Pressure transmitting fluids for brakes and hydraulic apparatus are characterized, among other things, by good anti-freezing qualities and high lubricating power. Insofar as such hydraulic fluids have appeared on the market in the past, they consisted, to a great extent, of castor oil, which at least gave high lubricating power but had the disadvantage of possessing only slight anti-freezing qualities. Developments are required and are in the direction of replacing castor oil because of this latter property.

On the other hand, the fluids having glycol (i.e., polyglycol or polyglycol-ether) bases, which have been used in large amounts heretofore, have good anti-freezing qualities but lack adequate lubricating power. Attempts have been made to increase the lubricating power by making mixtures, such as by adding castor oil to the aforementioned materials. However, it was not possible to maintain the anti-freezing qualities at the desired level when this was done. The problem is, therefore, to find additives, for hydraulic fluids having a polyglycol or polyglycol-ether base, which will increase the lubricating power but not affect the anti-freezing qualities.

Since, despite the disadvantage of having poor anti-freezing qualities, castor oil-containing fluids are still very often used in industry, it is necessary that hydraulic fluids containing a glycol base and containing castor oil be miscible with the castor oil in all proportions. It is therefore required that the additive for increasing lubricating power should not interfere with this miscibility. Under anhydrous conditions, polyglycol- or glycol ether-containing hydraulic fluids in suitable composition are miscible in all proportion with castor oil-containing fluids. Therefore, another condition is that the glycol-containing fluids be anhydrous.

It has now been established that hydraulic fluids which have good anti-freezing qualities and, furthermore, are compatible with castor oil-containing hydraulic fluids, are obtained if one adds, as a supplement to a liquid mixture having a base consisting essentially of anhydrous polyalcohols or ether-alcohols, certain quantities of phosphorous compounds, such as esters derived from the acids of phosphorous. Especially suitable as bases are di- and triethylene glycol or other alkylene glycols, as well as ethyl, propyl and butyl polyglycols, used either individually or in mixtures; the bases may also be mixed with anhydrous solvents such as diacetone alcohol, lower alcohols and the like.

Additives which substantially increase the lubricating power are organic phosphorous compounds containing oxygen or sulphur, such as esters of phosphonic acid, thioosphoric acid, phosphonic acid, phosphinous and phosphinic acid, phosphonic and phosphoric acid, as well as the esters of polyphosphorous acids. Especially simple to obtain and preferred because of their effective-ness, are the neutral and acidic phosphoric acid esters of aliphatic polyoxy- and polyhydroxy compounds, such as ethylene glycol, butylene glycol, glycerol and, particularly, polyethylene glycols. In the compounds mentioned, sulphur may replace oxygen. Very often the effect produced by individual components may be increased by using mixtures containing several of the above-described phosphorous compounds. In many cases, an increase in lubricating power may also be effected by a combination of phosphoric acid esters with boric acid esters or borates. In addition to the esters mentioned, oils, such as castor oil or other similar oils or derivatives thereof, may be added in such quantities that good anti-freezing qualities are preserved.

The phosphorus-containing esters mentioned are added in amounts which may differ a great deal depending on the purpose for which the hydraulic fluids are to be used. For ordinary requirements, in brake fluids which contain as a base, polyalcohols or their ethers and polyalkylene glycols (in admixture with other solvents if desired), an addition of 0.5 to 5.0% by weight is sufficient to increase the lubricating power of the base quite substantially.

Additives of the type described increase the lubricating power considerably without affecting miscibility with castor oil-containing fluids. Moreover, they do not cause any undesirable changes in viscosity of the fluid at high or low temperatures; and the swelling capacity of the normally employed sealing materials (e.g., gaskets, washers, etc.) is practically uninfluenced by these additives. To maintain the pH values necessary for satisfactory corrosion inhibition, the phosphoric acid esters are adjusted to pH 7-9 with ammonia, triethanolamine or other organic bases and to them are added the customary corrosion inhibitors, namely as inorganic or organic compounds giving a buffering effect, such as alkaline salts of boracic acid, benzoic acid, the phenyl glycinates and meroeptobenzthiazol, etc.

Example 1

A hydraulic fluid consisting of:
43 parts by weight butyl polyglycol
6 parts by weight ethyl polyglycol
17 parts by weight diethylene glycol
34 parts by weight triethylene glycol
0.3 parts by weight sodium meroeptobenzthiazol
and which shows very moderate lubricating power, can have its lubricating power improved considerably by adding 3 parts by weight pentaethyleneglycol secondary phosphate, adjusted to approximately pH 8.5 with triethanolamino in aqueous test solution (1:9). The freezing point of this liquid is —75 °C.

The ethylpolyglycol, mentioned in the above as well as the following examples, is essentially a mixture of diethylene and triethylene glycol monoethylether in the proportion of about 2:1; the butyl polyglycol, mentioned in the above as well as the following examples, is essentially a mixture of diethylene and triethylene glycol monobutylether in the proportion of about 2:1.

Example 2

A mixture of:
10 parts by weight ethyl glycol
70 parts by weight butyl polyglycol
19.5 parts by weight triethylene glycol
0.5 part by weight castor oil
provided with the customary corrosion inhibitor is significantly improved in lubricating power by adding 0.5 part by weight pentaethyleneglycol tertiary phosphate and 0.5 part by weight pentaethyleneglycol secondary
phosphate, both adjusted to about pH 8.5 (as in Example 1). The freezing point of the liquid is \(-70^\circ\) C.

**Example 3**

A mixture of:

70 parts by weight butyl polyglycol and
30 parts by weight triethylene glycol

including a minor quantity of corrosion inhibitor shows considerably increased lubricating power by adding to it 5 parts by weight of an alcoholysis product of castor oil with butyl diglycol and 0.5 part by weight pentaethyl-
ene glycol tertiary phosphate adjusted with triethanol-
amine to about pH 8.5 (as in Example 1). The freezing point of the liquid is \(-70^\circ\) C and it is miscible with castor oil-containing hydraulic fluids.

**Example 4**

A mixture of:

30 parts by weight diethylene glycol and
70 parts by weight butyl polyglycol

containing the customary corrosion inhibitor are sig-
nificantly improved in lubricating power by adding 4 parts by weight triethylene glycol tertiary phosphate, ad-
justed to pH 9 in aqueous test solution, and 3 parts by weight glycol triethanolaminate borate. The freezing point is \(-75^\circ\) C.

**Example 5**

A mixture of:

95 parts by weight ethyl polyglycol and
5 parts by weight triethylene glycol tertiary phosphate
adjusted to pH 8–9.5 in aqueous test solution is provided with a minor quantity of corrosion inhibitor. This liquid has a freezing point of \(-70^\circ\) C.

**Example 6**

A solution of 5 percent by weight pentaethylene glycol secondary phosphate (adjusted to about pH 9 in aqueous solution) in a mixture of 65 parts by weight diacetone alcohol and 30 parts by weight butyl polyglycol provided with the customary corrosion inhibitor results in a hy-
draulic fluid of good lubricating power having a freezing point of \(-70^\circ\) C.

**Example 7**

A mixture of:

55 parts by weight polyethylene glycol monobutyl ether
35 parts by weight diethylene glycol
8 parts by weight triethylene glycol

including a minor quantity of corrosion inhibitor is in-
creased in lubricating power by adding 2 parts by weight of a mixed poly-condensed tertiary ester formed by esteri-
fication of 1 mol phosphoric acid and 1 mol boric acid with 3 moles of a mixture of tetra and pentaeathy-
lene glycol having an average molecular weight of 200. The freezing point of this liquid is \(-70^\circ\) C. The liquid may be mixed with castor oil-containing hydraulic liquids.

The phosphoric acid-boric acid mixed ester may be replaced by corresponding esters of other glycols and polyglycols.

What is claimed is:

1. A hydraulic fluid consisting essentially of a mixture of at least one alcohol selected from the group consisting of lower alkyl polyglycols, lower alkylene glycols and lower polyalkylene glycol ether bases together with a minor but lubricating increasing proportion up to 5% by weight of an ester which is the reaction product of an acid selected from the group consisting of phosphoric acid, thiophosphoric acid, phosphonous acid, phosphonic acid, phosphonic acid, phosphorous acid, phosphonic acid, phosphoric acid and polyphosphoric acids, and an alcohol selected from the group consisting of ethylene glycol, butylene glycol, gly-
cerol and polyethylene glycols.

2. The hydraulic fluid of claim 1 which also contains diacetone alcohol as a solvent.

3. The hydraulic fluid of claim 1 which also contains triethanolamine as a pH adjuster.

4. A hydraulic fluid consisting essentially of a mixture of at least one alcohol selected from the group consisting of lower alkyl polyglycols, lower alkylene glycols and lower polyalkylene glycol ether bases together with a minor but lubricating increasing proportion up to 5% by weight of an ester which is the reaction product of an acid selected from the group consisting of phosphoric acid, thiophosphoric acid, phosphorous acid, phosphinic acid, phosphonic acid, phosphoric acid, phosphoronic acid and polyphosphoric acids, and an alcohol selected from the group consisting of ethylene glycol, butylene glycol, gly-
cerol and polyethylene glycols adjusted to a pH within the range 7–9 by the addition of a compound selected from the group consisting of the alkali salts of boric acid, phosphoric acid, phosphoric acid, phosphoric acid, phosphoric acid, phosphoric acid, phosphoric acid and mercaptobenz-thiazol.

5. A hydraulic fluid consisting essentially of polyethyl-
ene glycol monobutyl ether, a polyethylene glycol, and a minor but lubricating-increasing proportion up to 5% of a mixed poly-condensed tertiary ester formed by esteri-
fying a mixture containing 1 mol of phosphoric acid and 1 mol of boric acid with 3 mol of a mixture of tetra and pentaethy-
lene glycol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,916,457

December 8, 1959

Hilda Friedrich et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 36 to 39, should appear as shown below instead of as in the patent:

from the group consisting of ammonia and tri-
ethanol amine together with a minor, but
corrosion-inhibiting proportion by weight of
a corrosion inhibitor selected from the group
consisting of the alkali salts of boric acid,
benzoic acid, the phenyl glycines and mercap-
tobenzthiazol.

Signed and sealed this 27th day of September 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents