DTA equivalent ratio results in a material (ATPA A) that forms a clear, hard gel in PD 23 distillate (at 20% solids). Increasing this ratio to 75/25 (*see* ATPA B) and 80/20 (*see* ATPA C) decreases the ATPA's solubility in PD-23™ petroleum distillate, resulting in opaque, hard gels.

Table 1

PROPERTIES OF TERTIARY AMIDE TERMINATED POLYAMIDES

ATPA	Composition (eq. %)	Acid No.	Amine No.	S.P. (°C)	Appearance
A.	100% EMPOL™ 1008; 60% EDA, 40% DTA	20.8	25.1	82.2	clear, hard gel
B.	100% EMPOL™ 1008; 75% EDA, 25% DTA	11.3	10.9	101.9	opaque, hard gel
C.	100% EMPOL™ 1008; 80% EDA, 20 DTA	10.3	8.0	146.9	opaque, hard gel

COMPARATIVE EXAMPLE 1

SECONDARY AMIDE TERMINATED POLYAMIDE

As a comparative example, a polyamide at the same diamine/monoamine ratio as used in ATPA A (60/40, see Example 1) was prepared to determine if termination with a primary monoamine would result in polyamide that gelled hydrocarbons. This material, "Comp. A." was not compatible with PD-23™ petroleum distillate.

Table 2

PROPERTIES OF PRIMARY AMINE-TERMINATED POLYAMIDE

Resin	Composition (eq. %)	Acid No.	Amine No.	S.P. (°C)	Appearance
Comp. A.	100% EMPOL™ 1008; 60% EDA, 40% SA	5.5	0.9	--	two phases

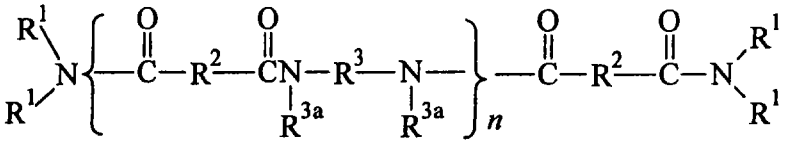
All publications and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually incorporated by reference.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the

particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

1. A tertiary amide terminated polyamide resin of the formula (1):



(1)

wherein,

n designates a number of repeating units such that terminal amide groups constitute from 10% to 50% of the total amide groups;

R^1 at each occurrence is independently selected from a C_{4-22} hydrocarbon group;

R^2 at each occurrence is independently selected from a C_{2-42} hydrocarbon group;

R^3 at each occurrence is independently selected from an organic group containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and

R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3.

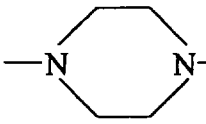
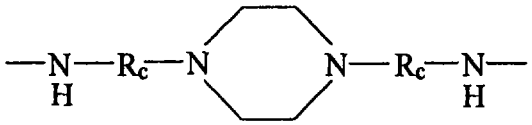
2. The resin of claim 1 wherein terminal amide groups of the formula $C(=O)N(R^1)(R^1)$ constitute from 20% to 35% of the total of the amide groups.

3. The resin of claim 1 wherein *n* is an integer from 1 to 5.

4. The resin of claim 1 wherein R^2 is a C_{30-42} hydrocarbon group having the structure of polymerized fatty acid with the carboxylic acid groups removed.

5. The resin of claim 1 wherein between 1% and 50% of the R^2 groups are a C_{4-19} hydrocarbon group.

6. The resin of claim 1 wherein R^3 is a C_{2-36} hydrocarbon group and R^{3a} is hydrogen.

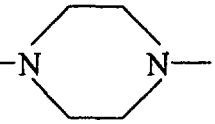
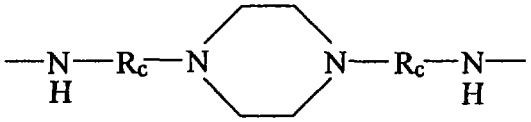
7. The resin of claim 1 wherein at least 1% of the $-N(R^{3a})-R^3-N(R^{3a})-$ groups are independently selected from polyalkylene amine, , and  wherein R_c is a C_{1-3}alkyl group.

8. The resin of claim 1 further comprising diamide having formula (1) wherein n=0, such that the ratio of terminal amide groups to the total of the amide groups in the resin is from 0.1 to 0.7.

9. A resin prepared by a method comprising reacting x equivalents of carboxylic acid from diacid or a reactive equivalent thereof, y equivalents of amine from diamine and z equivalents of a secondary amine-containing monoamine having no reactive functional groups except the secondary amine or a reactive equivalent thereof, where the monoamine is substantially the only monofunctional reactant used to form the resin, wherein at least about 50% of the carboxylic acid equivalents are from polymerized fatty acid and wherein each of x, y and z is greater than 0 such that $0.9 \leq \{x/(y+z)\} \leq 1.1$, and $0.1 \leq \{z/(y+z)\} \leq 0.7$.

