

CABLE GREASE COMPOSITION AND ARTICLES INCORPORATING SAME

Technical Field

5 The present invention relates to a grease composition that includes a colloidal particle filled, high molecular weight polyol base component with low levels of unsaturated mono-compounds, and to articles such as sheathed communication cables, especially those containing optical
10 fiber bundles, which include grease compositions such as those disclosed herein.

Background of the Invention

A grease typically is a solid or semi-liquid substance
15 which includes a thickening or gelling agent in a liquid carrier. Almost any oil having lubricating properties may be used with a suitable gelling agent to make a grease. Petroleum oils, fatty oils such as castor oil, polyalkylene glycols, synthetic diesters, silicones, fluorocarbons and
20 polyphenyl ethers are all found in commercial lubricating greases. (See, e.g., Braithwaite, "Lubrication and Lubricants," Elsevier Publishing Co., 1967, pages 181-183 and 223-228). The gelling agents frequently used in greases include fatty acid soaps, clays, silica, organic dyes,
25 amides, and urea derivatives. The gelling agent forms a network structure in which the carrier is held by capillary forces.

When a low stress is applied through a sample of grease, the material acts substantially like a solid. If a stress
30 above a critical value is supplied, the material flows and viscosity decreases rapidly. This decrease in viscosity is largely reversible since it is typically caused by the rupture of network junctions between filler particles, and these junctions can reform following the removal of the
35 source of the stress.

A desirable property of the grease is the absence of syneresis, i.e., its ability to maintain uniform consistency.

REPLACED SHEETS	SG
☒ Description : paged to paged15....	
☒ Claim(s) : paged16... to paged17....	
☒ Drawing(s) : paged18... to paged19....	
☒ Abstract : paged20... to paged21....	
DATE OF RECEIPT	

This Sheet Has Been Replaced



- 2 -

Generally, syneresis is controlled by assuring dispersion of an adequate amount of the gelling agent throughout the composition.

Grease compositions have been used as cable filling material in both conventional (electrical) communications as well as for optical fiber cables. U.S. Patent 4,701,016 discloses grease compositions comprising an oil, a gelling agent such as colloidal particles of silica or clay, and optionally a bleed inhibitor. The oils which are disclosed as being useful in the compositions of that patent include certain naphthenic or paraffinic oils having certain specific gravities and properties, polybutene oils of similar specific properties, triglyceride based vegetable oils, polypropylene oil, chlorinated paraffin oils, and polymerized esters. The colloidal particle filler material preferably comprises silica particles such as fumed silica or precipitated silica. Preferred bleed inhibitors include styrene-rubber, styrene rubberstyrene, or other block polymers, and/or semi-liquid rubbers such as high viscosity polyisobutylene. Other ingredients such as thermal oxidative stabilizers optionally may be present.

One disadvantage of the compositions of the above cited patent is that relatively large amounts of silica must be included to meet the appropriate service requirements for the grease. Thus, relatively stiff greases are obtained which are not entirely suitable for such fiber optic cables. In particular, such stiff greases will affect attenuation (microbending) of the fiber optic cable at relatively low temperatures (i.e., below about 50°F). Furthermore, if the amount of silica is reduced to lower the viscosity of the grease, the shear characteristics of the formulation are reduced to a value which is less than desirable. Moreover, such a reduction in silica often results in syneresis.

U.S. Patent 4,839,970 to Goetze et al. discloses a filling compound that can be utilized to fill light waveguide leads or light waveguide cable cores. The filling compound comprises polypropylene glycol to which a second compound

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0.1 to 1.0 weight percent of the filling compound.

While the greases of that patent can be used to seal
15 optical cable they are incapable of meeting current industry
specifications which require improved performance with
respect to bleed resistance and oxygen inhibition resistance.

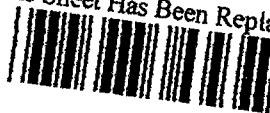
Accordingly, a need exists for novel polyol containing
grease compositions which are capable of providing an optimum
20 balance of viscosity and shearing characteristics such that
the compositions are suitable for use with fiber optic cables
even at lower temperatures. In addition, these formulations
must provide properties which are capable of passing the
appropriate drip tests, paper bleeding tests, and syneresis
25 requirements for such cable filling greases.

