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POLYSULFIDE POLYMER SEALANT AND LUBRICANT

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This invention relates to a new composition of matter and its method of preparation and is more particularly concerned with a lubricant and sealing composition which is chemically 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 composition is also resistant to weak mineral acids of about 10 percent concentration, with the exception of oxidizing acids, and weak alkalies up to pH of 13. The lubricant is resistant to aqueous solutions and water as well as mixtures of hydrocarbon liquids and gases and water. The compositions is a very satisfactory plug valve lubricating and sealing medium.

The lubrication of bearing contact parts, such as valves and like apparatus, when exposed to line fluids of strong solvent action, i. e., liquid hydrocarbons, has always presented a difficult problem. This problem is heightened when the line fluid consists of several types of chemicals, all possessing strong solvent action. Thus, mixtures of liquid hydrocarbons and water exert a solvent action and present problems that would not exist were either of these types of material encountered solely as the line fluid. The problem of lubricating bearing parts, such as valves, may be heightened further when the line fluid is under high pressure, may vary over a wide temperature range, may have a wide variation in pH (ranging from a solution corresponding to a 10 percent mineral acid concentration to one consisting of a weak alkali with a pH of 13), and may contain large amounts of hydrogen sulfide or mercaptans. All of the standard plug valve lubricants are usually readily disintegrated when used for oil field services where they encounter line fluids which are mixtures of hydrocarbons, water, acids, mercaptans, etc., thus necessitating frequent relubrication.

The lubrication of plug valves used in the oil fields has therefore created a demand for a lubricant and sealing medium which is particularly inert with respect to a wide range of solvents and line pressures, and one that will maintain a good lubricating and sealing film over a wide range of temperature. The invention provides a lubricant which is substantially resistant with respect to aliphatic hydrocarbons, manufactured and natural gases, oils, dilute acids, weak alkalies, mixtures of oils and hydrocarbons with water, and oils and gases containing large amounts of mercaptans and hydrogen sulfide, and which seals off the line fluid under wide variations in temperature and pressure.

The major object of the invention is to provide a novel composition of matter containing a major amount of synthetic liquid polysulfide polymer thickened by the addition of a metallic soap in the presence of uniformly dispersed carbon black, and the process of making the same.

A further object of the invention is to provide a novel composition of matter which has especial utility as a plug valve lubricant for general oil field services composed of a major amount of synthetic liquid polysulfide polymer having an average molecular weight of 1000–4000 thickened by solution therewith of a metallic soap and containing a dispersal of carbon black particles, and the process of making the same.

A further object of the invention is to provide a novel process for making the foregoing wherein the polymer, carbon black and soap are added to each other in a special order and under special controlled temperature conditions.

Further objects of the invention will appear as the description proceeds in connection with the appended claims.

This lubricant and sealing material is composed mainly of synthetic polysulfide polymers of the kind which are made by reacting dichloroethylformal and trichlorpropane together with a water dispersion of sodium hydrosulfide and sodium sulfite to produce a liquid synthetic polymer of average molecular weight of 1000–4000, and have the following average structure:

$$HS—(C_2H_4—O—CH_2—O—C_2H_4—S—S)_X—C_2H_4—O—CH_2—O—C_2H_4—SH$$

where X is an integer of about 6 for polymers of molecular weight of 1000 and X is an integer of about 23 for polymers of molecular weight of 4000. Occasionally in the chain of reoccurring units there is a side mercaptan group.

The synthetic polymers which I have used are those commercially known as Thiokol liquid polymer type LP–2 which has an average molecular weight of 4000, and Thiokol liquid polymer type LP–3 which has an average molecular weight of 1000. These polymers have different viscosities and they blend in the mixture to attain desired viscosity of the material.

