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(54) Title: LOW VOC NON-AQUEOUS DISPERSION COATINGS

(57) Abstract: A non-aqueous dispersion (NAD) resin from natural oils having solids content of greater than 90%, and more preferably, greater than 95%, fast cure, low VOC, and low bake temperatures, and wherein the inclusion of multifunctional isocyanates provide faster dry times and harder films.
LOW VOC NON-AQUEOUS DISPERSION COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/316,150 filed August 30, 2002.

FIELD OF THE INVENTION

The present invention relates to non-aqueous dispersion (NAD) resins having solids content of greater than 90%, and more preferably, greater than 95%, and coatings comprising these NADs.

BACKGROUND OF THE INVENTION

Although NADs having nearly 100% solids content are known in which oils such as soya oil, linseed oil, or castor oil are used as the carrier solvent, these NADs tend to exhibit very long dry times and very soft films, even with added metal driers to promote auto-oxidation. Typically, coatings produced from natural oils require high oven temperatures, and extended time to develop hard films. According to this invention, a fast cure, high solids, low VOC, low bake coating is taught, wherein the inclusion of multifunctional isocyanates, and optionally, metallic driers for oxidative cure, provide faster dry times and harder films.

Non-aqueous dispersions made from drying oils or blown oils to make nearly 100% solids coatings has been disclosed in British Patent 1408471 assigned to Dai Nippon Toryo Kabushiki Kaisha. The oils acted as the stabilizer for an acrylic core. These NADs were
promoted as sealants because as stated at page 4, lines 75-79 of the patent, "[a]fter coating and sealing, the surface becomes dry but the interior remains soft; therefore, cracks are not formed even after use for a long time." The '471 patent does not teach the use of hydroxyl-functional monomers and crosslinking agents such as isocyanates. British Patent 1319781 assigned to Imperial Chemical Industries, Limited describes an NAD prepared from a poly(methyl methacrylate) backbone grafted with linseed copolymer. Example 2 of the '781 patent describes the preparation of a 100% solids film forming NAD by evaporating ethyl acetate from a solution containing the dissolved NAD and linseed oil. The NAD was cured by auto-oxidation. The specification of the patent on page 3, lines 114-124, states, "[a]lthough micro-particles of the kind described can be used in stoving compositions and compositions in which the crosslinking reaction is broadly of the condensation type (for example hydroxyl/isocyanate, hydroxyl/N-methylol, epoxy/carboxy), they are particularly suitable for use in compositions in which the crosslinks are formed by an auto-oxidation reaction involving auto-oxidative groups such as those present in drying oils and derivatives thereof."

The addition of isocyanate or blocked isocyanate crosslinkers to NADs has been taught in several patents to cure NADs. Dai Nippon Toryo Company, Ltd.'s U.S. Patent Number 3,926,875, teaches acrylic core NADs stabilized with alkyls containing blocked isocyanates and isocyanate-reactive moieties such as hydroxyl groups either on the stabilizer or in the acrylic core or contained in both the stabilizer and acrylic core. All examples of the '875 patent contain hydrocarbon solvents.

U.S. Patent Number 4,138,376 to Imperial Chemical Industries describes the preparation of a coating from a blend of a polyisocyanate dispersion and a solution of an
alkyd resin. All alkyls were in a solvent comprising a major proportion of aliphatic hydrocarbons. The cure was between isocyanate groups and isocyanate reactive groups.

U.S. Patent Number 3,652,472 assigned to Balm Paints Limited describes NADs curable with crosslinking agents such as isocyanates, melamine resins, etc and optionally in addition to auto-oxidation. The dispersions all contained hydrocarbon solvents.

U.S. Patent Number 4,530,957 to Ford Motor Company describes NADs internally crosslinked with melamine resins, isocyanates, etc. and then blended with hydroxyl functional oligomers to form a cured coating when baked with melamine resins. All NADs contained organic solvents.

British patent application GB 2179047 assigned to Kansai Paint describes NADs containing perfluoroalkyl groups. Example 10 shows the NAD blended with another resin and cured with isocyanates. All examples contain solvent.

U.S. Patent Number 5,173,533 assigned to Kansai Paint describes storage stable NADs in which the core and shell contain complementary reactive groups such as hydroxyl/isocyanate. Upon evaporation of solvent, the complementary reactive groups on the shell and core interact to form cured coatings.

U.S. Patents 4,640,935 and 4,588,830 assigned to Dow Chemical describe NAD polyols containing addition polymerized monomers. The NADs are assumed to be 100% solids. These polyol NADs are reacted with isocyanates to make foams, elastomers and plastics. Natural oils are not mentioned.

