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VISCOSITY HYDRAULIC FLUID

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1 Claim. (Cl. 252—73)

The invention here presented is a new type of hydraulic fluid suitable for automobile brakes, airplane control mechanism and the like in locations in which the hydraulic fluid must be operative over a wide range of ambient temperatures; the composition of the invention containing a base fluid together with a viscosity booster and a viscosity reducer, as well as various other additives.

Many hydraulic fluid compositions are known to the art. The earliest improved fluids contained castor oil and a high boiling diluent in conjunction with various inhibitors. Later modifications included blown castor oil and castor oil-glycol reaction products. However, low-temperature usefulness, gum formation, and other factors led the art to find other materials.

A survey of the field of organic liquids which could possibly be suitable for use as hydraulic fluids from the standpoint of viscosity at high and low temperatures, low volatility and lack of corrosive action on metals, etc., immediately shows the paucity of compounds which are acceptable from the standpoint of attack on, or the swelling of rubber. The vast majority of otherwise acceptable liquids including esters, ketones, halides, acetals, acids, amines, ethers, hydrocarbons, etc., have far too great a degree of rubber attack. As a result of many studies, it has been shown that very few organic liquids are acceptable in this respect. Outstanding among those acceptable are certain alcohols and ether alcohols having a favorable oxygen to carbon ratio and distribution in the molecule, that is, an advantageous structural configuration.

To be suitable for use as a hydraulic fluid, a liquid composition must have the following characteristics: It must not exhibit too great a viscosity change under a wide range of temperatures. It must be reasonably viscous at the highest temperatures for which use it is contemplated, and it must remain fluid at the lowest temperatures likely to be encountered in automotive use, as at —50° F. In general, fluids which have a viscosity of at least 5 c.p.s. at 130° F. and a viscosity no greater than 1500 c.p.s. at —40° F. are considered suitable. A further requirement is that the fluid must have a lubricating action on most parts of the braking system in order to prevent undesirable wear during use. In this respect, fluids which allow the moving parts to wear not more than .001 of an inch during 200,000 braking cycles are usually considered adequate.

It is a primary prerequisite that a suitable fluid should not unduly attack any of the rubber or metal parts in the braking system. The attack on rubber is so undesirable that extensive research has gone into the manufacture of fluids which show a minimum of swelling or softening action on rubber. As to the attack on the metal parts, the fluid must have the correct pH value, usually in the range of 8.5 to 9.5. In this range, protection is obtained against the attack on acid sensitive metals, such as iron, tin, aluminum, zinc, etc., while this degree of alkalinity is not sufficiently high to cause the attack on the alkali sensitive materials, such as aluminum and zinc.

It is a further prerequisite that the fluid should have as low a volatility as is practical to achieve, in order to eliminate the possibilities of evaporation from the brake system storage unit as well as to prevent the undesirable evaporation of the fluid from the areas adjacent to hot braking surfaces.

In the past, these objections have been met, in part, through the use of various mixtures of aliphatic alcohols, and glycerine esters, such as castor oil, soya oil, etc., or with mixtures of various ether alcohols, such as, 2-butoxyethanol, the monoethyl ether of diethylene glycol and various polymers of ethylene oxide, propylene oxide, or interpolymers of ethylene and propylene oxides. The first-mentioned type consisting of alcohols and natural oils has certain shortcomings, like the lower aliphatic alcohols.

The degree of attack on rubber rapidly increases with the increase in chain length of the alcohol used in practice. It has been found that alcohols higher than the butyl alcohols cannot be used because of excessive attack on, or swelling of, the rubber parts in the braking system. The alcohols up to and including the butyl alcohols have, unfortunately, rather low boiling points and hydraulic brake fluids prepared with them show an undesirably high degree of volatility. In addition, the presence of natural glycerine esters, such as, castor oil and soya oil, and the like, is undesirable because, as is well known, these substances are subject to oxidation and in time form undesirable gummy materials in the system.

Because of the disadvantages, considerable effort has been made to develop improved fluids for hydraulic systems. One composition which has been suggested to overcome these disadvantages, comprises essentially a mixture of the above-mentioned components: "Carbitol," butyl 'Cellosolve," and interpolymers of ethylene oxide and propylene oxide.

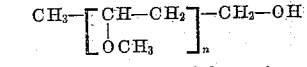
While fluids of this type are better than mixtures of alcohols and natural oils, they also have certain shortcomings. It has been established that the relatively low boiling points of two of the components used in such fluids, namely, butyl "Cellosolve" and "Carbitol," prevent such compositions from being considered for high temperature applications. It has been further established that such compositions will be prone to peroxide formation, a well known shortcoming characteristic of polyoxyethylenes, polyoxypropylenes, and the various interpolymers of ethylene oxide and propylene oxide.

We have found that the foregoing shortcomings and difficulties of the presently utilized fluids, particularly those containing polyoxyalkylenes and interpolymers of alkylene oxides are substantially overcome by employing an alkaline buffered mixture of 3-methoxy-1-butanol and 3,5,x-polymethoxy-1-alkanols as the principal ingredients with or without the presence of minor amounts of auxil-

iary components, such as anti-oxidants, corrosion inhibitors, viscosity regulators, and the like.

To the primary material as above outlined, we then add, according to the present invention, both a viscosity booster and viscosity reducer and find the unexpected phenomenon that under such circumstances the viscosity boosting effect is largely concentrated on the upper temperature range, whereas the viscosity lowering effect is largely concentrated on the lower end of the temperature range, resulting in a very much higher viscosity index of the finished fluid, and an adequate viscosity at the top of the temperature range, high enough to be fully satisfactory, and a low enough viscosity at the lower end of the temperature range, sufficiently low to prevent freezing of the mixture. In addition, the various components used exert no attack upon either metal or rubber in the system, do not precipitate or separate in any way, and do not volatilize out of the mixture.

The 3-methoxy-1-butanol and 3,5,x-polymethoxy-1-alkanols utilized as the major components in the mixture of the present invention are characterized by the following general formula:



where n represents an integer of from 1 to 10.

The alkanols characterized by the foregoing formula are prepared by reacting, in the known manner, vinyl methyl ether with methanol to yield dimethyl acetal and reacting the latter with additional vinyl methyl ether. The reaction ratio of methanol to vinyl methyl ether may vary from 2.0 to 1.0 to 20 to 1, preferably from 2.0 to 1 to 5.0 to 1, respectively. The crude acetal is then distilled to yield individual components which may be subjected to simultaneous hydrolysis-reduction to yield individual alkoxyalkanols such as 3-methoxy-1-butanol; 3,5-dimethoxy-1-hexanol; 3,5,7-trimethoxy-1-octanol; 3,5,7,9-tetramethoxy-1-decanol; 3,5,7,9,11-pentamethoxy-1-dodecanol and polymethoxy-1-alkanols as described in Examples 1, 4 and 5 of United States Patent 2,618,663. Alternatively, the crude acetal may be subjected to simultaneous hydrolysis-reduction as described in Example 3 of said patent and the mixture of alkanols employed as such in accordance with the present invention. The mixture of alkanols may be distilled to yield the individual components of the alkanols and the individual components may then be blended in the ratio of 20 to 40% of 3-methoxy-1-butanol and 60 to 80% of the remaining 3,5,x-polymethoxy-1-alkanols.

The alkanols are colorless liquids characterized by partial solubility in water, especially the methoxy derivatives which are completely soluble in water, and by complete miscibility in organic solvents, such as aliphatic alcohols, ketones, esters, glycol ethers, aromatic solvents, and aliphatic petroleum ethers and naphthas. The complete miscibility in aliphatic hydrocarbons is in sharp distinction to the polyethylene glycols which are virtually insoluble in these solvents.

All of the alkanols in the mixture, i.e., the 3-methoxy-1-alkanol and 3,5,x-polymethoxy-1-alkanols, when in contact with rubber have a very low swelling action thereon, considerably less than that tolerated in commercially available hydraulic fluids. In addition they possess an unusual inertness to oxidation attack. It is believed that the arrangement of atoms in the alkanols of the mixture contributes to this property. This is unexpected since it has been recognized by the art, as shown in U.S. Patents 2,492,955 and 2,481,278, that polymers of ethylene and propylene oxide have one serious drawback which limits their use as lubricants because the two-carbon-unit between the ether linkage in the polymer chain appears to make the polymer extremely sensitive to oxidation.

It is now found that the simultaneous addition to the above disclosed alkanols of a viscosity booster and a viscosity reducer further improves the performance of the hydraulic fluid. By use of a viscosity reducer in conjunction with a viscosity booster, it has been found possible to achieve the desired viscosity at both reference temperatures. This effect was unexpected because a viscosity booster, by itself, increases the viscosity at both temperatures, and a viscosity reducer, by itself, lowers the viscosity at both temperatures, whereas the use of the two, simultaneously concentrates the viscosity boosting effect onto the upper part of the temperature range, and the viscosity reducing effect onto the lower part of the temperature range.

As viscosity reducers there may be used bis(2-ethoxyethyl) ether, also called diethyl Carbitol, 1,2-diethoxyethane, also called diethyl Cellosolve, 1,1,3,5,X-alkoxyalkanes or compounds of the general formula $C_nH_{2n}+O_m$, butyrolactone and triethyl phosphate.

The exceptional performance obtained by relatively small amounts of what we have termed viscosity reducers was also an unexpected result. One would have expected the type of polyethers that we used as viscosity reducers to have had a deleterious swelling effect upon the rubber parts of the hydraulic brake system, but such was not the case in the concentrations needed to reduce viscosity to desirable values, nor do the materials show an undesirable volatility.

The presence of viscosity reducers, while mainly effective at the low temperature end of the temperature range, also acts to reduce slightly, but undesirably, the viscosity at the high end of the temperature range, that is, at 130° F. the viscosity tends to be substantially below the desired 6.0 c.p.s. Accordingly, we have found it desirable to add to the composition a viscosity booster; for which purpose we have found useful materials, such as methyl vinyl ether polymers, isobutyl vinyl ether polymers, 3-methoxybutyl vinyl ether polymers, interpolymers of isobutyl vinyl ether and cis-9-octadecenyl vinyl ether, various polyhydroxy compounds such as ethylene glycol, propylene glycol, 1,4-butanediol, etc., especially when used in conjunction with complex-forming inorganic salts such as borates, nickel and chromium salts.

The hydraulic fluids prepared in accordance with the present invention possess sufficient lubricity under operating conditions in various climates and extremes of temperatures. Tests have indicated that the lubricity is met by the presence, even in very small amounts, of the higher members of the 3,5,x-polymethoxy-1-alkanols series which are viscous liquids resembling glycerine and the low polyethylene glycols in consistency. These materials are free from gum formation which is a serious drawback to the use of lubricants of the like of castor oil and derived compounds.

The presence in the hydraulic fluid of low boiling diluents either as solvents or decomposition products may result in vapor lock and is, therefore, to be avoided. The lowest member of the alcohol series is 3-methoxybutanol with a boiling point of 159° C. at 760 mm. The presence of the higher members of the series increases the pot temperature at which such a mixture boils and may be varied depending on needs.

The wide solvent power of the 3,5,x-polymethoxy-1-alkanols makes it possible to secure homogeneous solutions on mixing with commercial hydraulic fluids. The water tolerance of the 3,5,x-polymethoxy alkanols is excellent.

The hygroscopicity of the 3,5,x-polymethoxy-1-alkanols is of a lower order than the glycols and polyethylene glycols in the same molecular weight range. Brake fluid mixtures containing these alkanols possess advantages over materials containing the polyethylene glycols.

Inasmuch as mixtures of 3-methoxy-1-alkanols and 3,5,x-polymethoxy-1-alkanols may in themselves serve as hydraulic brake fluids because of their desirable properties, it is at times desirable to fit certain needs to incorporate auxiliary substances, such as anti-oxidants, cor-

rosion inhibitors, viscosity modifiers, buffering agents, and the like.

As anti-oxidants, there may be used any of the materials commonly used to prevent the oxidation of oxidizable organic compounds, such as unsaturated hydrocarbons, e.g., rubber, unsaturated fuels, unsaturated esters, such as oxidizable vegetable oil, ethers, vinyl compounds, etc. Examples of these anti-oxidants are para-tertiary butylcatechols, hydroquinones, and various morpholine derivatives, such as N-phenyl-morpholine, N-(p-hydroxyphenyl)morpholine, N,N-diphenyl-p-phenylenediamine, diphenylamine, N-phenyl—naphthylamine, p-phenylphenol, o-phenylphenol, di-p-methoxydiphenylamine, m-toluylenediamine, various condensation products of aldehydes with aromatic amines: acetone-aniline and acetaldehyde-aniline and butylaldehyde-aniline, aldol-naphthylamine, hydroquinone monobenzyl ether, and isopropoxydiphenylamine.

As corrosion inhibitors, we may use inorganic nitrites, such as sodium nitrites, etc., organic nitrites, such as tertiary amine nitrites, chromates, such as sodium chromates and the like, inorganic boron compounds, such as sodium tetraborate, organic boron compounds, such as triethanolamine borate and the like, certain sulfur compounds, such as dialkylthiourea, mercaptans, organic disulfides, diarylamine phosphates, such as diphenylamine phosphate, long chain alkyl sulfonamide acetate sodium salt, phosphites, such as sodium phosphite, organic phosphoric acid and organic derivatives of phosphorous acids, such as benzenephosphenic acid, etc.

In addition to the components named above, auxiliary substances, such as viscosity modifiers, buffering agents, and coloring agents may be optionally added.

As viscosity modifiers, there may be used various polyhydroxy compounds, such as glycol, glycerine, 1,2,4-butanetriol, 1,4-butanediol, propylene glycol, etc., especially when used in conjunction with complex forming inorganic salts, such as borax, nickel and chromium salts, various polymeric materials, such as polyvinyl methyl ether, polyvinyl butyl ether, interpolymers of isobutyl vinyl ether and oleyl vinyl ether, various polyacrylates, such as polylauryl acrylate, polyolefines, such as polyisobutylene or interpolymers thereof, etc.

As buffering agents, the following inorganic compounds are useful: borates, such as sodium tetraborate, sodium metaborate, ammonium and organic borates, such as triethanolamine borates, sodium phosphite, tetraborate and the like, inorganic phosphate, such as the various sodium phosphates, such as trisodium o-phosphate, disodium hydrogen phosphate, sodium pyrophosphate, organic phosphate, e.g., triethanolamine phosphate, quinoline phosphate, salts of alkaline metals, organic acids, such as sodium acetate, sodium citrate, sodium benzoate, potassium tartrate and the like, and mixtures thereof to yield (when admixed in the brake fluid composition) a pH above 7 and not exceeding a pH of 11.

In order to dissolve sodium borate in the hydraulic brake fluid composition, it was found advantageous to use a solubilizing agent, such as ethylene glycol, in the formation. However, glycol is not essential in the hydraulic brake fluid. This agent can be omitted in compositions in which other buffers are incorporated. Also in place of ethylene glycol in borax formations, other solubilizing agents, such as "Carbitol" can be used.

The choice of coloring matter is not of critical importance in the finishing of the hydraulic brake fluid provided it does not cause a deleterious effect on the viscosity of the fluid or exhibit corrosive action on the rubber or metal parts of the braking system. Most dyestuffs are acceptable on these accounts since in most cases they are used only in minute quantities. Where coloring material or dyestuffs are added for identification or other purposes, the sole requirement is that the dyestuff be sufficiently soluble in the hydraulic fluid. It has been found that dyestuffs of any class may be used. These include vat dyestuffs, diphenylamine derivatives, azo dyes, triphenylmethane dyes, and the like.

From the standpoint of rubber swelling, we have found that the proportions of 3-methoxy-1-butanol in the mixture must range from 20 to 40% to yield good results. The 3-methoxy-1-butanol does not appear to give good results when employed alone or when incorporated with the foregoing auxiliary substances. An unusual and unexpected feature of the present invention is that the mixture, in addition to 20–40% of 3-methoxy-1-butanol, must contain 60 to 80% of at least one of the individual 3,5,x-polymethoxy-1-alkanols or a mixture thereof to yield good results. In these proportions the brake fluid does not cause any swelling or disintegration of rubber and completely eliminates brake failure through loss of fluid. Moreover, the blending of the individual alkanols of the mixture makes it readily possible to fit prescribed commercial needs or requirements of certain brake fluids with respect to non-volatility, viscosity, lubricity, and miscibility with auxiliary components. For general all around good results particularly in automotive hydraulic brake fluids, we have found that the following blend is ideal:

	Percent
3-methoxyl-1-butanol	20–40
3,5-dimethoxy-1-hexanol	25–35
3,5,7-trimethoxy-1-octanol	15–30
3,5,7,9-tetramethoxy-1-decanol	5–20
3,5,7,9,11-pentamethoxy-1-dodecanol	2.5–10
3,5,7,9,11,13- and higher	0.5–3.5

The higher polymethoxy alcohols of the type 3,5,7,9,-11,13,x-polymethoxy-1-alkanols, i.e., wherein n in the above formula equals 6 or greater, may be used in the range of 60 to 80% to 20 to 40% of 3-methoxy-1-butanol to yield a mixture which gives excellent results with respect to prevention of rubber swelling. A mixture of 20% of 3-methoxy-1-butanol and 80% of 3,5-dimethoxy-1-hexanol is comparable to a mixture of 40% of 3-methoxy-1-butanol and 60% of 3,5-dimethoxy-1-hexanol. Both mixtures possess sufficient lubricity under operating conditions in various climates and extremes of temperatures.

The viscosity-temperature relationships for any of these given base fluids is often not so good as desired. Two common reference temperatures used in characterizing these fluids as to viscosity are —40° F. (—40° C.) and 130° F. (54.4/9°C.). It is desirable to keep the viscosity at —40° F. as low as possible, and kinematic viscosities of 1000 centistokes or less are highly desirable to insure dependable operation of the hydraulic brake system in areas where such a temperature is occasionally reached. Usually, a base fluid will have a kinematic viscosity nearer 2000 centistokes, which is considered too high for reliable operation of the brake system. Hence, our viscosity reducers are extremely useful.

At the higher reference temperature, 130° F., it is desirable to maintain as reasonably high a viscosity as possible in order to minimize the tendency of the fluid to seep out of the hydraulic system. Most base fluids do not have very high viscosities at 140° F., for instance a kinematic viscosity of approximately 5 centistokes would be representative. The industry prefers the kinematic viscosity at 140° F. to be in excess of 6 centistokes, preferably 10 centistokes or higher. Viscosity boosters have been used to accomplish this. Examples are blown castor oil and interpolymers of ethylene oxide and propylene oxide.

As illustrative of the preparation of hydraulic brake fluids in accordance with the present invention, the following examples are given. The parts are by weight.

Example I

To 88.6 parts of a mixture of 3,5,x-polymethoxy

alkanols (prepared in accordance with Example 3, United States Patent 2,618,663), containing by weight the following components:

	Percent
3-methoxy-1-butanol	35.0
3,5-dimethoxy-1-hexanol	30.0
3,5,7-trimethoxy-1-octanol	22.0
3,5,7,9-tetramethoxy-1-decanol	7.5
3,5,7,9,11-pentamethoxy-1-dodecanol	3.6
Higher homologues characterized by the above formula wherein *n* equals 6 or more	2.9

A solution of 1 parts of borax, 0.3 part of N-phenylmorpholine, and 0.1 part of an organic nitrite corrosion inhibitor (sold under the trade name "V.P.I. 260 Crystals") in 10 parts of ethylene glycol was added. The resulting mixture was stirred until it became a homogeneous solution.

The viscosity of this mixture was then determined at temperatures of —40° F. and +130° F. and appropriate amounts of a viscosity booster in the form of methyl vinyl ether polymer, and the viscosity of the mixture was determined.

The results are shown in the following table together with the percent increase in viscosity:

Sample	Absolute viscosity in centipoises at —40° F. (—40° C.)	Kinematic viscosity in centistokes at 130° F. (54.4° C.)
3:1 polymethoxy-1-alkanols	470	3.32
94 g. 3:1 polymethoxy-1-alkanols	970	6.28
2 g. methyl. vinyl ether polymer		
Percent increase in viscosity	106	89

The portion of the same base fluid was then mixed with various amounts of substances including diethyl Carbitol, diethyl Cellosolve, 1,1,3-trimethoxybutane and 1,1,3,5-tetramethoxyhexane and the viscosities of the resulting mixtures were determined at —40° F. and at 130° F. The results are shown in the following table in which there is also shown the percentage lowering of viscosity, obtaining:

Property	47.50 parts 5:1 polymethoxy-1-alkanols				
	5:1 polymethoxy-1-alkanols	2.50 parts diethyl Carbitol	2.50 parts diethyl Cellosolve	2.50 parts 1,1,3,-Trimethoxybutane	2.50 parts 1,1,3,5-tetramethoxyhexane
Absolute viscosity in centipoises at —40° F. (—40° C.)	37,000	15,000	11,000	18,000	23,000
Kinematic viscosity in centistokes at 130° F. (54.4° C.)	12.2	9.50	8.86	9.92	12.2
Percent lowering of viscosity of 5:1 polymethoxy-1-alkanols by viscosity reducer:					
40° F		59.5	70.3	51.4	37.8
130° F		22.4	27.4	18.7	0

The viscosity booster and viscosity reducer substances were then combined in an appropriate amount of base fluid, as shown in the following table, and the viscosities determined at —40° F. and 130° F. The results are shown in the following table:

Formulations		Kinematic viscosity in centistokes at—	
Percent	Ingredient	—40° F. (—40° C.)	130° F. (54.4° C.)
0.3	4-phenylmorpholine	1,700	4.93
0.3	Anhydrous sodium tetraborate		
5.0	Distilled ethylene glycol		
0.2	Nuodex X-545		
94.2	3:1 polymethoxy-1-alkanols		
0.3	4-phenylmorpholine	1,450	6.57
0.60	Sodium tetraborate pentahydrate		
6.06	"Carbitol"		
2.00	Methyl vinyl ether polymer		
10.00	Diethyl "Carbitol"		
81.04	3:1 polymethoxy-1-alkanols		
2.0	Methyl vinyl ether polymer	910	6.10
1.5	Agent 460-BR		
5.0	1,1,3,5-tetramethoxyhexane		
91.5	3:1 polymethoxy-1-alkanols		

Thus the process of the invention adds to a viscous fluid designed to operate over a wide temperature range, a viscosity booster and a viscosity reducer, which combination shows the unexpected property of concentrating the viscosity raising effect on to the higher part of the temperature range, and the viscosity lowering effect on to the lower portion of the temperature range.

While there are above disclosed but a limited number of embodiments of the process of the invention it is possible to provide still other embodiments without departing from the inventive concept herein disclosed, and it is therefore desired that only such limitations be imposed upon the appended claim as are stated therein or required by the prior art.

The invention claimed is:

A hydraulic power fluid consisting essentially of a major amount of at least 80% by weight of a mixture of polymethoxy alcohols having the general formula

$$CH_3-\left[CH(OCH_3)-CH_2\right]_n-CH_2-OH$$

wherein *n* represents an integer of from 1 to 10, said poly methoxy alcohol mixture consisting essentially of 20–40% by weight of 3-methoxy-1-butanol, 25–35% by weight of 3,5-dimethoxy-1-hexanol, 15–30% by weight of 3,5,7-trimethoxy-1-octanol, 5–20% by weight of 3,5,7,9-tetramethoxy-1-decanol, 2.5–10% by weight of 3,5,7,9,11-pentamethoxy-1-dodecanol, and 0.5–3.5% by weight of 3,5,7,9,11,13- and higher homologs of said alcohols, and a minor amount of viscosity reducing agent selected from the group consisting of the ethyl ethers of ethylene glycol and diethylene glycol and 1,1,3,5-tetramethoxy hexane, and a minor amount of a methyl vinyl ether polymer as a viscosity boosting agent.

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