It is known that these synthetic liquid polysulfide polymers are resistant to oils and aliphatic hydrocarbons. However, these liquid polymers alone do not have the physical properties required to serve as satisfactory sealing mediums for lubricated plug type valves, particularly over a wide range of temperatures, and in the invention they are modified for suitable consistency. This has been accomplished by incorporating therewith a metallic soap such as aluminum stearate and a carbon black such as medium channel air-floated carbon black, whereby a plastic material is obtained which is satisfactory as a plug valve lubricant and seal and is satisfactorily resistant to the line fluids of the general oil field services. It has an effective operating range from 0° F. to 300° F. This new lubricant and seal maintains its viscosity up to as high as 450° F., but it is not usually recommended for temperatures in excess of 300° F., because when the polymers are subjected to sustained temperatures of above 300° F. there may occur thermal breakdowns which result in the separation and hardening of the carbon black and metallic soap and which completely change and make the lubricant unsatisfactory as a valve lubricant and sealing medium.

To obtain a lubricant with the desired characteristics which would be necessary for this type of service, the synthetic polymers had to be thickened with a thickening agent which would give it a wider temperature range. Various metallic soaps were tried for thickening the polymers, but all of the metallic soaps used proved at first to be insoluble in both types of the synthetic liquid polymer. An important discovery and feature of the invention is that I have found that by the incorporation of carbon black in the mixture, preferably of the medium channel air-floated grade, I am able to incorporate and dissolve metallic soaps into the synthetic polymer matrices and obtain a thickening and gelling action over a wide range of temperature. Without the addition of the carbon black, it was impossible to dissolve the soaps into the polymer.

The soaps that I have used are aluminum stearate of the mono, di, and tri types, mixtures of the mono, di and tri types, as well as mixtures of the tri and di, the di and

mono, and di and tri types, all of aluminum stearate. I have also used barium stearates, calcium stearates, magnesium stearates, lead oleates, naphthenate soaps of zinc, magnesium, lead, cobalt, and aluminum, oleate soaps of calcium, barium, aluminum, magnesium, and lithium, lithium stearate, strontium stearate. None of these soaps could be incorporated into the polymer in any noticeable proportion without the addition of the carbon black, but with the addition of the carbon black to the polymer, all of these soaps could be incorporated and added some thickening action to the polymer. Thus the invention contemplates the incorporation of substantially any metallic soap into a synthetic liquid polysulfide polymer in the presence of uniformly distributed carbon black which seems to make the solution possible. In addition I believe that the uniformly dispersed carbon black in the mixture retains the solution of the polysulfide and soap during its useful life.

In practicing the invention I have incorporated into the polymers, using the foregoing various types of metallic soaps, other carbon blacks to determine their properties in this polymer. The carbon blacks that have been tried are easy-process channel, medium-process channel, hard-process channel, low-flow channel, medium-color channel, high-color channel, fine-furnace, high-modulus furnace, semi-reinforced furnace and pure-tone furnace. All of these grades and types of carbon blacks could be incorporated into the polymer, but none produced as good or as pronounced thickening action as the channel blacks made by burning gas or oil and particularly the medium-channel air-floated carbon black.

In general I have found that substantially all of the foregoing carbon blacks could be incorporated to produce pronounced thickening of the polymer and soap mixtures. However, it seemed that where the average particle size was larger than 5 microns the carbon black acted more or less as fillers and did not impart worthwhile thickening or gelling of the polymer and soap mixture.

For substantially any given particle size of carbon black the optimum thickening action of the metallic soap occurs when the pH range of the carbon black is between 3.0 and 4.6. The carbon blacks which produced the greatest and most desirable thickening action and the most stable and non-bleeding lubricants are those having an average particle size of between 0.15 and 0.25 millimicron and having a medium acid pH of about 3 to 4.6. I found that carbon blacks having an acid pH of about 3 to 4.6 allowed the soap to be incorporated with the polymer very efficiently and desirably even when the average particle size was as high as 0.02 micron. The carbon blacks on the alkaline side with pH of about 7.9 to 10, which are mostly furnace blacks, permit rather limited solubility of the soap into the polymer and were not as desirable, and I found that in general the solubility of the soap in the polymer and consequently the thickening action decreased as the pH increases or decreases from the medium acid range of 3 to 4.6.

Actually the best results were obtained using an aluminum stearate with medium-channel air-floated carbon black having an average particle size of about 0.21 millimicron and a pH of about 3.7. This was rather unexpected since this type of carbon black is normally used as a paint or ink coloring and not for rubber reenforcing or the like. The soap which gave the widest temperature range in the lubricant and sealing material and gave the best sealing and film strength was an aluminum stearate of a mixture of di and tri with a total ash content of 6.10 to 6.25 percent.

It is my theory that the carbon black serves as a coupling agent promoting incorporation of the polymer and metallic soap, although this is the first time to my knowledge that carbon black has functioned as a coupling agent to any compounds.

For the preferred embodiment of the invention I prepare a satisfactory oil field service plug valve lubricant and sealing composition from Thiokol liquid polymers LP–2 and LP–3, carbon black (medium channel air floated), aluminum stearate (mixture of di and tri ash content 6.10 to 6.25 percent) and mica particles. The mica is not essential but it is highly desirable because it is inert with respect to the lubricant and the line fluid and is used in case the bearing or seating surfaces become void of lubricant and acts only as an anti-galling or anti-scoring substance.

The minimum and maximum percentage range for this general oil field lubricant is as follows:

	Percent
Thiokol liquid polymer LP–2	55–75
Thiokol liquid polymer LP–3	0–5
Carbon black, medium channel air-floated	14.5–6.0
Aluminum stearate, di and tri mixture (6.10–6.25% ash)	30–10
Mica	0.5–4.0

As this is the minimum and maximum percentage range of this formula, my preferred formula is as follows:

	Percent
Thiokol liquid polymer LP–2	67.5
Thiokol liquid polymer LP–3	2.5
Carbon black, medium-channel air-floated	9.0
Aluminum stearate, di and tri mixture	20.0
Mica	1.0

In the above illustrative embodiments of the invention, Thiokol liquid polymers LP–2 and LP–3 are identified as having substantially the following average structure:

$$HS—(C_2H_4—O—CH_2—O—C_2H_4—S—S)_X—$$
$$C_2H_4—O—CH_2—O—C_2H_4—SH$$

where X is an integer of about 6 for polymers of molecular weight of 1000 and X is an integer of about 23 for polymers of molecular weight of 4000. LP–2 has an average molecular weight of 4000 and LP–3 has an average molecular weight of 1000. These are the same organic liquid sulphide polymers identified and described hereinbefore in column 2.

In the preparation of lubricant composition of the invention, I found that a definite procedure must be followed. For example, if the carbon black is added to the liquid polymers first and the mixture heated above 150° F. before the aluminum stearate is added, an incomplete gelling of the aluminum soap results. I have also found that if the aluminum stearate is incorporated into the liquid polymer before the carbon black, there is a tendency for separation in the final product.

My preferred procedure for preparation is to first introduce the liquid polymers into a heat jacketed kettle having a paddle or other agitator. The agitator is started and the heat turned on. The polymer mixture is heated to approximately 125° F. The carbon black is then added into the kettle at a medium rate, while maintaining agitation and keeping the temperature of the mixture between 125–150° F. After all of the carbon black has been added, the mixture is agitated for ten minutes. Then the aluminum stearate is added, all the while maintaining agitation and keeping the temperature at approximately 150° F. Care should be taken not to let it exceed 150° F. by any substantial amount for any noticeable period. After all of the aluminum stearate has been added, the mica is added. As soon as all of the mica has been added, increase the heat on the kettle and heat the mixture to approximately 385° F., and maintain this temperature with agitation for 20 minutes. The composition is then discharged into cooling pans for rapid cooling and allowed to cool to room temperature.

After cooling to room temperature, the composition is rolled by three passes through a rubber mill roller or is shot through a homogenizer to break up the soap crystals. In practice and because of the odor of this composition, during the process I incorporate a masking agent which may be about 1¼ to 1½ percent of the total formula.

A satisfactory masking agent is composed of approximately 80 percent of Neutralizer 1A1, which is an odor depressing oil manufactured by Magnus, Mabee & Reynard, Inc., and 20 percent Santomask, which is an odor masking liquid manufactured by the Monsanto Chemical Company. The masking agent has no effect on the properties of the composition and it is there only to cut down the mercaptan and dithiol odors of the composition, so that any suitable masking agent inert with respect to the soap and polymers may be used.

The lubricant composition which I have just described is a general oil field lubricant and is resistant to those types of services, such as oils, gases, hydrocarbons, both liquids and gaseous, and mixtures of oils and water, hydrogen sulfide, and mercaptans, both mixed with hydrocarbons and unmixed, and also has excellent resistance to drilling mud services. This lubricant composition also is resistant to weak sulfuric, hydrochloric, and organic acids of about 10 percent strength and weak alkalies up to about a pH 13. It is completely unsuitable and is not recommended for strong oxidizing materials such as nitric acids or like oxidizing compounds. While it is not completely resistant to aromatic hydrocarbons, such as benzene and toluene, in the field this lubricant composition acts very satisfactorily as a seal and lubricating material in plug valves on aromatic services. One of the main properties of this lubricant and sealing composition of the invention, aside from its complete inertness to these aliphatic hydrocarbons, oils, and etc., is its preferential wetting action. Should the metal bearing or seating contact surfaces of the valve for example, become wetted with the line fluids, such as gasoline or oil, this lubricant composition will actually replace the line fluid on the metal and adhere tightly to the metal surfaces and exclude the line fluid from those surfaces.

It also exhibits a phenomena which gives it excellent load-carrying properties for high pressure gas lines such as are encountered in Christmas tree services. On the steel and iron types of valves, the lubricant composition actually chemically reacts on the seating surfaces to form a corrosive product, which in turn appears to have an attraction for the lubricant and resists being forced out by the line plug-loading pressures. It also has been found that once this corrosive product (which is of microscopic magnitude in thickness) is produced on the metal seating surfaces of the valve, the lubricant is almost impossible to remove during normal valve operation or by solvent action, even by the solvents to which it is not completely resistant, that is, it performs satisfactorily in service on lines carrying chlorinated hydrocarbons and aromatic hydrocarbons.

Field tests have been made on this lubricant for a number of months, and indications appear that it is the only one general oil field service lubricant with a wide temperature range of from 0° F. to plus 300° F. and resistant to the types of line fluid which are encountered in this type of service available today.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiment is 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 suitable for use in plug valves comprising substantially from 55 to 75 parts of a synthetic liquid organic polysulfide polymer having an average molecular weight of about 4000; from 0 to 5 parts of a synthetic liquid organic polysulfide polymer having an average molecular weight of about 1000; said polysulfide polymers having substantially the following average structure:

$$HS—(C_2H_4—O—CH_2—O—C_2H_4—S—S)_x—C_2H_4—O—CH_2—O—C_2H_4—SH$$

where X is an integer of about 6 for polymers of molecular weight of 1000 and X is an integer of about 23 for polymers of molecular weight of 4000; from 10 to 30 parts of at least one metallic non-water soluble soap selected from the group consisting of the soaps from stearic, oleic and naphthenic acids; and from 6 to 14.5 parts of medium-channel air-floated carbon black having an average particle size of less than 5 microns and a pH value of about 3 to 4.6.

2. The composition of claim 1 in which the metallic soap is aluminum stearate.

3. The composition of claim 1 in which there is present about 0.5 to 4 parts mica particles.

4. The process of making a flowable plastic mass suitable for use as a plug valve lubricant and sealant comprising heating to about 125° F., from 55 to 75 parts of a synthetic liquid organic polysulfide polymer having an average molecular weight of about 4000; and from 0 to 5 parts of a synthetic liquid organic polysulfide polymer having an average molecular weight of about 1000; said polysulfide polymers having substantially the following average structure:

$$HS—(C_2H_4—O—CH_2—O—C_2H_4—S—S)_x—C_2H_4—O—CH_2—O—C_2H_4—SH$$

where X is an integer of about 6 for polymers of molecular weight of 1000 and X is an interger of about 23 for polymers of molecular weight of 4000; then adding from 6 to 14.5 parts of carbon black having a pH of from 3.0 to 4.6 while keeping the temperature of the mixture between 125° F. and 150° F.; then adding from 10 to 30 parts of a metallic non-water soluble soap selected from the group consisting of the soaps from stearic, oleic and naphthenic acids, while maintaining the temperature of the mixture from substantially exceeding 150° F. to thicken the mixture to desired consistency; agitating and raising the temperature of the mixture to about 385° F., and then cooling the mixture to about room temperature.

5. In the process defined in claim 4, the further step of working the cooled mixture mechanically.

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