U.S. Patents 4,983,716 and 6,051,633 assigned to The Sherwin-Williams Company teach NADs in general.
None of the above patents teach fast cure, high solids, low VOC and low bake non-aqueous dispersions and coatings with high pencil hardness utilizing natural oils.

SUMMARY OF THE INVENTION

The present invention relates to a non-aqueous dispersion, which is formed in an alkyd medium by reactions comprising free radical polymerization of:

1. an alkyd formed from an acidolysis reaction product of a triglyceride oil with a trifunctional carboxylic acid or trifunctional anhydride, wherein the acidolysis reaction product is further reacted with a multi-functional alcohol;

2. at least one hydroxy-functional monomer; and

3. at least one monomer capable of copolymerizing with the hydroxy-functional monomer by a free radical addition reaction mechanism;

wherein the alkyd and a natural oil are used as a polymerization medium for the polymerizable monomers; and wherein the non-aqueous dispersion has a non-volatile materials content of greater than 90%. Preferably, the non-aqueous dispersion has a non-volatile materials content of greater than 95%.

The invention also relates to a coating composition comprising this non-aqueous dispersion. Further, this invention relates to a coating composition comprising the non-aqueous dispersion of this invention, and further crosslinked with a multifunctional isocyanate.

DETAILED DESCRIPTION OF THE INVENTION

The NAD of this invention comprises an oil-modified alkyd as the dispersing medium, either alone or in combination with a natural oil, for the polymerization of
unsaturated monomers in which the polymers formed from the free radical polymerization are predominantly insoluble in the alkyd medium.

**ALKYD**

The alkyd used in these NADs is not formed by any of the traditional processes such as fatty acid esterification or alcoholysis of a drying oil with later reaction with a di- or tribasic acid. Rather, the alkyds used in this invention are formed by a two-step process, wherein the first step comprises the acidolysis reaction of a triglyceride oil with a trifunctional carboxylic acid or a trifunctional anhydride, and the second step comprises reacting the product of the first step with a multifunctional alcohol. The alkyds of this invention differ from the conventional alkyds in that a much higher molecular weight can be achieved without an unacceptable increase in viscosity. Highly branched alkyds provide the basis for a high solids, low VOC composition. The high molecular weight of such a composition enables the air dry time of the composition to be very short.

The triglyceride oil used in the formation of the alkyd can be selected from the group consisting of linseed oil, soya oil, coconut oil, cottonseed oil, peanut oil, canola oil, corn oil, safflower oil, sunflower oil, epoxidized oils (such as epoxidized soya oil), dehydrated castor oil, fish oil, perilla, lard, walnut oil, tung oil and the like, and mixtures thereof. Particularly preferred for certain applications of this invention are those oils containing unsaturation in the glyceride chains, such as soya oil, dehydrated castor oil and linseed oil.

To form the alkyd, the triglyceride oil is first reacted via an acidolysis reaction with a trifunctional carboxylic acid such as trimellitic acid, trimesic acid, 1,3,5-pentane tri-carboxylic acid, citric acid or a trifunctional anhydride such as trimellitic anhydride, pyromellitic anhydride, or mixtures of such acids and/or anhydrides to produce an acid
functional alkyd reaction product. For many applications of this invention, it is especially preferred to utilize trifunctional anhydrides. The proportion of triglyceride oil to acid (or anhydride) and the processing conditions should be such that the reaction product will be acid functional. Frequently, the acid value of this product would be at least 20 and would frequently range from 20 to 120. Generally the ratio of moles trifunctional acid:oil should be approximately 1:1.75 to 1:1. The oil and the acid (or anhydride) should be charged into a reactor equipped with an inert gas blanket and a mechanical stirrer. The two reactants should be heated to a temperature greater than or equal to about 450° F, preferably to a temperature of about 480° F. This temperature should be held for a sufficient time period to allow for the desired degree of completion of the reaction of the two reactants. Typically, at this temperature, the reaction takes approximately one hour. If desired, a reaction catalyst such as lithium hydroxide monohydrate, barium hydroxide, or di-butyl tin oxide can be added in an amount of approximately 0.02% by weight of oil. The acid-functional intermediate produced by this acidolysis reaction should be cooled to about 350° F in preparation for the second step of the reaction.

