

ASSOCIATIVE THICKENERS

This invention relates to synthetic nonionic hydrophobically-modified water-soluble polyethers with the ability to viscosify water-based systems.

Water-soluble polymers (also commonly referred to as "thickeners" or "rheology modifiers") are widely used in many industrial water-borne systems as additives to modify their flow behavior. Thickeners increase and maintain viscosity at required levels under specified processing conditions and end use situations. Thickeners are useful, for example, in decorative and protective coatings, paper coatings, cosmetics and personal care items, detergents, pharmaceuticals, adhesives and sealants, agricultural formulations, and petroleum drilling fluids.

One such highly filled aqueous system where the thickener is used in a decorative and protective coating is latex paint, which is composed of a dispersion of a polymeric latex, pigments, clays, and other additives in water.

Thickeners can be materials that are either naturally occurring or synthetically manufactured. Natural thickeners, for example, include casein, alginates, gum tragacanth, guar, xanthan gum, locust bean gum, and modified celluloses, such as hydroxyethylcellulose, hydroxypropylcellulose, and carboxymethylcellulose. These natural products vary in their thickening efficiency. One of the drawbacks of natural product based thickeners is that they are subject to microbial attack and hence, addition of antimicrobial agents to the formulation is

required. Synthetic thickeners include various acrylic polymers, alkylene oxide polymers, amide polymers, and maleic anhydride polymers. These synthetic thickeners can be either homopolymers or copolymers. The hydrolytic stability of some of these polymers depends on the pH of the solution and others are sensitive to various components normally found in aqueous coatings.

Regardless of whether the thickener is natural or synthetic, it is desirable that it be water-soluble to have optimal properties as a thickener in various water-based systems. The term "water-soluble polymer" refers to any polymeric substance which is soluble in water and, by being soluble, produces a change in solution viscosity, refractive index, or surface tension of water.

Typically, a small amount (about 0.1-5 wt.%) of water-soluble polymers is added to latex paints to achieve the following performance characteristics during manufacturing, storage, and applications:

- a) Ease of formulation,
- b) Prevention of settling of the suspended particles (latex, pigment, etc.) during storage,
- c) Good film build during applications to achieve efficient hiding without excessive brush or roller drag,
- d) Good roller spatter resistance,
- e) No excessive sagging after application on a vertical surface, and
- f) Good flow and leveling for the formation of a smooth and continuous film with good appearance.

The above mentioned natural and synthetic thickeners provide different degrees of thickening efficiency and application properties. However, they invariably fail to provide all of the key performance properties in gloss paints. These key properties include good film build, flow and leveling, and gloss which are generally offered by solvent-based alkyd paints. Another drawback of these thickeners is that they may have poor compatibility with the various paint ingredients.

To eliminate some of the performance deficiencies of conventional thickeners, a new class of thickeners, commonly referred to as "associative thickeners", has been designed and commercialized (See E. J. Schaller and P. R. Sperry, in

"Handbook of Coatings Additives", Ed. L. J. Calbo, Vol. 2, p. 105, 1992; Marcel Dekker, Inc., New York). These thickeners are hydrophobically-modified water-soluble polymers. They undergo intermolecular association in aqueous solution and thereby exhibit enhanced solution viscosity. They can also adsorb onto the dispersed-phase particles of an aqueous dispersion and thereby form a three-dimensional network. Since they provide improved paint properties not offered by conventional thickeners, they have gained commercial importance.

Polysaccharide based associative thickeners are made by chemically grafting a small amount of a hydrophobic group (C_{10} - C_{24} alkyl) onto a modified polysaccharide. They are disclosed in U.S. Patents 4,228,277, 4,243,802, and EP 281,360.

Among commercial nonionic synthetic associative thickeners, hydrophobically modified ethoxylated urethane (HEUR) block copolymers constitute an important class. They are disclosed in U.S. Patents 4,079,028, 4,155,892, and 5,281,654.

These are low molecular weight polyurethanes made by condensing relatively low molecular weight polyethylene glycol (molecular weight $\sim 10,000$) with hydrophobic diisocyanates and end-capping the resulting copolymer with hydrophobic alcohols or amines. They are characterized by having three or more hydrophobes -- two of which are terminal and the remainder are internal. The hydrophobic groups are connected to the hydrophilic polyethylene oxide blocks through urethane linkages.

The preparation of HEURs is also disclosed in U.S. Patents 4,499,233 and 5,023,309. These HEURs are claimed to provide superior viscosifying properties and improved flow and leveling in aqueous systems.

Processes for the production of HEURs with pendant hydrophobes in bunches are described in U.S. Patents 4,426,485 and 4,496,708. These HEURs are believed to provide enhanced thickening to aqueous systems through micelle-like association.

HEURs with branched structure and terminal hydrophobes are disclosed in U.S. Patent 4,327,008. They are made by reacting polyalkylene oxides with a polyfunctional material, a diisocyanate, and water and end-capping the resulting product with a hydrophobic monofunctional active hydrogen-containing compound or a monoisocyanate.

Silicon-containing HEURs having particular utility in paints and coatings are disclosed in European Patent Application 0 498,442 A1. These are reaction products of an isocyanate functional material, a polyether polyol, a monofunctional
5 active hydrogen-containing hydrophobic compound, a silane-functional material, and water.

From applications and economic point of view, the major drawbacks of HEUR thickeners are their high cost, difficulty in handling, and tendency to destabilize the paint (separation of dispersed particles from the aqueous phase) (G.
10 D. Shay and A. F. Rich, J. Coatings Technology, Vol. 58, No. 7, p.43, 1986).

Random copolymers of ethylene oxide and long chain alkyl epoxides are disclosed in U. S. Patent 4,304,902. These copolymers provide enhanced aqueous viscosity, but do not provide good flow and leveling in latex paints.