11. The resin of claim 9 wherein all equivalents of carboxylic acid come from polymerized fatty acid.

12. The resin of claim 9 wherein the diamine has the formula $H_2N-R^3-NH_2$ and R^3 is a C_{2-36} hydrocarbon group.

13. The resin of claim 9 wherein at least 50% of the amine equivalents are contributed by a diamine of the formula $H_2N\text{-}R^3\text{-}NH_2$ wherein R^3 is a $C_{2\text{-}36}$ hydrocarbon group, and at least 1% of the amine equivalents are contributed by one or more diamines selected from  and $H_2N\text{-}R^3\text{-}NH_2$, wherein R^3 is selected from polyalkylene oxide, polyalkylene amine, and the formula  wherein R_C is a $C_{1\text{-}3}$ alkyl group.

14. The resin of claim 9 wherein the secondary amine-containing molecule has the formula $R^1\text{-}NH\text{-}R^1$, and R^1 is independently at each occurrence a $C_{12\text{-}22}$ hydrocarbon group.

15. A composition comprising a solvent and at least one resin selected from (a) the resin of claim 1, and (b) the resin of claim 9.

16. The composition of claim 15 wherein the solvent is selected from hydrocarbons and organic esters.

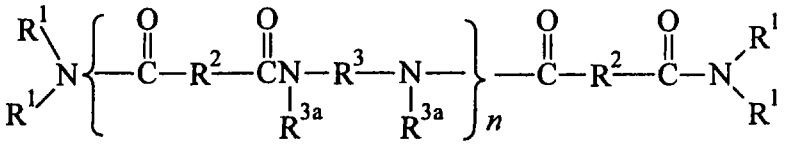
17. The composition of claim 16 wherein the hydrocarbon is an oil.

18. The composition of claim 16 wherein the ester comprises the structural formula $-C(=O)\text{-}O\text{-}R^5$ and R^5 is selected from $C_1\text{-}C_{22}$ hydrocarbyl.

19. The composition of claim 16 having at least about 5 weight percent and less than about 95 weight percent of resin, based on the total weight of resin and solvent.

20. A method for preparing a transparent or translucent gel, comprising combining a solvent with a resin according to claim 1 or according to claim 9.

21. A tertiary amide terminated polyamide resin of the formula (1):



(1)

wherein,

n designates a number of repeating units such that terminal amide groups constitute from 10% to 50% of the total amide groups;

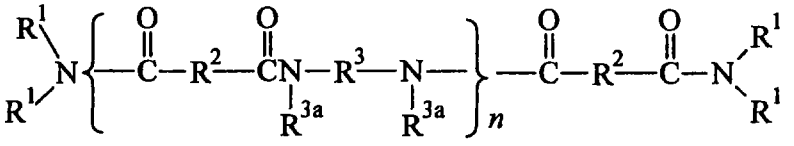
R^1 at each occurrence is independently selected from a C_{1-22} hydrocarbon group;

R^2 at each occurrence is independently selected from a C_{2-42} hydrocarbon group, where at least 50% of the R_2 groups have 30-42 carbon atoms;

R^3 at each occurrence is independently selected from an organic group containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and

R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3.

22. A tertiary amide terminated polyamide resin of the formula (1):



(1)

wherein,

n designates a number of repeating units such that terminal amide groups constitute from 10% to 50% of the total amide groups;

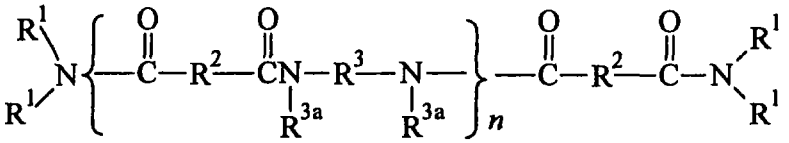
R^1 at each occurrence is independently selected from a C_{1-22} hydrocarbon group;

R^2 at each occurrence is independently selected from a C_{4-42} hydrocarbon group;

R^3 at each occurrence is independently selected from an organic group containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and

R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3.

23. A resin comprising a mixture of tertiary amide terminated polyamide compounds of the formula (1):



(1)

wherein,

n designates a number of repeating units such that terminal amide groups constitute from 10% to 50% of the total amide groups, and the composition comprises compounds of formula (1) having non-identical n values;

R^1 at each occurrence is independently selected from a C_{1-22} hydrocarbon group;

R^2 at each occurrence is independently selected from a C_{2-42} hydrocarbon group;

R^3 at each occurrence is independently selected from an organic group containing at least two carbon atoms in addition to hydrogen atoms, and optionally containing one or more oxygen and nitrogen atoms; and

R^{3a} at each occurrence is independently selected from hydrogen, C_{1-10} alkyl and a direct bond to R^3 or another R^{3a} such that the N atom to which R^3 and R^{3a} are both bonded is part of a heterocyclic structure defined in part by R^{3a}-N-R^3.

24. A composition comprising a solvent and the resin of claim 21, the composition having a gel consistency.

25. A composition comprising a solvent and the resin of claim 22, the composition having a gel consistency.

26. A composition comprising a solvent and the resin of claim 23, the composition having a gel consistency.

27. The composition of claim 16 wherein the organic ester is a triglyceride.

28. A candle comprising the resin of any of claims 1-14 and 21-23.

29. A candle comprising the composition of any of claims 15-19 and 24-27.

30. A cosmetic product comprising the resin of any of claims 1-14 and 21-23.

31. A cosmetic product comprising the composition of any of claims 15-19 and 24-27.