Summary of the Invention

The present invention relates to a gel for use in an
optical fiber buffer tube, which gel contains between about
30 75 and 95 parts by weight of a base component of a polyol
having a molecular weight of at least 4,000, and between
about 2 and 15 parts by weight of a thickening agent, such as
colloidal particles.

Preferably, the polyol is a polyether polyol having a
35 molecular weight of at least 4,000 up to as high as about
25,000. Preferably, the molecular weight is between 6,000
and 15,000 and more preferably between 8,000 and 12,000. To

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- 5 -

polyol or ester, such as colloidal particles. An antioxidant is generally used to improve the high temperature properties of the composition. If desired, although not critical to the invention, a bleed inhibitor of a thermoplastic elastomer can be added to the previously described components.

The preferred polyols of the invention include polyether polyols including polyoxypropylene glycol or polytetramethylene glycol, diol, triol, tetrol, etc., as well as hydroxyl terminated polyethers having a molecular weight of at least about 4,000. The upper limit for molecular weight is not critical, provided that the polyol is a liquid or at least is a semi-solid at room temperature. Solid polyols are more difficult to formulate and are not preferred for that reason. An upper limit for molecular weight can be as high as about 20-25,000. Those polyols having a molecular weight of about 6,000 to 15,000, and more particularly about 8,000 to 12,000, are preferred.

It is advantageous to use polyols having low levels of unsaturated mono-compounds. Polyalkylene oxides or polyether polyols for making polyurethanes are typically prepared from the polymerization of epoxides (most commonly propylene oxide or ethylene oxide) with an alkaline base catalyst such as potassium hydroxide. Polyhydric initiators of varying functionality are oxyalkylated to prepare polyether polyols with varying functionality. For example, difunctional alcohols such as propylene glycol, dipropylene glycol, or tripropylene glycol are commonly used as starters to prepare difunctional polyether polyols (triols). Trifunctional alcohols like glycerol and trimethylol propane are commonly used to prepare trifunctional polyether polyols (triols).

The base catalyzed polymerization of propylene oxide results in a competitive reaction between the desired attack at the oxirane ring, to form polyols by ring-opening polymerization, and a side reaction in which the base attacks at the methyl group, to form allyl alcohol. The allyl alcohol then acts as a monofunctional initiator, which propoxylates to form monol.

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- 6 -

The amount of monol in a polyol is measured by titration of the unsaturated end groups and reported as milliequivalents of unsaturation per gram of polyol. Since the molecular weight of the monol is less than one third the molecular weight of the triol, a small amount of terminal unsaturation translates into high mole percentages of monol. For example, a 6200 molecular weight poly(propylene oxide) triol capped with 5% ethylene oxide having an unsaturation value of 0.095 meq/g means the polyol contains 42.5 mole % monol or 20 weight % monol.

The monol species with unsaturated end groups act as chain terminators in elastomer formation. This limits the molecular weight of the elastomer and lowers the physical properties of the polyurethane. The formation of terminally
15 unsaturated end groups results in a substantial loss in hydroxyl functionality. For example, a 6200 molecular weight triol with 0.095 meq/g of unsaturation has a calculated functionality of only 2.14.

In polyols prepared with base catalysts, the amount of unsaturation formed increases as a direct function of equivalent weight and eventually conditions are established in which the amount of unsaturation being formed balances the additional molecular weight of the growing chain. The rate of unsaturation formation with KOH catalysis can be lowered by using lower temperature and longer reaction times, but this makes the process prohibitively expensive. In actual practice, 2200 is about the highest equivalent weight obtained with KOH catalysis (4400 MW diol, 6600 MW triol), and these polyols typically contain more than 0.09 meq/g of unsaturation.

In contrast, with double metal cyanide (DMC) catalysts, the amount of unsaturation formed increases very slowly with increasing polyol equivalent weight, which allows the synthesis of ultra high molecular weight polyols containing 35 low levels of monol, i.e., less than about 0.05 meq/g of unsaturation, and typically about 0.015 to 0.03 meq/g. Arco Chemicals as their R-18XX series, as well as from Polyols of

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- 7 -

this type are commercially available from Olin Corporation, as their POLY-LTM polyols. Such polyols have been found to be very useful in the present cable grease compositions.

The preferred polyether polyols are polyether diols, particularly polyoxypropylene diols. Generally, these polyether diols are prepared by condensing a large excess of an alkylene oxide, such as ethylene oxide or propylene oxide with a glycol, as is well known in the art. As noted above, to achieve a relatively low amount of unsaturated monocompounds, the reaction is conducted in the presence of double metal cyanide catalysts. The glycol can be a diol, such as the alkylene glycols, e.g., ethylene or propylene glycol, or an ether glycol, such as diethylene glycol. The Arco R-18XX series are the most preferred.

Among the thickening agents which are useful in the present invention are colloidal particles. Colloidal silica, either hydrophilic or hydrophobic, preferably a hydrophobic fumed silica having a BET surface area between about 50 and about 40 m²/gm, is preferred. An example of a hydrophobic fumed silica useful in the practice of the invention is a polydimethylsiloxane-coated fumed silica having a BET surface area of about 80-120 m²/gm, containing about 5% b.w. carbon, available from the Cabot Corporation of Tuscola, Ill., under the trade designation Cab-O-Sil TS 720. An exemplary hydrophilic colloidal material is fumed silica with a BET surface area of about 175-225 m²/gm, nominal particle size of 0.012 μ m, specific gravity 2.2, available from the Cabot Corporation under the trade designation Cab-o-Sil M-5.

Mixtures of these materials also may be used. Other colloidal fillers useful in the practice of the invention are precipitated silicas and clays such as bentonites, with or without surface treatment. Other inorganic colloidal particles may also be used, if desired, although the silicas are preferred.

Among the thermoplastic elastomers that may optionally be employed in the compositions according to the invention are the polyurethane elastomers which are based on polyether

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- 8 -

and/or polyester polyurethanes. In particular, the polyol used to form the polyurethane should be one of the polyols described above for optimum compatibility. Alternatively, any polypropylene glycol based polyether polyurethane can be used. Polyester polyurethanes, polyester elastomers or acrylic elastomers can also be used.

The thermoplastic elastomers are non-reactive, heat processable materials. One preferred elastomer is MILLATHANE E-34, a linear thermoplastic millable polyurethane elastomer which has a pendent group that contains an aliphatic, non-benzenoid $-O-O-$ moiety. Examples of these type thermoplastic elastomers are found in U.S. Patent 3,043,807. This component, which is not crosslinked, can be used to impart tack to the composition, which property enhances the ability of material to resist dripping after placement in the cable.

Other suitable elastomers include the LOMOD polyester and polyester copolymer elastomers made by General Electric, VALOX, a polybutylene terephthalate made by General Electric, the PELLATHANE thermoplastic polyurethanes made by Dow Chemical and the ESTANE thermoplastic polyurethanes made by B.F. Goodrich. These elastomers are generally used in an amount of about 1 to 15 parts by weight.

By following the combination of ingredients disclosed above, the grease of the present invention is characterized as being non-dripping with high penetration and a low yield stress. The high penetration capabilities as a grease allows a better fluidity. That is, lower viscosities may be used so that the cable may be more easily filled with the grease. Furthermore, the present invention provides distinct advantages over prior art formulations:

- 1) the processing properties as noted above are exceptional in that the material can thin out as much as possible under heat and shear for easy cable filling. Thus, the grease of the invention fills the cable more easily and faster, avoiding microbending difficulties which can cause attenuation in fiber optic cable.

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- 9 -

2) Conventional formulations at low viscosity require a reduced silica content to achieve the same degree of viscosity. However, this reduction causes syneresis, i.e., the gel becomes unstable and separates into an oil layer and a filler layer. This separation causes difficulties in the static properties of the fiber optic cable. The formulations of the present invention have not exhibited syneresis in any tests conducted so far.

When introducing the grease into the fiber optic cable, it is important to achieve as low a viscosity as possible so that the fibers are not moved. This is achieved by introducing the grease under high shear into the cable. This can be accomplished by retaining the grease composition in a reservoir such as a drum upon which a drum pump of the piston type is attached. This pump causes low shear and movement of the grease out of the drum and into a conduit or pipe which is traced and heated to maintain the temperature of the grease therein to at least about 80°C. The grease then is directed through a gear pump which is operated under high shear conditions of about 5,000 to as high as 20,000 revolutions per sec. A pipe exiting the gear pump directs the grease into a die which is positioned about the fiber optic cable in a manner such that the grease is extruded into the cable around the fibers. The grease is extruded into the cable at temperatures of about 500 to 600°F, preferably at about 550°F. Unlike prior art greases, the formulations of the invention are relatively stable at that temperature.