15 U. S. Patent 4,411,819 describes the preparation of polyethers which have branched chain structure and are characterized by having terminal hydrophobes. They are made by reacting a low molecular weight polyol with a mixture of ethylene oxide and at least one lower alkylene oxide having 3-4 carbon atoms. The polyethers are then end-capped with a mixture of C₁₂-C₁₈ alpha-olefin epoxides.

20 Low molecular weight (~9,000) hydrophobically end-capped polyether is disclosed in PCT Int. Appl. WO 92 08753. These are made by coupling low molecular weight (~4,500) surfactant with *m*-dichloromethylbenzene. Preparation of low molecular weight (~9,000) hydrophobically end-capped polyethers is also disclosed in U.S. Patent 5,045,230. These are made by reacting C₈-C₂₂ aliphatic
25 alcohols with a mixture of ethylene oxide and propylene oxide and subsequently coupling the alkoxyated alcohols with a diepoxide to form a polyether (MW ~ 9,000). Since these hydrophobically end-capped polyethers are of low molecular weight, they do not efficiently viscosify aqueous systems including latex paints.

Latex compositions containing low molecular weight (3,000-20,000) water-
30 soluble polyethers bearing terminal hydrophobes were disclosed in U. S. Patent 3,770, 684. They were claimed to provide improved leveling in latex paints.

However, these polyethers were not efficient in increasing the viscosity of water and did not provide other rheological properties demanded in various highly filled aqueous systems. Hence, they were not versatile and economical.

Commercial nonionic synthetic associative thickeners exhibit often poor and variable compatibility in paints, as exemplified by syneresis, poor color acceptance, variable paint viscosity over time, and inadequate hiding power. A need exists in the paint industry for a nonionic synthetic associative thickener that corrects these deficiencies at a cost-effective dosage level. No single thickener is known that provides all the desired performance characteristics required in water-borne coatings. Hence, very often, attempts are made to use blends of two or more different thickeners to achieve the targeted coating rheology. While this approach works in a limited way, blending of thickeners is often cumbersome and depending on mutual interactions between the individual thickener, the stability and performance of the coatings are often in jeopardy.

The present invention relates to a water-soluble copolymer composition comprising a backbone of acetal- or ketal-linked polyether which has ends that are capped with hydrophobic groups.

The present invention is also directed to a process for preparing a hydrophobically end-capped poly(acetal- or ketal-polyether) comprising

- a) reacting an alpha, omega-dihydroxy polyether with a gem-dihalide compound in the presence of a base to form an alpha, omega-dihydroxy poly[acetal- or ketal-polyether] backbone, and
- b) reacting the backbone with a hydrophobic reagent to form the hydrophobically end-capped poly(acetal- or ketal-polyether).

The present invention further relates to a film forming, coating composition comprising an aqueous solution of the hydrophobically end-capped poly[acetal- or ketal-polyether] composition mentioned above.

The polymers of the present invention have been found to efficiently thicken various water-based systems including latex paints and provide an improved combination of paint properties (stability, flow and leveling, film build, spatter resistance, and sag resistance).

"Flow and leveling" as used in this invention refers to the degree to which a coating flows out after application so as to obliterate any surface irregularities such as, for example, brush marks, an "orange peel" appearance, peaks, or craters, which are produced by the mechanical process of applying a coating.

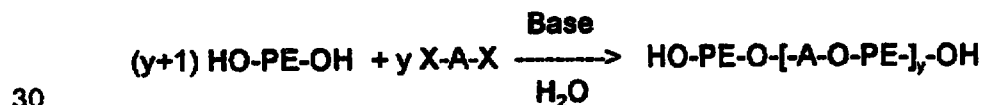
5 "Film build" means the formation of a continuous film to uniformly cover the surface of the substrate that is being coated.

"Spatter resistance" means the ability of the coating formulation to resist the formation of flying tiny droplets during application of the coating.

10 "Stability" means the ability to maintain the viscosity upon aging and to prevent phase separation.

"Sagging", as used herein, refers to the downward movement of a coating on a vertical surface between the time of application and setting, resulting in an uneven coating having a thick bottom edge. The resulting sag is usually restricted to a local area of a vertical surface and may have the characteristic appearance of a draped curtain. Sagging is aesthetically undesirable. In addition, coatings that resist the tendency to sag will not easily drip off a paint brush or a paint roller and will not easily drip off a horizontal surface, such as for example, a ceiling.

20 According to the invention, the water-soluble polymer backbone can be a preformed high molecular weight polyether, such as a polyalkylene glycol (also known as polyalkylene oxide) bearing terminal -OH groups. High molecular weight polyethylene glycols (molecular weight 17,000 and 35,000) are available from Fluka Chemical Corporation, Ronkonkoma, New York. Alternatively, a desired high molecular weight polyether precursor can be made in situ by condensing low molecular weight polyethers with a coupling agent, such as a gem-dihalogeno reagent or a mixture of gem-dihalogeno reagents as shown below. Various grades of low molecular weight polyethylene glycols (MW ~ 4,000-8000) are available from Union Carbide marketed under the trademark Carbowax.



where PE is a polyether; A is a moiety separating the halogen atoms (X). The terminal groups of the PE can also be -SH and -NH₂ groups.

Note that if X-A-X is a geminal dihalogeno-reagent, then the polyether blocks are connected through acetal or ketal linkages which are stable in alkaline environments.

So far as the type of terminal hydrophobe, R, is concerned, the polyether could bear either the same or different hydrophobes at its termini.