The intermediate from the acidolysis step is further reacted with a multifunctional alcohol. The amount of multifunctional alcohol should be such that the moles of hydroxyl equivalents contributed by the alcohol is in excess over the moles of carboxylic acid equivalents contributed by the acid or anhydride. Thus, the equivalent ratio of alcohol groups to acid groups for this reaction would typically be at least 1:1 and could range to about 1.5:1 or higher. The multifunctional alcohol can be selected from the group consisting of trimethylol propane, trimethylol ethane, glycerine, tris hydroxyethyl isocyanurate, and the like, and mixtures thereof, either alone or in combination with a difunctional alcohol selected
from the group consisting of ethylene glycol, propylene glycol, cyclohexane dimethanol, and mixtures thereof. Additionally, dimethylol propionic acid can be used in combination with the multifunctional alcohol. Trifunctional alcohols are particularly preferred due to the degree of branching they allow. Difunctional alcohols, if used, are preferably used as a minor component in combination with trifunctional alcohols. The alcohol is preferably added in bulk to the reaction vessel containing the product of the acidolysis reaction, although the alcohol can be added in two or more charging stages. The temperature is raised to between about 425° F and 500° F and these reaction conditions are maintained for so long as necessary to bring the acid value of the solution below about 15, preferably below about 10. If desired during this stage of the reaction, xylene or other azeotroping solvent can be added to the vessel to facilitate the removal of water from the reaction solution.

Depending on the desired molecular weight and viscosity, a portion of monofunctional alcohol, or monobasic acid such as soya fatty acid, linseed oil fatty acid or crotonic acid, up to about 20% by weight of the total alkyd can be added with the multifunctional alcohol to control molecular weight and act as a chain stopper.

The order of reactions, i.e. acidolysis with a trifunctional acid or anhydride, followed by reaction of that product with a multifunctional alcohol, is critical to the formation of the high molecular weight, low viscosity alkyd of this invention. The amounts of oil, acid and alcohol used should be such that the resulting alkyd has a high degree of branching, a z-average molecular weight, Mz, greater than or equal to about 20,000, an oil length of between about 65% and 85%, and a hydroxyl number less than 60, preferably less than 45. These alkyds have non-volatile materials contents approaching 100% NVM. The alkyd is especially suitable for use in non-aqueous dispersions as a dispersing medium, either alone or
in combination with some amount of natural oil, to act as the polymerizing medium and to disperse insoluble monomers and polymers.

**NON-AQUEOUS DISPERSION**

When preparing non-aqueous dispersions using the novel alkyd above, the monomers should be selected from monomers which would produce a polymer via a free radical addition reaction mechanism. More specifically, there should be at least one monomer containing hydroxy functionality, and at least one monomer capable of polymerizing with the hydroxy-functional monomer by a free radical additional reaction mechanism. The hydroxy-functional monomer can be present at levels greater than 5%. Most preferably, between about 5% and 35% by weight of the monomer charge comprises hydroxy functional monomers. Representative hydroxy-functional monomers include hydroxy ethyl acrylate and methacrylate, hydroxy propyl acrylate and methacrylate, and the like.

Representative monomers which are copolymerizable with the hydroxy functional monomers by a free radical addition reaction mechanism include: acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, itaconic acid, and esters of these acids, especially methyl acrylate and methacrylate, ethyl acrylate and methacrylate, butyl acrylate and methacrylate, lauryl acrylate and methacrylate, and the like, trimethylol propane triacrylate and trimethacrylate, hexanediol diacrylate, acrylamide, methacrylamide, vinyl chloride, vinylidene chloride, styrene, divinyl benzene, vinyl toluene, vinyl naphthalene and mixtures thereof. In addition to pure monomers, preformed polymers and polymeric intermediates can be included in the reaction charge. Other reactive materials including multifunctional epoxides, melamines and isocyanates could also be included. Preferably, the monomers copolymerizable with the hydroxy-functional monomer are present in the
monomer charge at levels greater than 5%, and preferably between about 65-95% by weight of the total monomer charge.

To prepare the non-aqueous dispersions of this invention, the alkyd dispersing medium is used as the polymerization medium for the monomer charge. The alkyd medium can be diluted with a natural oil such as soya oil or the other natural oils such as those useful in the production of the alkyd itself, if desired. Alternatively, reactive oils with low and high levels of conjugation (sunflower, soya, linseed, and castor oil) could be used to dilute the alkyd. If it is desired to include a natural oil as part of the dispersing medium, it can be included at levels up to about 40%, and generally at levels of 10 to 30% of the total weight of alkyd and natural oil.

All free radical addition reactants are preferably added via dropwise addition over a period of time to the alkyd dispersing medium. The monomer charge can be added pure, or, in an embodiment which is preferred for some applications, the monomers can be dispersed in an amount of the alkyd of this invention prior to addition to the dispersing medium. The amount of alkyd used for such a dispersion should be included in the calculation of the overall amount of alkyd present in the reaction vessel.

The total amount of alkyd contained in the reaction vessel, including any alkyd which may be added with the monomer charge, can comprise between about 25% to about 99%, preferably from about 30% to about 60%, most preferably between about 40% to about 55%, by weight of the combined total alkyd and total monomer charged to the vessel. The free radical addition monomer charge should, after completely added to the reaction vessel, account for approximately 1% to about 75%, preferably between about 40% to about 70%, by weight of the total alkyd and total monomer charged to the vessel, most preferably
between about 45% to about 60%. A chain transfer agent such as methyl mercapto-
propionate or 2-mercapto ethanol must also be added to the vessel in an amount from about
0.1% to about 6.0% by weight of monomer. An initiator, such as t-butyl peroctoate, t-amyl
peroctoate, cumene hydroperoxide, and t-butyl perbenzoate is also preferably added.

The temperature of the solution in the reaction vessel should be maintained between
about 200° F and 250° F for the entire period that monomer charge is being added. Upon
completion of the monomer addition, a chaser composition, such as vanadium naphthenate to
the reactor followed by cumene hydroperoxide is added over a period of about 90 minutes.
Upon completion of the chase composition, the temperature should be maintained between
200° F and 250° F for approximately one hour. At the end of that hour, the heat is removed
and the contents of the vessel are filtered. Although it is not our intent to be bound by
theory, it is believed that at least some graft copolymerization takes place between the
polymerization medium and the growing free-radical polymer thereby further enhancing the
performance of the final NAD.

The NADs made using these alkyds typically have NVM's of about 95% or more,
have very low viscosities, often less than about 7500 Cps, have volatile organic contents less
than 100 g/l, preferably less than 25 g/l, and exhibit excellent air dry times using
conventional metallic drier compounds. The NADs of this invention can be cured utilizing
drying agents well-known in the art. Drying agents can comprise standard metallic and rare
earth driers such as cobalt, calcium, potassium, barium, zinc, manganese, tin, aluminum,
zirconium and vanadium naphthenates, octoates, hexanates, and isodecanoates. A particularly
preferred drier composition is a combination of cobalt, calcium and zirconium driers present
in an amount from about 0.1% to about 2.5% by weight of the coating composition.
NADs CURED WITH ISOCYANATES

In a preferred embodiment, the NAD of this invention is blended with a polyisocyanate or blocked polyisocyanate crosslinking (curing) agent, which is capable of reacting with the hydroxy functionality present on the NAD to facilitate reduced curing time and/or temperatures, higher solids, a low VOC, and harder films. The polyisocyanate or blocked polyisocyanate crosslinking agent is at least about 1% by weight solids relative to the NAD. Useful ranges for the level of polyisocyanate are typically from 1% to about 60%, and frequently 10 to about 30%, by weight of the NAD. On an equivalents basis, the polyisocyanate should be present at a level to provide at least about 0.1 equivalents of isocyanate for each hydroxy equivalent, and typically, the NCO/OH ratio will range from at least 0.3/1.0 and to as high as about 1.5/1.0.

Typical isocyanate crosslinking agents which may be used for curing the composition include aliphatic, aromatic, cycloaliphatic diisocyanates, triisocyanates, polyisocyanates, and polymers, blocked and unblocked. Examples of suitable polyisocyanates include, but are not limited to, the adducts or prepolymer of those aliphatic and aromatic di- and tri-isocyanates which are already known to be useful in the preparation of coatings and can be selected from the group consisting of m- and p-phenylene diisocyanate, trimethylene diisocyanate; tetramethylene diisocyanate; pentamethylene diisocyanate; hexamethylene diisocyanate; ethylethylene diisocyanate, 2,3-dimethylenethylene diisocyanate; 1-methyltrimethylene diisocyanate; 1,3-dicyclopentylene diisocyanate; 1,4-cyclohexylene diisocyanate; 1,2-cyclohexylene diisocyanate; 1,3-phenylene diisocyanate; 1,4-phenylene diisocyanate; 2,4-toluylene diisocyanate; 2,6-toluylene diisocyanate; 4,4'-biphenylene diisocyanate; 1,5-naphthylene diisocyanate; 1,4-naphthylene diisocyanate; 1-isocyanatomethyl-5-isocyanato-
cyclohexyl)-methane; bis-(4-isocyanato-phenyl)-methane; 4,4'-diisocyanatodiphenyl ether; 2,3-bis-(8-isocyanatooctyl)-4-octyl-5-hexylcyclohexane; 1,3-bis(1-isocyanato-1-methylethyl)benzene; 4,4'- and 2,4'-diisocyanato-dipheylmethane, 4,4'-diisocyanato-2,2'-disphenylpropane, tetramethylene-1,4-diisocyanate; dicyclohexylmethane diisocyanate, isophorone diisocyanate, biurets, allophanates and isocyanurates of these polyisocyanates; and mixtures thereof. Particularly useful isocyanates are the biurets, allophanates and isocyanurates of 1,6-hexamethylene diisocyanate such as Desmodur N3600 polyisocyanate (commercially available from Bayer), polyisocyanate trimer (Tolonate® HDT-LV from Rhodia, Inc., Cranbury, New Jersey), or the like. The blend may contain a suitable catalyst for the reaction of the isocyanate groups, for example, dibutyl tin dilaurate, in a proportion of, for example, 0.01 – 0.5% by weight based on the weight of isocyanate.

The non-aqueous dispersions of this invention can be used alone as coating compositions, or, in the alternative, they can be formulated with other readily available, standard paint ingredients and components such as rheology modifiers, pigments, fillers, plasticizers, antioxidants, thixatropes, extenders, colors and pigments, solvents, diluents or reactive diluents, anti-skinning agents, drying agents, dispersants and surfactants, fungicides, mildewcides, preservatives, UV absorbers, anti-marring agents, flow and leveling agents, fragrances, defoaming agents, chelating agents, flattening agents, and anti-rusting agents.

Suitable rheology modifiers are well known in the art and can comprise organoclays, fumed silica, dehydrated castor oil organic derivatives (exemplary tradenames: Thixatrol® (Elementis Specialties, Inc., New Jersey); Flowtone® (English China Clay), polyamide resins, polyamide modified alkyds, MPA-60 (Elementis Specialties, Inc.), alkylbenzene sulphonate derivatives, aluminum, calcium and zinc stearates, calcium soyate, and the like.
Suitable extenders are also well known in the art and can comprise amorphous, diatomaceous, fumed, quartz and crystalline silica, clays, aluminum silicates, magnesium aluminum silicates, talc, mica, delaminated clays, calcium carbonates and silicates, gypsum, barium sulfate, zinc, calcium zinc molybdates, zinc oxide, phosphosilicates and borosilicates of calcium, barium and strontium, barium metaborate monohydrate, and the like.

Suitable pigments are well known in the art and can comprise for example, titanium dioxide, carbon black, graphite, ceramic black, antimony sulfide, black iron oxide, aluminum pastes, yellow iron oxide, red iron oxide, iron blue, phthal blue, nickel titanate, dianisidine orange, dinitroaniline orange, imidazole orange, quinacridone red, violet and magenta, toluidine red, molybdate orange, and the like.

Suitable dispersants and surfactants can comprise any of the readily available dispersants and surfactants to the coatings industry, including the anionic and nonionic surfactants, soya lecithin, alkyl ammonium salts of fatty acids, amine salts of alkyl aryl sulfonates, unsaturated organic acids, sulfonated castor oil, mixtures of high boiling point aromatic and ester solvents, sodium salts of aryl sulfonic acid, and the like.

Anti-skinning agents such as methyl ethyl ketoxime, o-cresol, and hydroquinone can be included.

The coatings of this invention may be used with or without driers at ambient cure, or at elevated temperatures. Preferably, the composition is typically baked in a range about 140° F – 160° F, for about 15-45 minutes, to form a coating about 0.1 to 3.0 mils thick.

Tables I – IV below exemplify the advantageous results obtained when 10-30% of a multifunctional isocyanate is blended with the NADs of this invention.
In addition to the above, the non-aqueous dispersions of this invention are particularly suited for blending with other polymers. If blended with a lower VOC polymer, the non-aqueous dispersions of this invention can produce extremely low VOC coating compositions. If blended with a higher VOC polymer, the non-aqueous dispersions of this invention can help to reduce the overall VOC of such polymer.

The following examples are intended to illustrate the invention but are not presented as limitations upon the scope of the claims.

**EXAMPLE ONE**

**PREPARATION OF ALKYD**

Charge 14,925 grams of alkali refined soya oil and 2240 grams of trimellitic anhydride to a reactor equipped with inert gas and a mechanical stirrer. Heat the contents to 480° F and hold for about one hour. Cool to about 350° F and add 1704 grams of trimethylol ethane and 368 grams of xylene. Heat the contents to about 480° F and hold for an Acid Value less than or equal to 10. Continue to hold the contents at this temperature until residual xylene is stripped off.

The resulting alkyd has an NVM of approximately 99.5%, a Gardner-Holdt viscosity of about X at 25° C, an Acid Value of about 9.9, an Mv of about 102,000, an oil length of about 79 and a Hydroxyl No. of about 47.

**EXAMPLE TWO**

**PREPARATION OF A CONVENTIONAL NAD**

Charge 265 grams of the alkyd prepared according to Example One and 186 grams of
mineral spirits to a reactor equipped with nitrogen and a mechanical stirrer. Heat to 110° C.

