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METHOD OF INHIBITING SQUAWKING IN MINERAL OIL TRANSMISSION FLUIDS

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This invention pertains to improved coolants and lubricants for use in power or force transmission mechanisms. More particularly this invention relates to mineral lubricating oil compositions for use in an apparatus by means of which mechanical forces are transmitted or absorbed such as in automotive transmissions, hydraulic brakes, clutches, and various other mechanical equipment.

In simple power transmitting mechanisms such as torque converters, among the various functions of the fluid employed therein is that of a heat transfer medium. However, in the more complicated automotive transmissions, fluid brake mechanisms and the like which also contain wet clutches, planetary gears and hydraulic control mechanisms, additional problems involving adequate cooling and lubrication are involved. Rigorous requirements have been set up to qualify fluids for this service. These include wide temperature stability at both high and low temperatures and a pour point of —30° F. maximum to insure proper pumpability and fluidity at low temperatures. The fluid must not have a detrimental effect on parts with which it comes in contact such as metal surfaces e.g., copper and solid organic surfaces such as organic resins and the like. The fluid must possess excellent anti-frictional and extreme pressure characteristics to afford proper lubrication of gears, clutch plates and other parts of automotive equipment. Also, the fluid must not cause chattering, squawking, squealing or produce other noises caused by the stick-slip phenomenon of clutch plates or other parts of these mechanisms.

Now, in accordance with the present invention, a lubricating and cooling power transmission fluid is provided, which satisfactorily meets the above requirements, and which consists essentially of a major amount of a mineral lubricating oil containing a minor amount sufficient to prevent chattering or squawking and stabilize the fluid composition, of an oil-soluble mono- or di-alkane phosphinic acid containing from 4 to 20, and preferably from 12 to 18, carbon atoms in the alkyl radical which can be straight or branched-chain.

Suitable alkane phosphinic acids include oil-soluble straight and branched-chain alkane phosphinic acids and include n-octane phosphinic acid, di-2-ethylhexyl phosphinic acid, dodecane phosphinic acid, pentadecane phosphinic acid, hexadecane phosphinic acid, octadecane phosphinic acid, dinonane phosphinic acid, didecane phosphinic acid, didodecane phosphinic acid, ditetradecane phosphinic acid, dioctadecane phosphinic acid, methylhexadecane phosphinic acid, and butyltetradecane phosphinic acid, and mixtures thereof.

The alkane phosphinic acids can be prepared by a number of suitable means such as described in Kosolapoff's "Organo Phosphorus Compounds" (John Wiley and Sons, Inc., 1950); Arbuzov (J. Gen. Chem. (U.S.S.R.), 4, 898–900 (1934); Kharasch et al. (J. Am. Chem. Soc. 67, 1864 (1954)); and U.S. Patent 2,724,718.

The following examples will serve to illustrate methods of preparing additives of this invention:

EXAMPLE I

Octane phosphinic acid

About equimols of sodium hypophosphite and 1-octene were added to methanol containing a catalytic amount of 2,2-bis(tert.-butyl peroxy) butane and the mixture reacted in an enclosed pressure-resistant vessel at a temperature of about 120° C. to 130° C. for about two hours under agitation. At the end of the reaction, a single liquid phase was observed which was sodium octane phosphinate dissolved in the methanol; acidification yielded octane phosphinic acid, $C_8H_{17}PH(O)OH$.

EXAMPLE II

Tetradecane phosphinic acid

About equimols of sodium hypophosphite and 1-tetradecent were added to methanol containing a catalytic amount of 2,2-bis(tert.-butyl peroxy)butane and the mixture reacted in an enclosed pressure-resistant vessel at around 210° C. At the end of the reaction the product was acidified as above, water-washed and the organic phase was dried. The crude product can be recrystallized from acetone to yield a major amount of tetradecane phosphinic acid and a minor amount of ditetradecane phosphinic acid and octacosane phosphinic acids having a melting point of 52.0–52.4° C. This entire mixture or the tetradecane phosphinic acid can be recovered by fractional crystallization from n-heptane and used as anti-chatter agents in hydraulic fluids or in other lubricants of this invention.

The oil-soluble alkane phosphinic acids can be used in compositions of this invention in amounts ranging from about 0.001% to about 5% or from 0.001% to 0.5% by weight, and preferably are used between 0.01% and 0.3% by weight.

The base oil is a mineral lubricating oil preferably having a high viscosity index and a low pour point. Such an oil can be illustrated by an SAE 10 mineral oil having the following properties:

Visc., SUS, at 100° F	175
Visc., SUS, at 210° F	45.2
Visc., index (V.I.)	106
Flash, ° F	395
Fire, ° F	440
Pour point	—35

Another suitable base oil is a refined, highly paraffinic transformer oil having the following properties:

Gr., ° API	30.9
Color	30
Visc., SUS, at 100° F	56.9
Flash, COC, ° F	290
Fire, COC, ° F	320
Pour point, ° F	Below —70

The oil can be obtained from various crudes such as Pennsylvania, Mid-Continent, Gulf Coast and California crudes.

The viscosity index of the oil can be adjusted when required by addition thereto of a small amount of a viscosity index improver such as polyisobutylene or methacrylate ester polymers such as those sold by Rohm and Haas under the name of "Acryloids" such as "Acryloid 710" which is predominantly a copolymer mixture of octyl and lauryl methacrylates having a molecular weight of from about 10,000 to 20,000 or "Acryloid 150" which is predominantly a copolymer mixture of cetyl, lauryl and octyl methacrylates having a molecular weight of about 10,000–15,000. These polymers are sold commercially as 40% concentrate of the polymer in a mineral lubricating oil base, to provide a viscous liquid having a viscosity at 210° F. of from about 600 to 850 centistokes. On an

oil-free basis the polymers when used in compositions of this invention vary from 0.001% to 5%.

Other auxiliary additives which can be used in compositions of this invention include phenolic and amine anti-oxidants such as alkyl phenols e.g., di- and tri-alkyl phenols, for instance 2,4-, 2,3-, 3,4-, 2,6- and 3,5-diamyl phenol, 2,4-dimethyl-6-tertbutyl phenol, 2,4-ditertbutyl-6-methyl phenol; arylamines such as phenyl-α-naphthylamine, phenyl-β-naphthylamine; fatty acids of from 10 to 20 carbon atoms such as lauric, palmitic or stearic acids and mixtures thereof. These auxiliary agents when used in compositions of this invention are employed in amounts of from 0.001% to 10% and preferably between 0.1% and 5%.

The following compositions illustrate compositions of the present invention:

	Percent
Composition A:	
Tetradecane phosphinic acid	0.03
Mineral lubricating oil (250 SUS at 100° F.)	Balance
Composition B:	
Tetradecane phosphinic acid	0.03
Polyisobutylene	2
SAE 10 mineral lubricating oil	Balance
Composition C:	
Tetradecane phosphinic acid	0.03
Methacrylate polymer (Acryloid 710)	5
SAE 10 mineral lubricating oil	Balance
Composition D:	
Tetradecane phosphinic acid	0.1
Methacrylate polymer (Acryloid 150)	0.5
SAE 10 mineral lubricating oil	Balance
Composition E:	
Tetradecane phosphinic acid	0.1
Transformer oil (56.95 SUS at 100° F.)	Balance
Composition F:	
Octadecane phosphinic acid	0.1
Transformer oil (56.95 SUS at 100° F.)	Balance
Composition G:	
Tetradecane phosphinic acid	0.1
Stearic acid	0.1
Transformer oil (56.95 SUS at 100° F.)	Balance
Composition H:	
Octadecane phosphinic acid	0.03
Mineral lubricating oil (250 SUS at 100° F.)	Balance
Composition I:	
Octadecane phosphinic acid	0.03
Methacrylate polymer (Acryloid 710)	5
SAE 10 mineral lubricating oil	Balance

The superiority of compositions of this invention as non-foaming, non-corrosive, oxidation stable, friction reducing and cooling lubricants and which are effective transmission and brake fluids and lubricants is shown by the data in Table I for six tests I through VI as follows:

Corrosion and stability were determined by the copper strip test (I) which consists of heating the test oil at 300° F. for 3 hours with a polished copper strip immersed in the oil. The appearance of the strip at the end of the test is noted. The anti-wear, friction-reducing and squawking inhibiting properties of this invention were determined by use of a modified 4-ball wear tester equipped with an aerostatic thrust bearing and modified by addition of a fly-wheel to the spindle carrying the rotating steel ball and using an electronic friction recording system, and in which the three lower balls of the 4-ball machine were replaced by a cup holding three discs punched from Dynaflow reverse drum bearing material, and the anti-chatter coefficient (II) was measured as the friction ratio

$$\frac{K-S}{S}\times 100$$

wherein K is the kinetic coefficient of friction and S is the static coefficient of friction. Some of the compositions were road tested in a Buick car equipped with

TABLE I

Test	I	II	III	IV		V	VI
				4-Ball [2] Friction, Noise (or Squealing)			
	Cu Corrosion and Stability Test	4-Ball (Anti-chatter Friction Ratios)	Road Chatter Test (1951 Buick Equipped With Dynaflow Transmission)	Kinetic (μ)	Static (μ)	25,000 Mile Road Test in Car Equipped With Brakes Containing Steel and Organic Resinous Clutch Plates (Noise or Squealing, 10—None, or Perfect, 0—Poor)	CRC-L-12 Foam Test
Composition A	Pass	116	None	.097	.042	8+	Passed.
Composition B	do	116	do	.097	.042	8+	Do.
Composition C	do	116	do	.097	.042	8+	Do.
Composition D	do	116	do	.097	.042	8+	Do.
Composition E	do	116	do			8+	Do.
Composition F	do	116	do			8+	Do.
Composition G	do	116	do			8+	Do.
Composition H	do	116	do			8+	Do.
Composition I	do	116	do			8+	Do.
SAE 10 mineral oil+0.1% octadecane phosphonic acid.		44	Moderate	.097	.058		
SAE mineral oil+0.1% P_2S_5—Chlorinated sperm oil reaction product.		14	Severe				
SAE 10 mineral oil+0.1% tributyl phosphite.		—2					
SAE 10 mineral oil+1% tributyl phosphate.		0					
SAE 10 mineral oil+1% tricresyl phosphate.		11					
SAE 10 mineral oil	Failed	6	Severe	.111	.103	1	Failed.
250 neutral (HVI) mineral oil	do	6	do	.111	.103		
Buick Dynaflow fluid [1]			do				

[1] Properties of Buick Dynaflow fluid:

Gr, API	28.3	Fire point, ° F	420
Vis., 100° F., SUS	177.6	Pour point, ° F	−40
Vis., 210° F., SUS	49.5	Sap. No	9.2
Flash point, ° F	370	TA N-E	0.1

[2] Static coefficient of friction (μ) must be significantly lower than kinetic coefficient of friction (μ).

Dynaflow transmission (III). The effectiveness of compositions of this invention as brake fluids was determined (*a*) in a modified 4-ball machine (IV) using rotating steel top balls and organic resinous discs as used in clutch plates and (*b*) in a 25,000 mile road test (V) using a car equipped with brakes containing steel and organic resinous clutch plates and provided with compositions of this invention to provide lubrication, cooling and prevention of noise (squeal). Foaming (VI) was determined by the CRC–L–12 foam test.

Other compositions of this invention which can pass the above tests include SAE 10 to SAE 30 motor oils, turbine oil, transformer oil or other refined mineral oils containing from 0.01% to 0.3% by weight of di-2-ethylhexyl phosphinic acid, or dodecane phosphinic acid, or didecane phosphinic acid, or didodecane phosphinic acid. To these compositions can be added minor amounts of from 0.01% to 5% of 2,4-ditertiary butyl-6-methyl phenol, phenyl-α-naphthylamine, stearic acid and/or methacrylate polymer such as "Acryloid 150 or 710."

Compositions of this invention may also include minor amounts of from 0.001% and 5% and preferably from 0.01% to 0.2% of a foam inhibitor, such as silicone liquids, e.g., dimethyl silicone polymers, fluoro organic compounds (fluoro paraffins); corrosion inhibitors, e.g., Zn dithiocyclohexyl phosphate; detergents, e.g., petroleum sulfonates, alkylaryl sulfonates, e.g., Ca or Ba petroleum sulfonate or alkylphenol sulfonate; extreme pressure agents, e.g., sulfurized terpenes; anti-wear agents, e.g., dibenzyl disulfide and the like.

This application is a continuation-in-part of my application Serial No. 260,937, filed December 10, 1951, which has been abandoned.

I claim as my invention:

1. A process of inhibiting squawking, chattering and squealing in power transmissions operated on mineral lubricating oil by addition thereto of from about 0.001% to about 1% by weight of an oil-soluble mono-alkane phosphinic acid, said alkane radical having from 4 to 20 carbon atoms and from about 0.001% to about 1% of a fatty acid selected from the group consisting of lauric acid, palmitic acid, and stearic acid.

2. The process of claim 1 wherein the oil-soluble monoalkane phosphinic acid is tetradecane phosphinic acid.

3. The process of claim 1 wherein the oil-soluble monoalkane phosphinic acid is octadecane phosphinic acid.

4. A process of inhibiting squawking, chattering and squealing in power transmissions operated on mineral lubricating oil by addition thereto of from about 0.1% to about 1% by weight each of tetradecane phosphinic acid and a saturated fatty acid selected from the group consisting of lauric acid, palmitic acid, and stearic acid.

5. A process of inhibiting squawking, chattering and squealing in power transmissions operated on mineral lubricating oil by addition thereto of from about 0.1% to about 1% by weight each of tetradecane phosphinic acid and stearic acid.

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