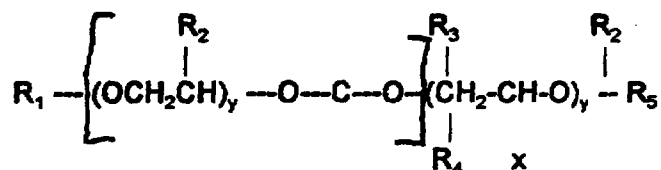
The hydrophobically-modified polyether can be made by reacting the terminal -OH, -SH, or -NH₂ groups of the polyether with an appropriate hydrophobic reagent in the presence of a base in an organic solvent.



where, — is the water-soluble polyether backbone, Z is a functional group capable of reacting with the terminal Y (Y = -OH, -SH and -NH₂) groups of the polyether, and R is a hydrophobic group.

To carry out the process, any solvent or solvent mixtures devoid of active hydrogens and stable to bases could be used. However, tetrahydrofuran, alkyl ethers of alkylene glycols or hydrocarbon solvents are preferred. Notwithstanding the above, the process can also be carried out in the absence of a solvent.

The polymer composition of the present invention has the following formula



where:

R₁ and R₅ are independently selected from the group consisting of a hydrophobic group or H. The hydrophobic groups can be either the same or different in the same molecule and are selected from hydrocarbyl, alkyl, aryl, arylalkyl, cycloaliphatic, perfluoroalkyl, carbosilyl, polycyclic groups, and complex dendritic hydrophobes. The preferred hydrophobic group is alkyl with a carbon range of 8-22 carbons, most preferred being 12-18 carbons. These hydrophobic

groups can be either saturated or unsaturated, branched or linear; the upper limit of the number of carbon atoms in the hydrophobic groups is 40 carbons, preferably 27 carbons, and more preferably 22 carbons; the lower limit of the number of carbon atoms in the hydrophobic groups is 1 carbon, preferably 4 carbons, more preferably 8 carbons. Specific examples of the hydrophobic groups are octyl, dodecyl, hexadecyl, and octodecyl groups.

When the hydrophobic groups are independently selected from alkyl, perfluoroalkyl and carbosilyl, the carbon range is from 1 to 40 carbons. When the hydrophobic groups are aryl, arylalkyl, cycloaliphatic, and polycyclic groups, the carbon range is 3 to 40 with the preferred range being from 6 to 29 carbons, and most preferred range being 14 to 25 carbons.

R_2 is selected from the group consisting of H, alkyl groups having 1-3 carbons, or a combination thereof;

R_3 and R_4 are independently selected from the group consisting of H, alkyl groups of 1-6 carbons, and phenyl;

y is an integer having values from about 1 to about 500; and

x is an integer having values from about 1 to about 50.

The composition of the present invention has a poly(acetal- or ketal- polyether) backbone that is either linear or branched, with the linear one being preferred. The polyethers that can be used in this invention include any water-soluble polyalkylene oxide or copolymers of polyalkylene oxides; the preferred polyether backbone is polyethylene oxide or water-soluble copolymers of ethylene oxide with another comonomer such as propylene oxide and butylene oxide.

The weight average molecular weight of the copolymer has an upper limit of 2,000,000, preferably 500,000, and most preferably 100,000. The lower limit of the molecular weight of the polymer is 500, preferably 15,000, and most preferably 20,000.

According to the present invention, a wide variety of hydrophobically end-capped poly(acetal- or ketal- polyethers) could be made by appropriately selecting various reaction conditions and manipulating the stoichiometry and molecular weight of the reactants.

Generally, any gem-dihalide can be used in the process for preparing the poly(acetal- or ketal-polyether) of the instant invention. However, dihalogenomethanes, such as dibromomethane and dichloromethane are preferred. Examples of other dihalides include: 1,1-dichlorotoluene ($C_6H_5CHCl_2$).

5 1,1-dichloroethane (CH_3CHCl_2) and 1,1-dibromoethane (CH_3CHBr_2). When a solvent is used, any solvent devoid of active hydrogens can be used in the process of this invention with oxygenated hydrocarbon solvents bearing 2 to 30 carbons are preferred. Examples of solvents that can be used in the instant invention are: toluene, xylene, aliphatic hydrocarbons, dialkyl ethers of alkylene glycols and
10 diethoxymethane. Any strong base capable of reacting with the terminal active hydrogens of the poly(acetal- or ketal-polyether) to form poly(acetal- or ketal-polyether) dianion, could be used in the process. Examples of bases that can be used in this invention are alkali metal hydrides, alkali metal hydroxides, alkali metal carbonates, and organic bases.

15 The preferred process of making hydrophobically end-capped poly(acetal-polyethers) comprises mixing molten polyether with caustic at elevated temperatures, followed by copolymerizing the polyether with a gem-dihalide, and subsequently end-capping the poly(acetal-polyether) with a hydrophobic reagent.

In accordance with this invention, the hydrophobically end-capped
20 poly(acetal- or ketal-polyether) compositions can be used in film forming coating compositions such as latex paints, the pigment volume concentration (PVC) of the latex paint can have a lower limit of 5, preferably 10 and an upper limit of 85, preferably 80. More particularly, when the latex paint is a high gloss paint, the PVC is from about 15 to about 30; when the paint is a semi-gloss paint, the PVC is from
25 about 20 to about 35; and when it is a flat paint, the PVC is from about 40 to about 80. Also, for latex paints the ICI viscosity should be above about 1.5 Pa.s at 25°C for good performance.

The following examples illustrate the preparation of hydrophobe end-capped poly(acetal-polyethers) of the present invention. However, they should not be
30 construed as the only ones limiting the invention, as other process variations are possible.

EXAMPLE 1**Preparation of PEG-8000/Methylene Copolymer**

To a three-necked round-bottomed flask (1000 ml) equipped with a Dean-Stark separator (at the top of which was attached a condenser whose top was
5 connected to a nitrogen source), magnetic stirrer, and thermometer were added polyethylene glycol (MW ~ 8000) (PEG-8000) (45 g) and toluene (100 ml). Moisture from PEG-8000 was azeotropically removed by distilling out toluene. The residual toluene, which could not be distilled out of the reaction flask at atmospheric pressure, was removed by passing a stream of nitrogen over the viscous solution of
10 PEG-8000 and keeping one of the necks of the reaction flask open. Then the flask containing dry PEG-8000 was cooled to room temperature and the Dean-Stark separator removed.

