HYDRAULIC BRAKE FLUIDS

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2 Claims

ABSTRACT OF THE DISCLOSURE

A hydraulic brake fluid consisting essentially of a poly(oxyethylene-oxy-1,2-propylene) glycol monomethygly etyl ether having an average molecular weight of from about 160 to about 230 and the formula

\[ \text{CH}_3-O-(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CH}_2\text{CHO})_m-\text{H} \]

wherein \( n \) averages from 1 to 3.7, \( m \) averages from 0.3 to 3 and the average total of \( n \) and \( m \) is from 3.1 to 3.9 and the oxyethylene groups constitute from 65 to 90% by weight of the total weight of oxalkylene groups present.

This application is a continuation-in-part of Ser. No. 638,557, now abandoned.

The present invention relates to a novel hydraulic brake fluid and to the method of applying pressure to a hydraulic brake by the use of that fluid.

In these days of growing use of automotive vehicles of greater weight and horsepower and operation thereof at higher speeds and throughout the winter in areas having very cold winters, there is an ever greater need for hydraulic brake fluids which not only have a higher boiling point and a suitable viscosity at high temperatures as well as being low in rubber-swelling but which also have a relatively low viscosity at low temperatures and a low freezing point.

Conventional hydraulic brake fluid compositions have very high viscosity at low temperatures which results in poor brake operation at those temperatures. In order to overcome this defect, additional components, such as diethylene glycol monooxyether, ethylene glycol mono-butyether and the like may be added to the hydraulic brake fluids as a viscosity depressant. However, if these are added in amounts sufficient for lowering viscosity, the boiling point of the fluid is depressed to an undesirable degree.

Also in the prior art there has been proposed for use as hydraulic brake fluids polyoxyalkylene glycol monomethyl ethers of high boiling point and somewhat lower than conventional viscosity at low temperatures. In this respect, reference may be made to U.S. Pat. Nos. 3,062,747 and 3,324,035.

According to the present invention, there are provided as hydraulic brake fluids polyoxyalkylene glycol monomethyl ethers superior to those provided in the aforementioned two patents, particularly with respect to having low viscosity at very low temperatures, while at the same time meeting the other requirements for hydraulic brake fluids. More particularly, there is provided according to the invention a hydraulic brake fluid consisting essentially of a poly(oxyethylene-oxy-1,2-propylene) glycol monomethyl ether having an average molecular weight of from about 160 to about 230 and the formula

\[ \text{CH}_3-O-(\text{CH}_2\text{CH}_2\text{O})_n-(\text{CH}_2\text{CHO})_m-\text{H} \]

wherein \( n \) averages from 1 to 3.7, \( m \) averages from 0.3 to 3 and the average total of \( n \) and \( m \) is from 3.1 to 3.9 and the oxyethylene groups constitute from 65 to 90% by weight of the total weight of oxalkylene groups present.

The block character of the polymers represented by the above formula and the arrangement of the ethylene oxide and propylene oxide units in the molecule, also as represented in the above formula, are critical to the present invention. In this regard, in the preparation of the polyoxyalkylene glycol monomethyl ethers which serve as brake fluids according to the invention, a procedure is always followed such that this particular block copolymer structure will result. Thus, for example, in conventional processes for the preparation of polyoxyalkylene glycol monomethyl ethers, the procedure is to be followed for the preparation of the block copolymers according to the invention is initially to carry out the addition reaction of ethylene oxide with methanol to form a polyoxyethylene glycol monomethyl ether and then to carry out the addition reaction with that ether of propylene oxide. These reactions are ordinarily carried out in the presence of a catalytic amount of an alkaline catalyst, such as sodium hydroxide or potassium hydroxide, under moderate pressure and at a reaction temperature of about 80°C. to about 140°C. If desired, the reaction mixture may subsequently be subjected to neutralization, dehydration and elimination of low boiling materials.

The preparation of polyoxyalkylene glycol monomethyl ethers according to the invention for hydraulic brake fluid use is illustrated by the following example:

**EXAMPLE**

0.8 gram of potassium hydroxide is added to 32 grams of methanol and the mixture is stirred at 60°C. under a nitrogen atmosphere until a clear solution is formed, whereupon this solution is heated to 100°C. To the solution is added 106.5 grams of ethylene oxide (2.42 moles) slowly while maintaining the temperature at 100°C and the mixture is stirred at that temperature under a pressure of 2 to 4 kg/cm² for 2 hours. Thereafter, 57.3 grams of 1,2-propylene oxide (0.98 mol) is added slowly and reacted under the same conditions. After the reaction is completed, the polymer product is distilled at a reduced pressure of 5 mm. Hg at 65°C. and any low boiling components are thus eliminated. The residue is neutralized by the addition thereto of a 5% by weight sulfuric acid solution and then dehydrated under reduced pressure. To the dried residue, 3% by weight of magnesium silicate absorbent (Allegheny Industrial Chemical Co.) is added and further drying is carried out at reduced pressure and a temperature of 80°C. The absorbent is then separated from the now dry polymer product.

The products produced in the preparation of polyoxyalkylene glycol monomethyl ethers by this method reflect exactly the mol ratios of the reactants.

In the following table, there is set forth a comparison of polyoxyalkylene glycol monomethyl ethers within the scope of the invention with polyoxyalkylene glycol monomethyl ethers outside the scope of the invention. Samples within the scope of the invention are distinguished from samples outside the scope of the invention by the employing of "C" as a prefix to designate the samples outside the scope of the invention, i.e., comparative samples. It is noted that according to Japanese Industrial Standard K2233, for hydraulic brake fluids the following are some of the requirements: viscosity at −40°C., less than 1800 centistokes; viscosity at 50°C., greater than 4.2 centistokes; boiling point, greater than 190°C.; and rubber swelling, 0.5 to 5.0%. The corresponding specifications of the Society of Automotive Engineers (U.S.), as referred
3,528,920

to in U.S. Pat. No. 3,062,747, are quite similar, namely: maximum viscosity at -40°F, 1800 centistokes; minimum viscosity at 130°F, 4.0 centistokes; minimum boiling point, 375°F; and rubber swelling, 4.0% (maximum). Of course, to exceed these requirements, as, for example, by providing a lower viscosity at very low temperatures, is highly desirable.

Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-10</th>
<th>C-12</th>
<th>C-13</th>
<th>C-14</th>
<th>C-15</th>
<th>C-16</th>
<th>C-17</th>
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A comparison of viscosities at -40°C for sample 1 with sample C-2 to C-5, for sample 8 with sample C-15, for sample 11 with sample C-16 and for sample 14 with C-17 clearly shows the importance of the teachings of the present invention to first react with the methanol the ethylene oxide and then add to the reaction mixture propylene oxide and subsequently not to add any more ethylene oxide, thereby to provide a block copolymer of the above formula in order to obtain particularly low viscosities at very low temperatures. The comparison of sample 1 with samples C-2 to C-5 is particularly significant in showing the criticality of first reacting the ethylene oxide with the methanol before adding thereto propylene oxide and subsequently not adding thereto any more ethylene oxide. In U.S. Pat. No. 3,062,747, the main thrust of the disclosure is to polyoxyalkylene glycol monomethyl ethers which are block copolymers, i.e., which are prepared by reacting the alkyl alcohol with a mixture of alkylene oxides. There is brief mention that the reaction of the alkyl alcohol with ethylene oxide and 1,2-propylene oxide may be sequential but there is no recognition whatever of the criticality of the sequence being ethylene oxide-propylene oxide as in the present invention rather than propylene oxide-ethylene oxide or ethylene oxide-propylene oxide-ethylene oxide or propylene oxide-ethylene oxide-propylene oxide.

A comparison of the viscosities at -40°C of sample 1 with samples C-6 and C-7, of sample 8 with samples C-9 and C-10, and of sample 11 with samples C-12 and C-13 clearly shows the importance of the obtaining of particularly low viscosity at very low temperatures of providing that the alkylene oxide to methanol molar ratio be less than 4.0; it is seen that this becomes particularly important as the oxy-1,2-propylene weight ratio is increased. In contrast to this aspect of the present invention, in U.S. Pat. No. 3,324,035, while among the samples therein are included polyoxyalkylene glycol monomethyl ethers in which first ethylene oxide and then 1,2-propylene oxide is added to methanol, in certain specific embodiments thereof, it is to be understood that the scope of the invention is not to be considered limited by the specific embodiments disclosed but rather is to be determined by the reference to the appended claims.

What we claim is:

1. A hydraulic brake fluid consisting essentially of a poly(oxyethylene-oxy-1,2-propylene) glycol monomethyl ether having an average molecular weight of from about 160 to about 230 and the formula

\[
\text{CH}_n\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_{m-1}\left(\text{CH}_2\text{CHO}\right)_{m-1}\overline{\text{H}}
\]

wherein \( n \) averages from 1 to 3.7, \( m \) averages from 0.3 to 3 and the average total of \( n \) and \( m \) is from 3.1 to 3.9 and the oxyethylene groups constitute from 65 to 90% by weight of the total weight of oxyalkylene groups present.

2. In a method for applying pressure to a hydraulic brake through a hydraulic brake fluid, the improvement wherein the hydraulic brake fluid consists essentially of a poly(oxyethylene-oxy-1,2-propylene) glycol monomethyl ether having an average molecular weight of from about 160 to about 230 and the formula

\[
\text{CH}_n\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_{m-1}\left(\text{CH}_2\text{CHO}\right)_{m-1}\overline{\text{H}}
\]

wherein \( n \) averages from 1 to 3.7, \( m \) averages from 0.3 to 3 and the average total of \( n \) and \( m \) is from 3.1 to 3.9 and the oxyethylene groups constitute from 65 to 90% by weight of the total weight of oxyalkylene groups present.

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260—615