As noted above, an antioxidant may be used to impart enhanced stability to the grease at such elevated extruding temperatures. The most preferred antioxidant is Ciba-Geigy Irganox 245, a sterically hindered phenolic compound in the form of a white crystalline powder having the empirical formula $C_{24}H_{30}O_4$. This compound is also known as triethylene glycol bis [3-(31-tert-butyl-4'-hydroxy-5'-methylphenyl) propionate] or ethylene bis (oxyethylene) bis (3-tert-butyl-4-hydroxy-5-methyl hydro cinnamate). Other bis hindered phenol rings connected by a polyether linkage should provide

- 10 -

comparable results, but the Irganox 245 is preferred due to its ready commercial availability.

To determine whether or not a particular antioxidant is suitable for use in the present invention, a modified Belcore oxygen inhibition test may be conducted. A sample of the grease is put in a calorimeter in a boat under nitrogen pressure and is conditioned at 190°C. Thereafter, pure oxygen is pumped into the calorimeter and changes in the grease are measured. In order to provide a suitable grease, the material must be able to withstand approximately 10 minutes at 190°C in a pure oxygen environment. The use of 1% by weight of Irganox 245 in the grease formulations of the present invention allows the grease to withstand approximately 8 minutes in the modified Belcore test. Increasing that level to about 2% increases the resistance of the grease to the test environment to about 12 minutes. Finally, an addition of about 3% Irganox 245 allows the greases of the present invention to achieve a 30 minute or higher rating in the previously described test: this is an optimum condition which is quite unexpected for these types of materials.

Thus, the compositions of the present invention are capable of passing the appropriate tests for obtaining suitable grease compositions for filling fiber optic cable. These tests include a syneresis observation, an 80°C drip test, and a bleeding test utilizing a 0.1 millimeter penetrant at 25°C.

A conventional optical fiber buffer tube or cable includes a plurality of glass fiber cores, each of which typically has a polymerized coating thereon for moisture protection. These fiber cores are color coded so that operators can select the proper ones for splicing or other connections. Thus, a pigmented material, usually of an uncrosslinked PVC material, is applied to the exterior of each fiber core to impart a desired color thereto. The fiber cores are collected and placed into a cable. Thus, the cable grease must be one which is compatible with the ink. For

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- 11 -

example, inks are soluble in certain polyols, and can "run" or dissolve therein. To minimize this problem the polyol should have a molecular weight of at least 4,000 and preferably at least 6,000 for compatibility with these types of ink.

A syneresis observation at ambient temperature is conducted as follows: the formulations are prepared, retained in a suitable container, and observed for oil separation over a period of one month. The formulations of the instant invention exhibit no syneresis over a period of at least six months; it is unlikely that any syneresis will be encountered for longer times of use of the grease.

The 80° drip test is described as follows:

1. Use a 12 inch long buffer tube;
- 15 2. Insert three 12 inch long optical fibers into the tube.
3. Fill the tube with the grease to be tested by injecting the sample of the composition with a 5 cc syringe. No air should be trapped in the tube;
- 20 4. Place the tube in a horizontal position for 2 hours at room temperature;
5. Place the tube in a horizontal position for 2 hours at 80°C (A forced air oven is preferably used);
- 25 6. Clean any amount of grease that comes out of the tips of the tube due to thermal expansion;
7. Weigh a clean, empty aluminum dish in grams (W1);
8. Place the tube in a vertical position at 80°C;
9. Place the aluminum dish under the tube in such a way that the tip of the tube is a few millimeters from the center of the bottom of the dish;
- 30 10. Leave the system at 80°C for 24 hours;
11. Reweigh the aluminum dish in grams (W2). Inspect the dish for any traces of liquid;
12. The difference in weight (W2 - W1) is the dripping reading in grams.
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The paper bleeding test is described as follows:

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- 12 -

MATERIALS

1. 5 ml syringe
2. 11 cm diameter, type 1 filter paper
3. Pyrex watchglass (12 cm diameter)
- 5 4. 600 ml Pyrex beaker
5. Lab spatula
6. Analytical balance
7. Tweezers
8. Scissors
- 10 9. Forced draft oven set to 80°C

PROCEDURE

1. Load the grease compound into the syringe with a spatula. Slowly press the plunger to eliminate air bubbles.
2. Cut a 1 in. by 1 in. filter paper square; weight 15 (WT 1) and record (to 0.0001 grams).
3. Slowly apply 1 ml of the compound from the syringe onto the filter paper square in a circular dab. (Leave some room around the edges to allow the dab to spread.) Weigh this "sample square" and record this value as WT 2.
- 20 4. Weigh an 11 cm diameter filter paper circle (WT 3), and place it on the watchglass. Put the "sample square" on the center of the filter paper, and cover with a 600 ml beaker.
5. Let the sample lie undisturbed at room temperature 25 for 16 hours.
6. Weigh the sample square (WT 2A) and the large filter paper circle (WT 3A).
7. Replace the sample square under the beaker, and place the entire assembly in the oven. Do not disturb for 24 30 hours.
8. Remove from the oven and allow to cool for 5 minutes on a marble surface. Weigh the sample square (WT 2B) and the filter paper circle (WT 3B). Note any color changes.
9. Discard sample square and filter paper.
- 35 10. When handling the sample square and the filter paper circle, use only tweezers. Take care to keep moisture and all foreign particles away from the sample square.

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- 14 -

Examples 1-3

The following samples were prepared for testing according to the modified Belcore test.

5	COMPONENT	EXAMPLE (in parts per weight)		
		<u>1</u>	<u>2</u>	<u>3</u>
	Polypropylene Glycol 4000 mol. wt.	89	87	87
	Silica particles Cab-O-Sil TS-720	10	10	10
10	Antioxidant			
	Irganox 1076	1	3	-
	Irganox 245	-	-	3
	Belcore Test Results (minutes)	1.6	7.9	36

15 These tests show the unexpected performance achievable with the Irganox 245 antioxidant, whereby the use of three parts of this component enables the grease to withstand 36 minutes in the test. In general, however, the present invention discloses that greater amounts of antioxidant are
20 needed compared to those taught by the prior art (e.g., by U.S. Patent 4,839,970) in order to achieve the desired level of performance in the Belcore test. However, one skilled in the art can select the optimum amount of any particular antioxidant by routine testing.

25 Example 4

The following examples were prepared using higher molecular weight polyols that have a reduced level of mono unsaturated compounds. The specific procedure is as follows:
30 2.5 g (1%) of the antioxidant (Irganox 245) is dissolved in 222.5 g (89%) of polyol on a hot plate. The mix is cooled to room temperature and blended with 25 g (10%) silica (Cabot 720) until homogeneous. The mix is then taken out of the blender and milled twice on a three roll mill. Three fibers
35 were tested in each grease as described above. Also performed was a paper oil bleeding test with the same greases. POLYOLS: Arco R-1857 (2,000 MW diol); Arco R-1885

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- 16 -

THE CLAIMS



What is claimed is:

1. A buffer tube gel consisting essentially of about
5 75 to 95 parts by weight of a polyol having a molecular
weight of at least 4000 and a reduced content of unsaturated
mono compounds; about 2 to 15 parts by weight of a thickening
agent; and about 1 to 5 parts by weight of an antioxidant so
that the composition can withstand at least about 10 minutes
10 at 190°C in a pure oxygen environment.
2. The gel of claim 1 wherein the thickening agent
comprises colloidal particles.
3. The gel of claim 2 wherein the colloidal particles
are silica, clay or a mixture thereof.
- 15 4. The gel of claim 2 wherein the colloidal particles
comprise hydrophobic fumed silica, precipitated silica, clay
or a mixture thereof.
5. The gel of claim 2 wherein the colloidal particles
are present in an amount of about 4 to 12 parts by weight.
- 20 6. The gel of claim 1 wherein the polyol is present
in an amount of between about 80 and 95 parts by weight and
has a molecular weight of between 4,000 and 25,000.
7. The gel of claim 1 wherein the polyol has a
molecular weight of between about 6,000 and 15,000 and a
25 content of mono unsaturated compounds of no greater than
0.05 meq/g.
8. The gel of claim 1 wherein the polyol has a
molecular weight of between about 8,000 and 12,000 and a
content of mono unsaturated compounds of no greater than
30 0.03 meq/g.
9. The gel of claim 1 further consisting essentially
of up to about 15 parts by weight of an elastomer to act as a
bleed inhibitor.
10. The gel of claim 9 wherein the elastomer is a
35 polyurethane elastomer.

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