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POLYSULFIDE LUBRICANT AND SEALANT COMPOSITION

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12 Claims. (Cl. 252—28)

This invention relates to a new composition of matter and its preparation and is more particularly concerned with a lubricating and sealing composition which is chemically relatively inert to aliphatic hydrocarbons, mineral and vegetable oils, natural and manufactured gases, oils and hydrocarbon gases containing large amounts of hydrogen sulfide or mercaptans. This lubricant is also relatively resistant to water and dilute aqueous solutions of mineral acids up to about 10% concentration and alkalis up to a pH of 13, as well as to mixtures of liquid and gaseous hydrocarbons and water. It is particularly suited as a lubricating and sealing composition for plug type valves intended for general oil field or petroleum refinery service and drilling in mud line valves, etc.

The lubrication of bearing contact parts, such as valves and like apparatus, when exposed to line fluids having strong solvent actions, e.g., liquid hydrocarbons, has presented a difficult problem. This problem is more difficult if the line fluid consists of a mixture of chemicals of widely different types, all possessing strong solvent action. Thus, mixtures of liquid hydrocarbon and water or aqueous solutions exert a solvent action that would not exist were either of the materials encountered solely as line fluid. The problem is further complicated if the line fluids encountered are under high pressure and are subject to wide variations in temperature. These conditions are commonly encountered in general oil field and petroleum refinery service, and most of the standard lubricating and sealing compositions available are not entirely satisfactory in that they are either largely dissolved or disintegrated by the line fluids or are incapable of withstanding high line pressures or function efficiently only over a narrow temperature range. To our knowledge, the only lubricating and sealing composition which functions satisfactorily under the conditions recited above is the lubricant and sealant disclosed by Perkins in co-pending application, Serial No. 361,080, filed June 11, 1953, now U.S. Patent No. 2,818,384.

The composition described in the above application comprises as its essential ingredients a synthetic liquid organic polysulfide polymer of molecular weight 1000–4000, thickened by the admixture of a metallic soap which has been solubilized by the use of finely divided carbon black of a specified size and pH value. This composition has given excellent service in oil field and petroleum refinery practice under a wide variety of field conditions; however, it has an objectionable odor even after reodorizing. Furthermore, the carbon black in the composition imparts a tenacious stain to workmen's clothing, tools and the like which may come in contact with the lubricant during its application. The objectionable odor and tenacious staining properties are disliked by workmen, which often results in improper maintenance of the apparatus in which such a lubricant is used.

An object of this invention is to provide a novel lubricating and sealing composition particularly suited for plug valves which comprises a major portion of a synthetic liquid organic polysulfide polymer thickened with minor portions of microsilica and polytetrafluoroethylene resin.

A further object of this invention is to provide a valve lubricant and sealant which is resistant to the solvent action of a wide variety of line fluids which are under high temperatures and pressures.

Another object of this invention is to provide a lubricant and sealant composition containing a major portion of a synthetic liquid organic polysulfide polymer, the lubricant and sealant having no substantial objectionable odor, nor substantial staining properties.

Other objects of the invention will, in part, be obvious, and will, in part, appear hereinafter.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The novel lubricating and sealing composition of this invention comprises as its essential ingredients, substantially from 75 to 95 parts by weight of a synthetic liquid organic polysulfide polymer having an average molecular weight of from 1000 to 4000, from 2 to 7 parts by weight of microsilica, and from 0.1 to 1.5 parts by weight of polytetrafluoroethylene resin.

Liquid organic polysulfide polymers are particularly suitable for the preparation of plug valve sealing and lubricating compositions intended for use in general oil field and refinery practice since they are insoluble in both liquid hydrocarbons and water or dilute aqueous solutions.

The microsilica is used to thicken the synthetic liquid organic polysulfide polymer to a consistency which will make it useful as a lubricant and sealant composition. Microsilicas have been found to be efficient thickeners for polysulfide polymers; however, the resulting composition hardens when exposed to temperatures of 200° F. or higher for periods ranging from several days to one week. This hardening apparently is caused by oxidation of the polymer or polymerization of the polymer catalyzed by the microsilica, or both. In practicing this invention, the tendency for the polysulfide polymer to harden at elevated temperatures when thickened with microsilica is controlled by adding to the formulation a small amount of polytetrafluoroethylene resin which functions to keep the concentration of microsilica at a low level.