Begin a three hour dropwise addition of Solutions #1 and #2 below:

Solution #1: 629 grams of alkyd prepared according to Example One, 795 grams of methyl methacrylate, 298 grams of hydroxy ethyl acrylate, and 5.8 grams of 2-mercaptop ethanol (chain transfer agent).

Solution #2: 34.8 grams of mineral spirits and 8.2 grams of t-butyl peroctoate (initiator).

Upon completion of the addition of Solutions #1 and #2, hold for one hour at 110° C, add four (4) drops of vanadium naphthenate to the reactor, and begin a three hour addition of a "chase" comprising 57.1 grams of mineral spirits, and 30.5 grams of cumene hydroperoxide. Hold the temperature at 110° C for approximately one hour after the chase has been completely added.

The resulting non-aqueous dispersion has a NVM of approximately 86.3% and a viscosity of 1500 centipoise at 25° C using the Brookfield LVT Spindle #3 at 30 rpm.

EXAMPLE THREE (Soya Oil)

PREPARATION OF AN OIL MODIFIED NAD

Charge 418 grams of the alkyd prepared according to Example One and 294 grams of alkali-refined soybean oil to a reactor equipped with nitrogen and a mechanical stirrer. Heat to 110° C. Begin a three hour dropwise addition of Solutions #1 and #2 below:

Solution #1: 993 grams of alkyd prepared according to Example One, 1254 grams of methyl methacrylate, 470 grams of hydroxy ethyl acrylate, and 9.3 grams of 2-mercaptop ethanol (chain transfer agent).
Solution #2: 54.9 grams of alkali-refined soybean oil and 12.9 grams of t-butyl peroctoate (initiator).

Upon completion of the addition of Solutions #1 and #2, hold temperature for one hour at 110° C, add two (2) drops of vanadium naphthenate to the reactor, then flush reaction lines with alkali-refined soybean oil. Begin a three hour addition of a "chase" comprising 90 grams of alkali refined soybean oil, and 48.1 grams of cumene hydroperoxide. Hold the temperature at 110° C for approximately 45 minutes after the chase has been completely added.

The resulting non-aqueous dispersion has a NVM of approximately 97.7% and a viscosity of 8180 centipoise at 25° C using the Brookfield LVT Spindle #3 at 12 rpm.

**EXAMPLE FOUR (Linseed Oil)**

**PREPARATION OF AN OIL MODIFIED NAD**

Charge 325 grams of the alkyd prepared according to Example One and 229 grams of supreme linseed oil to a reactor equipped with nitrogen and a mechanical stirrer. Heat to 110° C. Begin a three hour dropwise addition of Solutions #1 and #2 below:

Solution #1: 772 grams of alkyd prepared according to Example One, 976 grams of methyl methacrylate, 366 grams of hydroxy ethyl acrylate, and 7.2 grams of 2-mercaptop ethanol (chain transfer agent).

Solution #2: 42.7 grams of supreme linseed oil and 10.1 grams of t-butyl peroctoate (initiator).

Upon completion of the addition of Solutions #1 and #2, hold temperature for one hour at 110° C, add five (5) drops of vanadium naphthenate to the reactor, then flush reaction lines.
with supreme linseed oil. Begin a three hour addition of a "chase" comprising 70 grams of
supreme linseed oil and 37.4 grams of cumene hydroperoxide. Hold the temperature at 110°
C for approximately 45 minutes after the chase has been completely added.

The resulting non-aqueous dispersion has a NVM of approximately 98.1% and a
viscosity of 6,320 centipoise at 25° C using the Brookfield LVT Spindle #3 at 12 rpm.

EXAMPLE FIVE (Castor Oil)

PREPARATION OF AN OIL MODIFIED NAD

Charge 265 grams of the alkyd prepared according to Example One and 186 grams of
raw castor oil to a reactor equipped with nitrogen and a mechanical stirrer. Heat to 110° C.

Begin a three hour dropwise addition of Solutions #1 and #2 below:

Solution #1: 629 grams of alkyd prepared according to Example One, 795 grams of
methyl methacrylate, 298 grams of hydroxy ethyl acrylate, and 5.8
grams of 2-mercapto ethanol (chain transfer agent).

Solution #2: 34.8 grams of raw castor oil and 8.2 grams of t-butyl peroctoate
(initiator).

Upon completion of the addition of Solutions #1 and #2, hold temperature for one hour at
110° C, five (5) drops of vanadium naphthenate to the reactor, then flush reaction lines with
raw castor oil. Begin a three hour addition of a "chase" comprising 57.1 grams of raw castor
oil, and 30.5 grams of cumene hydroperoxide. Hold the temperature at 110° C for
approximately 45 minutes after the chase has been completely added.

The resulting non-aqueous dispersion has a NVM of approximately 96.0% and a
viscosity of 6800 centipoise at 25° C using the Brookfield LVT Spindle #3 at 12 rpm.
COMPARATIVE EXAMPLES OF ISOCYANATE-CURED
CONVENTIONAL ALKYDS AND OIL-MODIFIED ALKYDS

Conventional NAD of Example Two and the Oil Modified NAD of Example Three were blended with 10-30% (by weight of NAD solids) of polyisocyanates HDT-LV (available from Rhodia), or alternatively, Desmodur N3600 (available from Bayer). The isocyanates were added to the NADs with 0.01 weight percent dibutyl tin dilaurate, manually stirred, coated on Bonderite panels and allowed to dry at ambient temperature. The coated panels were aged for 7 days and then tested for pencil hardness.

<table>
<thead>
<tr>
<th>NAD</th>
<th>Isocyanate</th>
<th>Pencil Hardness</th>
<th>VOC</th>
<th>NVM</th>
<th>Dry Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>-0-</td>
<td>&lt; B</td>
<td>250</td>
<td>85%</td>
<td>4 hours</td>
</tr>
<tr>
<td>86% NVM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% NVM</td>
<td>-0-</td>
<td>&lt; 6B</td>
<td>~ 0</td>
<td>97.5</td>
<td>tacky</td>
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<td>Conventional</td>
<td>10% HDT-LV</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>30 min</td>
</tr>
<tr>
<td>86% NVM</td>
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<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>20% HDT-LV</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min.</td>
</tr>
<tr>
<td>86% NVM</td>
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<tr>
<td>Conventional</td>
<td>10% N-3600</td>
<td>HB</td>
<td>&lt; 150</td>
<td>85%</td>
<td>30 min.</td>
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<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min.</td>
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<tr>
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<tr>
<td>100% NVM</td>
<td>10% HDT-LV</td>
<td>2B</td>
<td>~ 0</td>
<td>97.5%</td>
<td>30 min.</td>
</tr>
<tr>
<td>100% NVM</td>
<td>20% HDT-LV</td>
<td>2B</td>
<td>~ 0</td>
<td>97.5%</td>
<td>15 min.</td>
</tr>
<tr>
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<td>2B</td>
<td>~ 0</td>
<td>97.5%</td>
<td>45 min.</td>
</tr>
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<td>20% N-3600</td>
<td>2B</td>
<td>~ 0</td>
<td>97.5%</td>
<td>30 min.</td>
</tr>
</tbody>
</table>
Low Bake Tests

I. Low Bake Test: 30 minutes at 140° F

<table>
<thead>
<tr>
<th>NAD</th>
<th>Isocyanate</th>
<th>Gloss</th>
<th>Pencil Hardness</th>
<th>VOC</th>
<th>NVM</th>
<th>Dry Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional 86%</td>
<td>10% HDT-LV</td>
<td>97</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>30 min</td>
</tr>
<tr>
<td>Conventional 86%</td>
<td>10% N-3600</td>
<td>97</td>
<td>HB</td>
<td>&lt; 150</td>
<td>85%</td>
<td>30 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>10% HDT-LV</td>
<td>90</td>
<td>2B</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>45 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>10% N-3600</td>
<td>90</td>
<td>2B</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>45 min</td>
</tr>
</tbody>
</table>

II. Low Bake Test: 15 minutes at 155° F with Driers (1)

<table>
<thead>
<tr>
<th>NAD</th>
<th>Isocyanate</th>
<th>Gloss</th>
<th>Pencil Hardness</th>
<th>VOC</th>
<th>NVM</th>
<th>Dry Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional 86%</td>
<td>20% HDT-LV</td>
<td>97</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min</td>
</tr>
<tr>
<td>Conventional 86%</td>
<td>20% N-3600</td>
<td>98</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>20% HDT-LV</td>
<td>95</td>
<td>2B</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>30 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>20% N-3600</td>
<td>97</td>
<td>2B</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>30 min</td>
</tr>
</tbody>
</table>

III. Low Bake Test: 15 minutes at 140° F with Drier (1)

<table>
<thead>
<tr>
<th>NAD</th>
<th>Isocyanate</th>
<th>Gloss</th>
<th>Pencil Hardness</th>
<th>VOC</th>
<th>NVM</th>
<th>Dry Time</th>
</tr>
</thead>
<tbody>
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<td>30% HDT-LV</td>
<td>102</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min</td>
</tr>
<tr>
<td>Conventional 86%</td>
<td>30% N-3600</td>
<td>103</td>
<td>B</td>
<td>&lt; 150</td>
<td>85%</td>
<td>15 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>30% HDT-LV</td>
<td>100</td>
<td>B</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>15 min</td>
</tr>
<tr>
<td>100% NVM</td>
<td>30% N-3600</td>
<td>N/a</td>
<td>N/a</td>
<td>&lt; 25</td>
<td>97.5%</td>
<td>15 min</td>
</tr>
</tbody>
</table>

(1) driers were a combination of Co/CA/ZR
CLAIMS:

1. A non-aqueous dispersion which is formed in an alkyd medium by reactions comprising free radical polymerization of:

   (i) an alkyd formed from an acidolysis reaction product of a triglyceride oil with a trifunctional carboxylic acid or trifunctional anhydride, wherein the acidolysis reaction product is further reacted with a multi-functional alcohol;

   (ii) at least one hydroxy-functional monomer;

   (iii) at least one monomer capable of copolymerizing with the hydroxy-functional monomer by a free radical addition reaction mechanism;

wherein the alkyd and a natural oil are used as a polymerization medium for the polymerizable monomers;

wherein the non-aqueous dispersion has a non-volatile materials content of greater than 90%.

2. The non-aqueous dispersion of claim 1, wherein the alkyd has a non-volatile materials content greater than 95%.

3. The non-aqueous dispersion of claim 1, wherein the alkyd has a z-average molecular weight, 
   $M_z$, greater than about 20,000.

4. The non-aqueous dispersion of claim 1, wherein the alkyd has an oil length of between about 65% to about 85%.

5. The non-aqueous dispersion of claim 1, wherein the alkyd has an hydroxyl number of less than 60.

6. The non-aqueous dispersion of claim 1, further comprising a multifunctional isocyanate.
7. The non-aqueous dispersion of claim 6, wherein the multi-functional isocyanate is present at between about 1-60% by weight of the non-aqueous dispersion.

8. A non-aqueous dispersion obtained by polymerizing under free radical addition polymerization conditions, in a polymerization medium comprising an alkyd and optionally a natural oil, a polymerization mixture comprising:
   (i) at least one hydroxy-functional unsaturated monomer; and
   (ii) at least one unsaturated monomer capable of copolymerizing with the hydroxy-functional monomer;

and wherein the alkyd is formed from an acidolysis reaction product of a triglyceride oil with a trifunctional carboxylic acid or trifunctional anhydride, wherein the acidolysis reaction product is further reacted with a multifunctional alcohol.

9. The non-aqueous dispersion of claim 8 wherein the polymerization mixture also comprises a chain transfer agent.

10. The non-aqueous dispersion of claim 8 wherein the polymerization mixture also comprises the alkyd.

11. The non-aqueous dispersion of claim 8, wherein the natural oil has low conjugation.

12. The non-aqueous dispersion of claim 8, wherein the natural oil has high conjugation.

13. A coating composition comprising:
   (a) a non-aqueous dispersion which is formed in an alkyd medium by reactions comprising free radical polymerization of:
       (i) an alkyd formed from an acidolysis reaction product of a triglyceride oil with a trifunctional carboxylic acid or trifunctional anhydride, wherein the
acidolysis reaction product is further reacted with a multi-functional alcohol;

(ii) at least one hydroxy-functional monomer;

(iii) at least one monomer capable of copolymerizing with the hydroxy-functional monomer by a free radical addition reaction mechanism;

wherein the alkyd and a natural oil are used as a polymerization medium for the polymerizable monomers; and wherein the non-aqueous dispersion has a non-volatile materials content of greater than 90%.

14. The coating composition of claim 13, further comprising a multifunctional isocyanate.

15. The coating composition of claim 14, wherein the multi-functional isocyanate is present at between about 1-60% by weight of the non-aqueous dispersion.

16. The coating composition of claim 13, further comprising rheology modifiers, pigments, fillers, plasticizers, antioxidants, thixatropes, extenders, colors and pigments, solvents, diluents or reactive diluents, anti-skinning agents, drying agents, dispersants and surfactants, fungicides, mildewcides, preservatives, UV absorbers, anti-marring agents, flow and leveling agents, fragrances, defoaming agents, chelating agents, flattening agents, and/or anti-rusting agents.

17. An alkyd comprising an acidolysis reaction product of a triglyceride oil with a trifunctional carboxylic acid or trifunctional anhydride, wherein the acidolysis reaction product is further reacted with a multi-functional alcohol.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G63/48 C09D167/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 0 555 504 A (SHERWIN WILLIAMS CO) 18 August 1993 (1993-08-18) page 3, column 3, paragraph 7 - page 4, column 5, paragraph 1; claims 1,6; examples</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier document but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

  *"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  "&" document member of the same patent family

Date of the actual completion of the international search: 28 October 2002
Date of mailing of the international search report: 06/11/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 eipo nl,
Fax: (+31-70) 340-3016

Authorized officer
Engel, S
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