To the dry PEG-8000 at room temperature were added dry (HPLC grade) tetrahydrofuran (THF) (650 ml) and sodium hydride dispersion (60% in mineral oil)
15 (0.85 g). The resulting reaction mixture was heated under reflux for 0.5 hour.

Following this, a solution of dibromomethane (0.98 g) in THF (50 ml) was added dropwise to the PEG-8000/NaH reaction mixture over a period of 2 hours under nitrogen atmosphere through an addition funnel. The resulting reaction mixture was heated under reflux for 24 hours. After evaporation of solvent, a fluffy
20 white solid was isolated.

The weight average molecular weight of the PEG-8000/methylene copolymer was 53,000 with polydispersity index of 1.94. It was soluble in water to form a clear solution.

EXAMPLE 2

25 **Preparation of C₁₈ End-Capped PEG-8000/Methylene
Copolymer in Tetrahydrofuran (THF)**

The PEG-8000/methylene copolymer (described in Example 1) (13 g) was dried by dissolving it in boiling toluene (60 ml) and azeotropically distilling out toluene from the polymer solution. This "dry" PEG-8000/methylene copolymer was
30 heated under reflux with sodium hydride dispersion (60% in mineral oil) (0.25 g) and 1-bromooctadecane (0.5 g) in THF (150 ml) for 22 hours under nitrogen

atmosphere. After evaporation of solvent from the reaction mixture, a tan solid was isolated.

The C₁₈ end-capped PEG-8000/methylene copolymer thus obtained was soluble in water (2% solution BF viscosity at 30 rpm ~ 1080 cps). The C₁₈ hydrophobe content of the product was 1.42%.

EXAMPLE 3

Preparation of C₁₈ End-Capped PEG-8000/Methylene Copolymer Using Dichloromethane

To a three-necked round-bottomed flask (500 ml) equipped with a Dean-Stark separator (at the top of which was attached a condenser whose top was connected to a nitrogen source), magnetic stirrer, and thermometer were added PEG-8000 (18 g) and toluene (70 ml). Moisture from PEG-8000 was azeotropically removed by distilling out toluene. The residual toluene, which could not be distilled out of the reaction flask at atmospheric pressure, was removed by passing a stream of nitrogen over the viscous solution of PEG-8000 and keeping one of the necks of the reaction flask open. Then the flask containing dry PEG-8000 was cooled to room temperature and the Dean-Stark separator removed.

To the dry PEG-8000 at room temperature were added dry (HPLC grade) tetrahydrofuran (THF) (170 ml) and sodium hydride dispersion (60% in mineral oil) (0.4 g). The resulting reaction mixture was heated under reflux for 1.5 hour.

Following this, dichloromethane (0.15 g) was added to the PEG-8000/NaH reaction mixture and the resulting reaction mixture under reflux for 18 hours to form the PEG-8000/methylene copolymer.

Then sodium hydride (60% dispersion in mineral oil) (0.3 g) and 1-bromooctadecane were added to the reaction mixture containing the PEG-8000/methylene copolymer. After heating the resulting mixture under reflux for 8 hours, it was cooled to room temperature and transferred into a plastic tray. After evaporation of solvent inside the hood, a slightly brown solid was isolated.

The weight average molecular weight of the C₁₈ end-capped PEG-8000/methylene copolymer was 31,947 with polydispersity index of 1.91. It was

soluble in water to form a clear solution (2% solution BF viscosity at 30 rpm ~ 1780 cps). The octadecyl ($C_{18}H_{37}$) content of the polymer was 2.02 wt%.

EXAMPLE 4

Preparation of C_{12}/C_{16} Mixed End-Capped

PEG-8000/Methylene Copolymer

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To a stainless steel pressure reactor (Chemco type) were added PEG-8000 (750 g), THF (750 ml) and sodium hydride (60% dispersion in mineral oil) (22 g). After sealing the reactor, the resulting mixture was heated at 80°C for 1 hour and then cooled to 40°C. Following this, dibromomethane (13 g) was added to the reaction mixture at 40°C and the resulting reaction mixture heated at 80°C for 4 hours.

10

To this reaction mixture at 80°C was added a mixture of 1-bromododecane (8 g) and 1-bromohexadecane (15 g). The resulting reaction mixture was heated at 120°C for 2 hours, cooled to room temperature and the reactor charge transferred into a plastic tray. After evaporation of solvent, a buff solid was isolated.

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The C_{12}/C_{16} mixed end-capped PEG-8000/methylene copolymer thus formed was soluble in water (2% solution BF viscosity at 30 rpm ~ 60 cps).

EXAMPLE 5

Preparation of C_{16} End-Capped PEG-8000/Methylene Copolymer

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The procedure described in Example 4 was repeated using the following reagents.

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1. PEG-8000 - 750 g,
2. Tetrahydrofuran - 750 ml,
3. Sodium hydride (60% dispersion in mineral oil) - 22 g and
4. Dibromomethane - 11 g, and
5. 1-Bromohexadecane (Fluka; 97% pure) - 42 g

The C_{16} end-capped PEG-8000/methylene copolymer was soluble in water (2% solution BF viscosity at 30 rpm ~ 590 cps). The cetyl ($C_{16}H_{33}$) content of the copolymer was 1.52 wt%.

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EXAMPLE 6**Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in Dipropylene Glycol Dimethyl Ether**

Example 5 was repeated using Proglyde® DMM dipropylene glycol dimethyl ether (Dow Chemical) as the reaction solvent.

The C₁₆ end-capped PEG-8000/methylene copolymer was soluble in water (2% solution BF viscosity at 30 rpm ~ 120 cps).

EXAMPLE 7**Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in Diethoxymethane**

Example 5 was repeated using diethoxymethane (Eastman Chemical) as the reaction solvent.

The C₁₆ end-capped PEG-8000/methylene copolymer was soluble in water (2% solution BF viscosity at 30 rpm ~ 720 cps).

EXAMPLE 8**Preparation of C₁₆ End-Capped PEG-8000/Jeffamine® ED-6000/Methylene Terpolymer in THF**

A PEG-8000/Jeffamine® ED-6000/methylene Terpolymer was made by copolymerizing PEG-8000 (600 g), Jeffamine® ED-6000 (a polyoxyalkylene amine available from Huntsman Corporation) (150 g) and dibromomethane (12 g) in the presence of sodium hydride (60% dispersion; 22 g) in tetrahydrofuran (750 ml) according to the procedure described in Example 4. This Terpolymer was then reacted in situ with 1-bromohexadecane (42 g) at 120°C for 2 hours. After evaporation of solvent, a fluffy solid was isolated.

The C₁₆ end-capped PEG-8000/Jeffamine® ED-6000/methylene copolymer was soluble in water (2% solution BF viscosity at 30 rpm ~ 300 cps). The cetyl (C₁₆H₃₃) content of the copolymer was 0.95 wt%.

EXAMPLE 9**Preparation of C₁₈ End-Capped EMKAROX HV 105 Polyalkylene Glycol/Methylene Copolymer**

Example 2 was repeated using the following reagents.

- 5 a. EMKAROX HV 19 Polyalkylene glycol (nominal molecular weight ~ 20,000; available from ICI Americas) - 18 g
- b. Toluene - 100 ml
- c. THF - 170 ml
- d. Sodium hydride (60% dispersion) - 0.5 g
- 10 e. Dibromomethane - 0.2 g
- f. 1-Bromooctadecane - 1.0 g.

The 2% solution BF viscosity of the C₁₈ end-capped EMKAROX HV 105 polyalkylene glycol/methylene copolymer was 140 cps.

Paint Properties of Hydrophobe End-Capped Polyethers

- 15 The following Examples illustrate the thickeners of the present invention being incorporated into a vinyl-acrylic latex (UCAR 367 or POLYCO 2161) based flat paint (pigment volume concentration = 60%) and an all-acrylic (Rhoplex AC-417 or 417M) semigloss paint (pigment volume concentration = 24%) to achieve an initial Stormer viscosity of 90-95 Kreb Units. The ingredients used in the vinyl-acrylic
- 20 flat and the all-acrylic semigloss paint are shown in Table 1 and 2 respectively.
- The significance and scale of various paint properties are as follows:

- a) Stormer viscosity (initial and after overnight storage) is measured by a Stormer viscometer at 200 sec⁻¹ shear rate and expressed in Kreb Units (KU).
- 25 b) ICI viscosity is measured by an ICI plate and cone viscometer at 12,000 sec⁻¹ and expressed in poise.
- c) Thickening efficiency (TE) measured as dry wt % thickener needed in the paint to achieve the initial Stormer viscosity.
- d) Leveling by Leneta method (measured on a scale of 0-10; 0 = worst and
- 30 10 = best).
- e) Sag resistance by Leneta method, mid-range bar, wet film thickness (WFT) (in mils) above which sag occurs.
- f) Spatter resistance by roll-out over a black panel (compared on a scale of 0-10; 0 = worst and 10 = best).

g) 60° Gloss is specular gloss viewed at 60°.

Table 1

Interior Flat White and Light Tint Base

	Materials	Pounds	Gallons
5	Water	200.0	24.00
	Dispersant (Potassium tripolyphosphate)	2.0	0.10
	Ross & Rowe 551	2.0	0.23
	Dispersant (Tamol 731)	5.0	0.56
	Defoamer (Hercules SGL defoamer)	2.0	0.27
10	Ethylene glycol	20.0	2.18
	Carbitol acetate	10.0	1.19
	Titanium dioxide (Ti-Pure® R-901)	175.0	5.12
	Calcium carbonate (Camel CARB)	150.0	6.64
	Iceberg Clay	125.0	5.74
15	1160 silica	25.0	1.13

Grind to a Hegman of 4 and let-down at slower speed as follows:

	Materials	Pounds	Gallons
	Ephoxylated nonylphenol (Makon 10)	3.0	0.34
20	Vinyl-acrylic latex (Polyco 2161)	200.0	22.00
	Biocide (Proxel GXL)	1.0	0.11
	Water and/or thickener solution	250.5	30.07
	Total	1170.5	99.68

25

Formula Constants

Weight/gallon, lbs.	11.74
Pigment Volume Concentration, %	62.7
Nonvolatile Volume, %	31.3
Nonvolatile Weight, %	49.9
Stormer Viscosity, KU (Initial)	95 ± 2

30

Table 2
Interior White Semigloss

Materials	Pounds	Gallons
Propylene glycol	80.0	9.30
Dispersant (Tamol® SG-1)	8.5	0.89
Defoamer (Hercules SGL defoamer)	2.0	0.26
Titanium dioxide (Ti-Pure® R-900)	240.0	7.03
Silica (Imsil A-15)	25.0	1.13

Grind to a Hegman of 7+ and let-down at slower speed as follows:

Materials	Pounds	Gallons
Acrylic latex emulsion (Rhoplex AC-417M) (48% solids)	500.0	56.00
Antifoaming agent (Hercules SGL defoamer)	2.7	0.37
Propylene glycol	10.0	1.16
Biocide (Proxel GXL)	1.0	0.11
Coalescent (Texanok®)	21.6	2.73
Anionic surfactant (Triton GR-7M Premix)	0.5	0.06
Water	20.8	2.50
Water and/or thickener solution	153.7	18.46
Total	1065.8	100.00

Formula Constants

Weight/gallon, lbs.	10.66
Pigment Volume Concentration, %	24.8
Nonvolatile Volume, %	32.9
Nonvolatile Weight, %	48.0
Stormer Viscosity, KU (Initial)	90 ± 2
Gloss 60°	40 ± 5

EXAMPLES 10-27**Preparation of Various Hydrophobe End-Capped
PEG-8000/Methylene Copolymers**

Following the procedures described in Examples 1 and 2, a series of
5 hydrophobe end-capped PEG-8000/methylene copolymers with different molecular
weights (17,000-150,000) and bearing various amounts of different hydrophobes
(C₁₆-C₂₂) were made by varying the amount of appropriate reagents and reaction
conditions.

The solution viscosity of a given hydrophobe end-capped polyether depended
10 on its molecular weight, hydrophobe type, and the hydrophobe content.

The paint properties of various thickeners with different compositions are given
in Tables 3 and 4. All of the molecular weights (indicated in Tables 3 and 4) refer to
the weight average molecular weight of the sample.

Procedures for Determining the Weight Average**15 Molecular Weight of Poly(acetal-polyethers)**

The weight average molecular weights of poly(acetal-polyethers) were
measured by size exclusion chromatography (SEC). The SEC measurements were
performed in a 0.20M lithium acetate buffer (pH 4.8) plus 0.5% β -cyclodextrin plus
0.1% N-methyl pyrrolidone (NMP) mobile phase with both the columns and the
20 refractive index detector thermostated at 40°C. The polymers were
chromatographed through a set of four Shodex PROTEIN® columns (2 KW-802.5 +
1 KW-803 + 1 KW-804) in series at a flow rate of 1.0 ml/min. A sample
concentration of 0.20% was used with an injection volume of 200 liters. The
molecular weight distribution data are based on polyethylene oxide/polyethylene
25 glycol standards and are not absolute.

TABLE 3
ALL-ACRYLIC (RHOPLEX AC-417M) SEMIGLOSS PAINT PROPERTIES OF
END-CAPPED METHYLENE/PEG-8000 COPOLYMERS

Examples	Hydrophobe	M _w x 10 ⁻³	Viscosity (2%) (cps)	TE (%)	KU	ICI	Level	Sag	Spatter	60° Gloss
10	C ₁₈	62	3560	0.29	93/105	0.9	10	6	9	51.6
11	C ₁₈	53	3800	0.33	90/104	1.0	10	6	8	51.7
12	C ₁₈	53	2120	0.36	90/101	1.1	9	8	7	55.6
13	C ₁₈	74	600	0.55	89/105	1.5	10	6	9	53.1
14	C ₁₈	109	1720	0.29	88/102	1.1	10	6	9	50.9
15	C ₁₈	67	1720	0.39	88/106	1.1	10	6	7	54.9
16	C ₁₈	71	4100	0.24	90/103	0.9	9	8	7	55.8
17	C ₁₈	74	4100	0.29	92/109	1.0	10	8	8	58.2
18	C ₁₈	59	3000	0.31	90/107	1.0	10	8	8	58.2
19	C ₁₈	57	2000	0.36	91/101	1.1	9	8	7	55.6
20	C ₁₈	56	1000	0.73	93/116	1.9	10	6	9	54.8
21	C ₁₈	78	410	0.47	88/101	1.9	9	8	9	54.2
22	C ₁₈	72	420	0.43	90/102	1.8	10	8	9	51.8
23	C ₁₈	53	280	0.58	90/102	1.8	10	8	9	51.6
24	C ₁₈	67	220	0.65	90/113	2.2	10	8	8	51.3
25	C ₁₈	48	180	0.73	90/106	2.4	10	8	8	51.3
26	C ₁₈	61	120	0.73	91/113	2.5	10	6	9	51.0
27	C ₁₈	35	30	1.16	90/101	2.7	10	6	8	55.4

TABLE 4

Vinyl-Acrylic (UCAR 367) Flat Paint Properties of
End-Capped Methylene/PEG-8000 Copolymers

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Example	Hydrophobe	$M_w \times 10^{-4}$	Viscosity (2%) (cps)	TE (%)	KU	ICI	Level	Sag	Spatter
10	C ₁₈	62	3560	0.45	97/104	1.5	8	12	9
11	C ₁₈	53	3800	0.51	96/104	1.8	10	9	9
12	C ₁₈	53	2120	0.54	94/101	1.5	7	11	7
13	C ₁₈	74	600	0.98	95/110	2.3	8	12	9
14	C ₁₈	109	1720	0.81	97/108	1.9	8	12	9
15	C ₁₈	67	1720	0.63	93/106	1.6	7	10	8
16	C ₁₈	71	4100	0.48	96/109	1.5	8	8	8
17	C ₁₈	74	4100	0.47	96/112	1.5	7	8	8
18	C ₁₈	59	3000	0.50	93/106	1.3	7	8	8
19	C ₁₈	57	2000	0.55	94/102	1.4	8	11	7
20	C ₁₈	56	1000	0.89	97/113	2.2	8	12	9
21	C ₁₈	78	410	0.82	94/102	1.7	7	12	9
22	C ₁₈	72	420	0.62	93/107	2.8	8	10	8
23	C ₁₈	53	280	0.64	93/102	2.9	8	9	8
24	C ₁₈	67	220	0.75	94/109	3.0	8	10	9
25	C ₁₈	48	180	0.82	96/110	3.3	7	12	7
26	C ₁₈	61	120	0.86	97/115	3.5	8	11	9

As can be seen, the paint properties are controlled by the molecular weight, hydrophobe type and solution viscosity. The paint data clearly show that by appropriately adjusting these molecular parameters, one can achieve a balance of paint properties.

EXAMPLE 28

Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base

To an Abbe ribbon blender were added PEG-8000 (1250 g) and sodium hydroxide (37 g). After sealing the reactor, the mixture was heated at 80°C for one hour. Then dibromomethane (18.5 g) was added to the PEG-8000/NaOH mixture and the resulting reaction mixture heated at 80°C for 4 hours to form the PEG-8000/methylene copolymer.

To the PEG-8000/methylene copolymer at 80°C was added 1-bromohexadecane (65 g) and the resulting reaction mixture was heated at 120°C for 2 hours. Following this, the reactor was opened and the molten reaction mixture poured into a plastic tray. Upon cooling to room temperature, the reaction mixture solidified.

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm ~ 410 cps).

EXAMPLE 29

Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base With Shorter Reaction Time

To an Abbe ribbon blender were added PEG-8000 (1250 g) and sodium hydroxide (37 g). After sealing the reactor, the mixture was heated at 80°C for 1 hour. Then dibromomethane (18.5 g) was added to the PEG-8000/NaOH mixture and the resulting reaction mixture heated at 100°C for 2 hours to form the PEG-8000/methylene copolymer.

To the PEG-8000/methylene copolymer at 100°C was added 1-bromohexadecane (65 g) and the resulting reaction mixture heated at 120°C for 2 hours. Following this, the reactor was opened and the molten reaction mixture poured into a plastic tray. Upon cooling to room temperature, the reaction mixture solidified.

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm ~ 410 cps).

EXAMPLE 30

Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base

Example 28 was repeated using less sodium hydroxide. The reagents used were:

- a. PEG-8000 - 1250 g
- b. Sodium hydroxide - 25 g
- c. Dibromomethane - 18.5 g
- d. 1-Bromohexadecane - 65 g

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm ~ 60 cps).

EXAMPLE 31

Preparation of C₁₆ End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydride as the Base

Example 28 was repeated using the following reagents.

- a. PEG-8000 - 1250 g
- b. Sodium hydride (60% dispersion in mineral oil) - 36.5 g
- c. Dibromomethane - 18.5 g
- d. 1-Bromohexadecane - 70 g

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm ~ 620 cps).

EXAMPLE 32**Preparation of C₁₂ End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base**

Example 28 was repeated using the following reagents.

- 5
- a. PEG-8000 - 1250 g
 - b. Sodium hydroxide - 37 g
 - c. Dibromomethane - 17 g
 - d. 1-Bromododecane - 83 g

10 The crude reaction mixture was soluble in water (20% solution BF viscosity at 30 rpm ~ 4400 cps). The dodecyl (C₁₂H₂₅) content of the copolymer was 1.75 wt%.

EXAMPLE 33**Preparation of C₁₂/C₁₆ Mixed End-Capped PEG-8000/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base**

15 Example 28 was repeated using a mixture of 1-bromododecane and 1-bromohexadecane as the end-capping agents. The reagents used were:

- a. PEG-8000 - 1250 g
- b. Sodium hydroxide - 37 g
- c. Dibromomethane - 18.5 g
- 20 d. 1-Bromododecane - 20 g
- e. 1-Bromohexadecane - 60 g

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm ~ 165 cps).

EXAMPLE 34

25 **Preparation of Nonylphenyl/C₁₆ Mixed End-Capped PEG/Methylene Copolymer in a Solvent-Free Process Using Sodium Hydroxide as the Base**

Example 28 was repeated using a mixture of PEG-8000 and ethoxylated nonylphenol, C₉H₁₉-C₆H₄-O(CH₂CH₂O)₄₀-H (IGEPAL CO-890; available from GAF

Corporation) as the polyethylene glycol substrates. The other reagents used are shown below:

- a. PEG-8000 - 1250 g
- b. IGEPAL CO-890 - 25 g
- c. Sodium Hydroxide - 37 g
- d. Dibromomethane - 18.5 g
- e. 1-Bromohexadecane - 60 g

The crude reaction mixture was soluble in water (2% solution BF viscosity at 30 rpm - 195 cps).

10 **Effect of the Degree of Hydrophobe End-Capping on the Paint
 Properties of Poly(Acetal-Polyethers)**

15 It was surprising to find that the degree of hydrophobe end-capping, i.e., the fraction of chain ends capped with a hydrophobe, of the poly(acetal-polyether) of a given molecular weight dramatically affected its key paint properties (thickening efficiency, ICI viscosity, leveling, and spatter resistance). This is exemplified by comparing paint properties of various poly(acetal-polyethers) of identical molecular weight (weight average molecular weight ~ 31,000) prepared according to the procedure described in Example 28 but containing different degrees C₁₆-capping (see data in Table 5).

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TABLE 5

Rhoplex AC-417M Semigloss Paint Properties of C₁₈ End-Capped
Poly(Acetal-Polyethers) (MW ~ 31000) with Different Levels of C₁₈ Hydrophobe

Samples	C ₁₈ Content (wt %)	TE (%)	KU	ICI	Level	Sag	Spatter	60° Gloss
a	1.45	0.73	91/105	2.0	10	9	9	47.0
b	1.90	0.51	90/104	1.6	9	8	9	45.8
c	2.00	0.30	88/96	1.0	6	9	8	47.5
d	2.28	0.32	90/105	1.1	6	12	9	46.4

The data in Table 5 show that the best balance of paint properties is achieved at an intermediate level of hydrophobe content of about 1.9 wt. % corresponding to a degree of end-capping of about 70%. Lower hydrophobe weight percents provide poor thickening efficiency and higher levels lead to poor leveling and lower ICI viscosity. The optimum degree of end-capping to achieve a balance of paint properties would vary with molecular weight of the poly(acetal-polyether).



What is claimed:

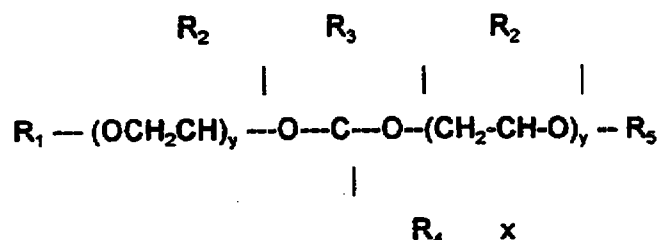
1. A water-soluble polymer composition comprising a backbone of poly(acetal or ketal-polyether) which has ends that are capped with hydrophobic groups.
- 5 2. The polymer composition of claim 1 wherein the hydrophobic groups are independently selected from the group consisting of alkyl, aryl, arylalkyl, cycloaliphatic, perfluoroalkyl, carbosilyl, polycyclyl, and complex dendritic groups.
3. The polymer composition of claim 2, wherein the alkyl, perfluoroalkyl, and carbosilyl hydrophobic groups comprise 1 to 40 carbons.
- 10 4. The polymer composition of claim 2 wherein the aryl, arylalkyl, cycloaliphatic, and polycyclic hydrophobic groups comprise 3 to 40 carbons.
5. The polymer composition of claim 3 wherein the hydrophobic group is an alkyl group of 8 to 22 carbons.
6. The polymer composition of claim 5 wherein the hydrophobic group is an
15 alkyl of 12 to 18 carbons.
7. The polymer composition of claim 4 wherein the hydrophobic group is selected from the group consisting of aryl, arylalkyl, cycloaliphatic and polycyclic of 6 to 29 carbons.
8. The polymer composition of claim 7 wherein the hydrophobic group is
20 selected from the group consisting of aryl, arylalkyl, cycloaliphatic and polycyclic of 14 to 25 carbons.
9. The polymer composition of claim 1, wherein the upper limit of the molecular weight of the polymer is about 2,000,000.
10. The polymer composition of claim 1 wherein the upper limit of the
25 molecular weight is about 500,000.
11. The polymer composition of claim 1 wherein the upper limit of the molecular weight is about 100,000.
12. The polymer composition of claim 1 wherein the lower limit of the molecular weight is about 500.



13. The polymer composition of claim 1, wherein the lower limit of the molecular weight of the polymer is about 15,000.

14. The polymer composition of claim 1 wherein the lower limit of the molecular weight is about 20,000.

5 15. A polymer composition having the following formula



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where

R_1 and R_5 are independently selected from the group consisting of a hydrophobic group having 1 to 40 carbons or H,

15 R_2 is selected from the group consisting of H, alkyl having 1-3 carbons, or a combination thereof,

R_3 and R_4 are independently selected from the group consisting of H, alkyl of 1-6 carbons, and phenyl,

y is an integer of from about 5 to about 500, and

x is an integer of from about 1 to about 50.

20

16. The polymer composition of claim 15 wherein R_2 is H.

17. The polymer composition of claim 15 wherein R_2 is an alkyl having 1 to 2 carbons.

18. The polymer composition of claim 15 wherein R_3 and R_4 are both H.

25 19. The polymer composition of claim 16 wherein R_3 and R_4 are alkyl groups having 1 to 2 carbons.

20. The polymer composition of claim 15 wherein y is about 180.

21. The polymer composition of claim 15 wherein y is about 100.

22. The polymer composition of claim 15 wherein x is about 15.

23. The polymer composition of claim 15 wherein x is about 5.



24. A process for preparing a hydrophobically end capped poly(acetal- or ketal - polyether) comprising

- 5 a) reacting an alpha, omega-dihydroxy, -dithiol or -diamino polyether or a mixture of them with a gem-dihalide compound in the presence of a base to form an alpha, omega- dihydroxy poly(acetal- or ketal-polyether) backbone, and
- b) reacting the backbone with a hydrophobic reagent to form the hydrophobically end capped poly(acetal or ketal-polyether).

25. The process of claim 24 wherein the hydrophobic groups are independently selected from the group consisting of alkyl, aryl, arylalkyl, cycloaliphatic, perfluoroalkyl, carbosilyl, polycyclyl, and dendritic groups.

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26. The process of claim 25, wherein the alkyl, perfluoroalkyl, and carbosilyl hydrophobic groups comprise 1 to 40 carbons.

27. The process of claim 25 wherein the aryl, arylalkyl, cycloaliphatic, and polycyclic hydrophobic groups comprise 3 to 40 carbons.

15 28. The process of claim 26 wherein the hydrophobic group is an alkyl of 8 to 22 carbons.

29. The polymer composition of claim 28 wherein the hydrophobic group is an alkyl of 12 to 18 carbons.

20 30. The process of claim 27 wherein the hydrophobic group is selected from the group consisting of aryl, arylalkyl, cycloaliphatic, polycyclic, and dendritic of 6 to 29 carbons.

31. The process of claim 30 wherein the hydrophobic group is selected from the group consisting of aryl, arylalkyl, cycloaliphatic and polycyclic of 14 to 25 carbons.

25 32. The process of claim 24, wherein the upper limit of the molecular weight of the polymer is about 2,000,000.

33. The process of claim 24 wherein the upper limit of the molecular weight is about 500,000.



34. The process of claim 24 wherein the upper limit of the molecular weight is about 100,000.

35. The process of claim 24 wherein the lower limit of the molecular weight is about 500.

5 36. The process of claim 24, wherein the lower limit of the molecular weight of the polymer is about 15,000.

37. The process of claim 24 wherein the lower limit of the molecular weight is about 20,000.

10 38. A film forming coating composition comprising the hydrophobically end capped poly(acetal- or ketal-polyether) composition of claim 1.

39. The film forming coating composition of claim 38 wherein the composition is a latex paint.

40. The film forming coating composition of claim 39 wherein the latex paint has a pigment volume concentration of from about 15 to about 80.

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