The organic polysulfides used in this invention are those synthetic polymers produced by the reaction of sodium polysulfide and an organic dihalide. A large number of dihalides may be used in the production of the polysulfite polymers referred to. The following dihalides are particularly useful: methylene dichloride, ethylene dichloride, propylene dichloride, glycerol dichlorohydrin, dichloroethyl ether, dichloroethyl formal and triglycol dichloride. Particularly good results have been obtained with "Thiokol, LP–32" a liquid organic polysulfide polymer prepared with 99.5 mol percent of dichloroethyl formal (bis-2-chloroethyl formal), and 0.5 mol percent of trichloropropane as a cross-linking agent. "Thiokol, LP–32" has an average molecular weight of 4000, a viscosity at 77° F. of approximately 400 poises, a pour point of 45° F., a flash point (open cup) of 455° F., fire point (open cup) of 485° F., and a maximum moisture content of 0.2%.

"Thiokol" liquid organic polysulfide polymers are

manufactured by the Thiokol Chemical Corporation of Trenton, New Jersey, and are further designated in accordance with their molecular weight and tri-chloropropane content. Of course, synthetic liquid organic polysulfide polymers of other manufacturers may be used with equally good results.

For a more complete description of the preparation of synthetic liquid organic polysulfide polymers of desired molecular weight, reference should be had to U.S. Patent 2,466,963 issued April 12, 1949.

We have found that best results are obtained by using an air floated microsilica having substantially the following specifications: Silica content 99.0—99.7%; ignition loss (1000° C.) 0.2; sp. gr.—2.1; and pH (10% aq.) 4.5–6.0. Such a microsilica is available on the market as "Cabosil." The resulting lubricant is made less susceptible to hardening than if a silica having a larger particle size and lower pH is used. We have also found that the rate of hardening is proportional to the concentration of microsilica. Thus by keeping the microsilica concentration as low practicable, the tendency to harden or thicken excessively is markedly diminished.

Effective thickening of the liquid organic polysulfide polymer, by the use of microsilica in low concentrations ranging from 2 to 7 parts by weight of the composition, is accomplished by employing small but effective amounts of polytetrafluoroethylene resin. An example of such a resin available commercially is "Teflon" which has been estimated to have a molecular weight between 142,000 to 534,000. The resin may be either in the form of finely divided solid particles, or more conveniently in the form of an aqueous dispersion containing about 60% resin solids. Only a small amount of polytetrafluoroethylene resin is necessary to bring about a marked thickening of the organic polysulfide-microsilica matrix. The amount of resin yielding consistencies suitable for use as valve lubricating and sealing compositions is in the range of from 0.2 to 1.5 parts by weight of the composition. The amount of polytetrafluoroethylene resin used must be carefully controlled in preparing the lubricant and sealant compositions of this invention in order to provide desirable consistencies for proper functioning under particular service conditions. If the amount of resin used is too high, the liquid organic polysulfide-microsilica suspension sets to a very thick rubbery mass entirely unsuitable as a lubricant and sealant.

The amount of resin used is also dependent upon other additives which may be incorporated into the composition to tailor the resulting lubricant and sealant for a particular service condition. For example, it has been found that polytetrafluoroethylene resin will also thicken a suspension of finely divided mica in a liquid organic polysulfide polymer. While the thickening action is much less pronounced than with microsilica suspensions, this fact must be taken into account when formulating lubricants containing mica as an anti-galling agent. As little as 0.5 part by weight of mica will provide beneficial results and the amount may be varied up to 6 parts by weight; however, about 3 parts by weight will provide excellent load bearing qualities in the lubricant and sealant when used in high pressure valves and will prevent seizing and galling should the valve plug become devoid of lubricant.

In formulating the compositions of this invention, it has been found useful to use additives such as chlorine or oxygen-bearing compounds in order to extend the useful temperature range and to increase metal adhesion and film strength of the resulting lubricant and sealant. Examples of such compounds are bis(ethoxyethoxyethyl-phthalate) which may also be designated bis(diethyl-eneglycolmonoethyl ether) and is commonly known in the trade as "dicarbitolphthalate," chlorinated polyphenyls (distillation range 435° C. to 450° C.) such as chlorinated biphenyl containing 65%–70% by weight

combined chlorine and mixed isomeric terphenyls containing meta and para terphenyls (melting range 60° C. to 140° C.) which are available on the market as "Santowax." These compounds may be used separately or in combination with each other and in amounts varying up to 10 parts by weight of the composition.

The objectional odor present in the lubricant and sealant of co-pending application Serial No. 361,080, referred to hereinbefore, is substantially reduced in preparing the lubricant and sealant of this invention because during its preparation it is not necessary to raise the temperature above 250° F. Presumably, the dithiols and mercaptans which are largely responsible for the objectional odor are formed at temperatures above 250° F. In the co-pending application, temperature as high as 385° F. were used in preparing the lubricants and sealants disclosed therein.

The following Example I is illustrative of the practice of this invention:

Example I

	Parts by wt. (lbs.)
Synthetic organic polysulfide polymer (dichloroethyl formal 99.5 mol percent trichloropropane 0.5 mol percent); (average molecular weight 4000)	89.7
Chlorinated biphenyl (ASTM distillation range 435–450° C.)	5.0
Airfloated microsilica (pH 5; average particle size—0.01 to 0.02 micron)	2.6
Mica	2.0
Polytetrafluoroethylene resin aqueous dispersion (60% resin solids)	0.7

A lubricant and sealant was prepared from the above formulation, in which the ingredients are the same as those described in more detail hereinbefore, by introducing the polysulfide polymer into a suitable vessel equipped with a paddle mixing device and means for heating and cooling said vessel. Agitation was commenced and the chlorinated biphenyl and mica were introduced with continued agitation. The mixture was then heated to a temperature of about 250° F. until the chlorinated biphenyl was dissolved. The heating was stopped and cooling commenced. The microsilica was then added and blended in thoroughly. After the temperature of the mixture dropped to 120° F., the polytetrafluoroethylene resin dispersion was added and thoroughly mixed. The mass was again heated to 250° F. in order to drive off the water and to set the final gel and structure of the plastic mass. It is essential that the resin be added at about 120° F. since it is liable to precipitate and not function as a thickener if added at a higher temperature. Although the chlorinated biphenyl is soluble in the common hydrocarbon solvents, it has been found that the small amount used in the formulation of this invention does not seriously interfere with the functioning of the lubricant in the presence of hydrocarbon solvents. The above lubricant has performed satisfactorily in the temperature range of 0° F. to 200° F. and pressures of 1000 p.s.i.g. nitrogen. It has performed satisfactorily at 5000 p.s.i.g pressure at room temperature

In the preparation of the above formulation, any suitable non-volatile reodorant, compatible with the finished lubricant may be used in order to overcome the slight objectionable odor of the polymer used Such reodorants may be incorporated in the lubricant and sealant in an amount of from 0.25 to 1.0 part by weight of the composition by simple thorough mixing with the finished product. Examples of reodorants available on the market are "Thiokol Mask 1093 and 1046" and "Neutralizer 7919" manufactured by Polak & Schwartz, and "Santomask" manufactured by Monsanto Chemical Company.

Another formulation which we have found to be effective as a valve lubricant and sealant is illustrated as follows:

Example II

	Parts by wt. (lbs.)
Synthetic organic polysulfide polymer (dichloroethyl formal 99.5 mol percent, trichloropropane 0.5 mol percent); (average molecular weight 4000)	86.2
Mixed isomers of terphenyl (melting range 60° C.–140° C.)	5.0
Bis(ethoxyethoxyethylphthalate)	2.0
Airfloated microsilica (pH 5, average particle size 0.01 to 0.02 micron)	6.5
Polytetrafluoroethylene resin aqueous dispersion (60% resin solids)	0.3

A lubricant and sealant was prepared from the above formulation, in which the ingredients are the same as those described in more detail hereinbefore, by introducing the polysulfide polymer, mixed isomeric terphenyls, and bis(ethoxyethoxyethylphthalate) into a vessel equipped with a device for agitation and heating means. The mixture was heated to a temperature of about 250° F. to bring the terphenyls into solution. The heat was then turned off, and the microsilica added with continued agitation, and the mass cooled to 120° F. The polytetrafluoroethylene dispersion was then added and the mass heated to 250° F. with continued agitation. It is essential that the resin be added at 120° F. since it is liable to precipitate and not function as a thickener if added at a higher temperature. The lubricant is then cooled and is ready for use or packaging.

In Example II the terphenyls act as a softener and the bis(ethoxyethoxyethylphthalate) eliminates a minimum in consistency which occurs in the lubricant at about 100° F. in its absence.

In the preparation of the above formulation, any suitable reodorant compatible with the finished lubricant, may be used in order to overcome the slight objectionable odor of the polymer used. Such reodorant may be incorporated in the finished product in amounts of from 0.25 to 1.0 part by weight of its composition by simple thorough mixing with the finished product.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. A lubricating and sealing composition comprising as its essential ingredients a major portion of a synthetic liquid organic polysulfide polymer, and substantially from two to seven parts by weight of microsilica, and substantially from 0.1 to 1.5 parts by weight of polytetrafluoroethylene to thicken said liquid polymer to a consistency that the composition will be suitable for use as a plug valve lubricant and sealant.

2. A lubricating and sealing composition for use in plug valves comprising as its essential ingredients substantially from 75 to 95 parts by weight of a synthetic liquid organic polysulfide polymer having an average molecular weight of from 1000 to 4000, substantially from 2 to 7 parts by weight of microsilica, and substantially from 0.1 to 1.5 parts by weight of polytetrafluoroethylene resin.

3. The composition of claim 2 in which the microsilica is an air floated microsilica having a silica content of from 99.0 to 99.7% by weight.

4. The composition of claim 2 in which the microsilica has an average particle size of from 0.5 to 0.020 micron.

5. The composition of claim 2 in which there is present not more than 10 parts by weight of a chlorinated polyphenyl.

6. The composition of claim 2 in which there is present not more than 10 parts by weight of bis(ethoxyethoxyethylphthalate).

7. The composition of claim 2 in which there is present not more than 10 parts by weight of mixed isomeric terphenyls.

8. The composition of claim 2 in which there is present not more than substantially 10 parts by weight of at least one compound selected from the group consisting of chlorinated polyphenyl, bis(ethoxyethoxyethylphthalate), and isomeric terphenyls.

9. The composition of claim 2 in which there is present from 0.5 to 6 parts by weight of mica.

10. A lubricating and sealing composition for use in plug valves comprising substantially from 75 to 95 parts by weight of a synthetic liquid organic polysulfide polymer; substantially from 2 to 7 parts by weight of microsilica; substantially from 0.1 to 1.5 parts by weight of polytetrafluoroethylene resin; not more than substantially 10 parts by weight of at least one compound selected from the group consisting of chlorinated polyphenyl, bis(ethoxyethoxyethylphthalate), and isomeric terphenyls; and substantially from 0.5 to 6 parts by weight of mica.

11. A lubricating and sealing composition for use in plug valves formulated from substantially the following ingredients:

	Parts by wt.
Synthetic liquid organic polysulfide polymer	90
Chlorinated biphenyl	5
Microsilica	3
Mica	2
Polytetrafluoroethylene resin aqueous dispersion (60% resin solids)	0.7

12. A lubricating and sealing composition for use in plug valves formulated from substantially the following ingredients:

	Parts by wt.
Synthetic liquid organic polysulfide polymer	86
Mixed isomeric terphenyls	5
Bis(ethoxyethoxyethylphthalate)	2
Microsilica	6.5
Polytetrafluoroethylene resin aqueous dispersion (60% resin solids)	0.3

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,979,457 April 11, 1961

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

Column 2, line 54, for "polysulfite" read -- polysulfide --; column 3, line 21, after "low" insert -- as --.

Signed and sealed this 10th day of October 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC