Patented Sept. 14, 1954

2,689,223

UNITED STATES PATENT OFFICE

2,689,223

VISCOSITY INDEX IMPROVERS

Alexander H. Popkin, New York, N. Y., and Thomas S. Tutwiler, Watchung, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application June 22, 1951, Serial No. 233,110

11 Claims. (Cl. 252—42.7)

1

This invention relates to improved lubricating oil compositions. Particularly the invention relates to lubricating oil concentrates of a sulfur reactive hydrocarbon copolymer of an aliphatic isoolefin of low molecular weight with a low molecular weight diolefin and containing also combined therein as a stabilizer for said concentrate a minor amount of the reaction product of phosphorus and sulfur with the metal salt of an alkyl phenol sulfide.

It is known in the art that lubricating oils may be improved in their rate of change of viscosity with temperature, that is, their viscosity index may be improved, by adding thereto minor amounts of various additive materials which are known as viscosity index improvers. One especially efficient viscosity index improver has been found to be a copolymer of a low molecular weight isoolefin with a low molecular weight diolefin. These multi-olefinic copolymers are usually prepared by a low temperature copolymerization process. One such process is defined in United States Patent No. 2,356,128, issued to Thomas and Sparks on August 22, 1944, the specification of which is herein combined by reference.

The copolymeric materials referred to in the above mentioned patent have been most economically prepared in molecular weight ranges in the order to 40,000 to 250,000. It has been found that the copolymeric materials within this molecular weight range are less desirable as viscosity index improvers than copolymers having a lower molecular weight, such as 10,000 to 30,000 Staudinger, because they are relatively unstable to shearing forces. Thus, after continued use in automotive engines, they break down and lose their ability to thicken or improve the viscosity characteristics of the lubricating oil containing them.

One solution of the problem of shear instability of these high molecular weight copolymeric materials is presented in United States Patent No. 2,466,301. In this patent it is taught that the high molecular weight copolymers may be degraded as to molecular weight by milling the copolymeric material in the presence of an aryl mercaptan as an assisting agent. By this procedure the molecular weight is reduced to one within the desired range.

A second method of reduction of molecular weight is presented in United States Patent No. 2,239,501. In this patent it is taught that the molecular weight of these copolymeric materials may be reduced by extrusion through an orifice.

2

It is the common practice in the lubricating oil manufacturing art to prepare oil concentrates of lubricant additives for ease in handling, storage, and the like. These concentrates are prepared by blending with a suitable base oil from 10% to 90% of the particular additive material. These concentrates are then added to a lubricating formulation in amounts sufficient to give the desired weight percent of additive in the finished blend.

It has been found that lubricating oil concentrates of these copolymeric viscosity index improvers which have been degraded in molecular weight from about 40,000 to 250,000 to one of about 10,000 to 30,000 are thermally unstable to some degree, that is, these oil concentrates show a decrease in viscosity upon continued standing at high temperatures. This, of course, is undesirable, loss of viscosity indicating a loss of thickening power, or viscosity index improving potency. It is toward this phase of the over all problem that this invention is directed.

It has now been found and forms the object of this invention that concentrated oil solutions of these degraded multi-olefinic copolymeric materials may be stabilized against thermal degradation by adding to the concentrates minor amounts of the phosphorous and sulfur reaction product of the metal salts of alkyl phenol sulfides.

The improved lubricating oil concentrates of this invention consist essentially of the following three components:

A. A lubricating oil
B. A degraded copolymer of an aliphatic isoolefin and a low molecular weight dioolefin, and
C. A phosphorized sulfur metal salt of an alkyl phenol sulfide.

The lubricating oil component of this invention may consist of any of the commonly known lubricating oils, either natural or synthetic. They may be straight mineral oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes. If desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali, and/or clay or other agents such as aluminum

chloride. They may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloroethyl ether, nitrobenzene, and the like. Hydrogenated oils or while oils may be employed. Synthetic oil prepared by the polymerization of olefins, by the reaction of oxides of carbon with hydrogen, by the hydrogenation of coal or its products are operable. Other types of synthetic oils such as the complex synthetic esters, ethers, ether esters, or ester ethers may be used.

Although a wide range of lubricating oils may be used in the preparation of the concentrates of this invention, as outlined above, it is preferred to use mineral lubricating oils having a viscosity within a range of from 34 to 300 S. U. S. at 210° F.

As the copolymeric material operable in this invention one may employ any of the copolymers described in United States Patent 2,356,128 referred to above. These include copolymers of a low molecular weight aliphatic isoolefin having from 4 to 7 carbon atoms, such as isobutylene, with a low molecular weight conjugated aliphatic diolefin having from 4 to 8 carbon atoms such as butadiene, isoprene, dimethyl butadiene, and the like. These copolymeric materials are prepared by subjecting a mixture of a major proportion, say from 70 to 99 parts of the isoolefin and the minor proportion, say 1 to 30 parts of the diolefin, to a low temperature process, that is, temperatures below 0° C., in the presence of the suitable catalyst such as aluminum chloride dissolved in a lower alkyl halide. These copolymeric materials and their preparation do not form a part of this invention.

As was stated above, for the maximum viscosity index improving potency it is essential that these copolymeric materials have molecular weights in the order of 10,000 to 30,000 Staudinger. Although the temperatures and other conditions of preparation of the copolymers may be controlled so as to result in a product having molecular weights within this range, it is found to be advantageous from a practical point of view to degrade the commercially available copolymeric materials having a molecular weight within a range of from 40,000 to 250,000 Staudinger to one within the desired range. It has also been found that these degraded copolymers have superior viscosity index improving properties than copolymeric materials which have been prepared initially of the desired molecular weight range.

Accordingly, in the preferred embodiment of this invention, the copolymeric material is one which has been reduced in molecular weight from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger.

The amounts of the copolymeric materials which are blended with a lubricating oil base to form the concentrates will depend upon various factors. Ordinarily, it is preferred to combine with the lubricating oil from 10% to 90.0% by weight, based on the weight of the total composition, of the copolymer. In the preferred embodiment, using a copolymer having a molecular weight within the range of from 10,000 to 30,000 Staudinger and using a mineral lubricating oil as a base, from 10% to 50% by weight of the copolymer is used.

The third component of the improved lubricating oil compositions of this invention, hereinafter referred to as a stabilizing agent, is the reaction product of phosphorus and sulfur with a metal salt of an alkyl phenol sulfide. These products are described in detail in United States

Patent 2,451,345, issued to McNab and Rogers on October 12, 1948. Although it has been found that the metal salts of alkyl phenol sulfides themselves have some stabilizing effect, the phosphorus sulfided treated products are superior and are preferred.

Exemplary of the compounds which may be reacted with phosphorus and sulfur or a phosphorus sulfide such as P_2S_5, P_4S_3, P_4S_7 or the like are the metal salts such as calcium, barium, strontium, magnesium, zinc, tin, lead, aluminum, cobalt, or nickel salts of the following:

Calcium tert.-octyl phenol sulfide
Barium 2,4-di-tert.-amyl phenol sulfide
Cobalt tert.-amyl phenol sulfide
Barium salt of 2-hydroxy-3,5-di-tert.-amyl-4-diethylamino diphenyl sulfide
Zinc salt of salicylic acid sulfide octyl ester
Barium 2-stearoyl-4-amyl phenol sulfide
Mixed calcium-barium tert.-octyl phenol sulfide
Tin salt of C_{16}–C_{20} branched chain alkyl phenol sulfide
Barium salt of bis(2,4-diamyl phenol)-4-amyl-phenol dithioether (prepared from 2 mols of 2,4-di-tert.-amyl phenol and one mol of p-tert.-amyl phenol, sulfurized with sulfur chloride and neutralized with barium hydroxide)

When the salts employed are those of polyvalent metals, it is not essential that all of the valences be satisfied by hydroxyaryl sulfide groups; some of them may be satisfied by other acidic organic groups such as carboxy, aroxy, alkoxy, organo-substituted inorganic acid groups such as phosphoric, phosphorus, thiophosphoric, thiophosphorus, phosphonic, phosphinic, sulfonic, sulfinic, and the like.

Thus, for example, the present invention also includes reaction products of phosphorus sulfide with such compounds as:

Calcium mixed salt of tert.-amyl phenol sulfide and iso-octyl salicylate
Aluminum mixed salt of tert.-octyl phenol sulfide and stearic acid
Tin mixed salt of di-tert.-amyl phenol sulfide and naphthenic acids
Barium mixed salt of tert.-octyl phenol sulfide and petroleum mahogany sulfonic acids
Nickel mixed salt of tert.-amyl phenol sulfide and amyl xanthic acid
Zinc mixed salt of isododecyl phenol sulfide and methyl cyclohexyl thiophosphoric acid
Nickel mixed salt of tert.-amyl phenol sulfide and oleic acid
Magnesium mixed salt of tert.-octyl phenol sulfide and cetyl phenol

These materials and their preparation are described in detail in United States Patent No. 2,451,345 referred to above and do not form a part of the instant invention.

Although the amounts of the stabilizing agent added to the oil solution of the copolymeric material will depend upon several factors, usually from 0.05% to 10% by weight, based on the weight of the copolymeric material, is used. In the preferred embodiment of the invention, that is, a mineral lubricating oil containing combined therein from 10% to 40% by weight of a copolymer of a lower molecular weight isoolefin and a low molecular weight diolefin which has been reduced in molecular weight from about 40,000 to 250,000 Staudinger to a molecular weight within a range of from 10,000 to 30,000 Staudinger, from 0.1% to 2.5% by weight of the phosphorus

sulfide reaction product of the metal salt of an alkyl phenol sulfide, based on the weight of the copolymeric material, will be used.

In order to point out the remarkable thermal stability of the lubricating oil concentrates of this invention, a blend of a Mid-Continent base oil containing 20% by weight of a degraded copolymer of isobutylene and isoprene having a molecular weight of about 22,000 was divided into several portions. Into separate portions were added various commercially available stabilizing agents along with the stabilizing agent of this invention. The blends were stored for twenty days at a temperature of 210° F. After that time a viscosity determination was made and the present loss of viscosity reported. The results of the test are set out in Table I below.

TABLE I

Stability data

Chemical Structure of Inhibitor	Wt. Percent	Solution Degradation, Percent Loss Vis./210° F., S. U. S., After 20 Days' Storage at 210° F.
	none	11.0
P_2S_5-treated barium salt of diisobutylphenol sulfide	1.6	3.5
Di-tert.-butyl-p-cresol	1.0	9.0
Di-tert.-butyl-p-cresol	3.0	16.0
	1.0	17.0
Phenol-aldehyde condensate	1.0	24.0
A polyaromatic alkylated with para-cresol	1.0	28.0
2-tert.-Butyl-4-methoxyphenol	1.0	42.0

Upon examination of the results of the storage stability test data of Table I above, it is seen very clearly that unusal results are obtained with the compositions of this invention. The lubricating oil concentrate, according to the concept of this invention, showed only 3.5% loss in viscosity after 20 days storage at 210 compared to 9% loss shown by the tertiary butyl-p-cresol, the most advantageous stabilizer of the prior art.

From the stability point of view, one extremely desirable viscosity index improver is a commercially available polymer of isobutylene having a molecular weight within a range of from about 10,000 to 30,000 Staudinger. It has been found, however, that the lubricating oil compositions of this invention are considerably more stable at high temperature storage than this commercial polymer having about the same molecular weight range. This is shown by the data in Table II below:

TABLE II

Stability data

Polymer	Inhibitor	Solution Degradation, Percent Loss Vis./210° F., After 20 Days' Storage at 210° F.
Degraded Copolymer of Isobutylene-Isoprene, 27,000 M. W.	None	29
Degraded Copolymer of Isobutylene-Isoprene, 27,000 M. W.	1.6% P_2S_5-treated barium salt of diisobutyl phenol sulfide.	5
Degraded Copolymer of Isobutylene-Isoprene, 27,000 M. W.	0.5% P_2S_5-treated barium salt of diisobutyl phenol sulfide.	10
19,000 M. W. Polybutene	None	11
23,000 M. W. Polybutene	None	22

To show that the stabilizing effect of the agent is not lost upon dilution with mineral oil to a finished formulation a concentrate of a copolymer of isobutylene and isoprene was diluted with a solvent extracted Mid-Continent distillate having a viscosity at 210° F. of 36 S. U. S. until a blend was obtained containing approximately 10.0% of the copolymeric material. This blend was divided into two portions, and to one was added 1.8% by weight, based on the weight of the copolymer, of the inhibitor of Table II above. The samples were allowed to stand for 26 days at 210° F. and viscosity determinations made. It was found that at the end of that period the sample containing the inhibitor had lost no viscosity units whereas the control had lost 8.0% of its viscosity.

It is also within the concept of this invention to prepare these concentrates of the viscosity index improving copolymers described above, in such a manner that the finished oil concentrates exhibit the high degree of thermal stability as shown above. According to this concept of the invention, the copolymeric material having a molecular weight within the range of 40,000 to 250,000 Staudinger are degraded to a molecular weight within the range of from 10,000 to 30,000 according to any of the procedures with which the art is familiar. As is pointed out above, this includes milling in the presence of an aryl mercaptan, extrusion through an orifice, and the like. After the degradation is completed there is then added to the concentrate a stabilizing amount of the phosphorus sulfide reaction product of the metal salt of an alkyl phenol sulfide. In this instance, as described above, from 0.05% to 10% of the stabilizing agent may be added.

Another phase of this invention relates to the preparation of these multi-olefinic copolymers having viscosity index improving characteristics in an oil solution in the presence of an inert atmosphere such as nitrogen. In this instance the degradation is carried out under a nitrogen blanket or by some other means which excludes oxygen. The presence of the inert atmosphere excludes oxygen and the characteristic formation of peroxides in the polymer, the peroxide formation contributing to the over all instability of the oil concentrates. In this concept, as in the two above described phases of the invention, the stabilizing agents are added to insure complete thermal stability.

To summarize briefly, this invention relates to thermally stable lubricating oil concentrates of multi-olefinic copolymers which have been reduced or degraded in molecular weight from about 40,000 to 250,000 Staudinger to about 10,000 to 30,000 Staudinger. This thermal stabilization is accomplished by incorporating minor amounts of the phosphorus sulfide reaction products of metal salts of alkyl phenol sulfides. It is also within the concept of this invention to prepare these stabilized oil concentrates by degrading the copolymeric materials in an oil solution in the presence of an inert atmosphere such as a nitrogen blanket and stabilizing said concentrates by the addition of the stabilizing agent.

What is claimed is:

1. A lubricating oil concentrate useful for blending purposes which consists essentially of a mineral base lubricating oil containing combined therein from 10% to 90% by weight of a copolymer of a low molecular weight aliphatic isoolefin and a low molecular weight aliphatic conjugated diolefin, said copolymer having vis-

cosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing a minor amount, sufficient to improve the thermal stability characteristics thereof, of a phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

2. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 90% by weight of a copolymer of a low molecular weight aliphatic isoolefin and a low molecular weight aliphatic conjugated diolefin, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing a minor amount, sufficient to improve the thermal stability characteristics thereof, of a phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

3. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 50% by weight of a copolymer of a low molecular weight aliphatic isoolefin having from 4 to 7 carbon atoms per molecule and a low molecular weight aliphatic conjugated diolefin having from 4 to 8 carbon atoms per molecule, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing a minor amount, sufficient to improve the thermal stability characteristics thereof, of a phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

4. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 50% by weight of a copolymer of from 70 to 99 parts by weight of isobutylene and from 30 to 1 parts by weight of isoprene, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Stuadinger and containing a minor amount, sufficient to improve the thermal stability characteristics thereof, of a phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

5. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 50% by weight of a copolymer of from 70 to 99 parts by weight of isobutylene and from 30 to 1 parts by weight of isoprene, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing from 0.05% to 10.0% by weight, based on the weight of the copolymer, of a phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

6. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 50% by weight of a copolymer of from 70 to 99 parts by weight of isobutylene and from 30 to 1 parts by weight of isoprene, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing from 0.05% to 10.0% by weight, based on the weight of the copolymer, of a P_2S_5 reaction product of a metal salt of an alkyl phenol sulfide.

7. A lubricating oil concentrate consisting essentially of a mineral base lubricating oil having a viscosity at 210° F. of from 34 to 300 S. U. S. containing combined therein from 10% to 50% by weight of a copolymer of from 70 to 99 parts by weight of isobutylene and from 30 to 1 parts by weight of isoprene, said copolymer having viscosity index improving characteristics and having been reduced in molecular weight from one within a range of from about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and containing from 0.05% to 10.0% by weight, based on the weight of the copolymer, of a P_2S_5 reaction product of the barium salt of diisobutyl phenol sulfide.

8. A process for the preparation of thermally stable oil concentrates of a copolymer of a low molecular weight aliphatic isoolefin having from 4 to 7 carbon atoms and a low molecular weight aliphatic conjugated diolefin having 4 to 8 carbon atoms, said copolymer having viscosity index improving characteristics, which comprises degrading said copolymer in the presence of a mineral oil from a molecular weight of about 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and adding to said oil solution of the degraded copolymer a minor proportion, sufficient to stabilize the copolymer against thermal degradation, of the phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

9. A process for the preparation of thermally stable oil concentrates of a copolymer of from 70 to 99 parts by weight of a low molecular weight aliphatic isoolefin having from 4 to 7 carbon atoms and from 1 to 30 parts by weight of a low molecular weight aliphatic conjugated diolefin having from 4 to 8 carbon atoms, said copolymer having viscosity index improving characteristics, which comprises degrading said copolymer in the presence of a mineral oil from a molecular weight of from 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and adding to said oil solution of the copolymer from 0.05% to 10.0% by weight, based on the weight of the degraded copolymer, of the phosphorus sulfide reaction product of a metal salt of an alkyl phenol sulfide.

10. A process for the preparation of thermally stable oil concentrates of a copolymer of from 70 to 99 parts by weight of a low molecular weight aliphatic isoolefin having from 4 to 7 carbon atoms and from 1 to 30 parts by weight of a low molecular weight aliphatic conjugated diolefin having from 4 to 8 carbon atoms, said copolymer having viscosity index improving characteristics, which comprises degrading said copolymer in the presence of a mineral oil from a molecular

weight of from 40,000 to 250,000 Staudinger to one within a range of from about 10,000 to 30,000 Staudinger and adding to said oil solution of the copolymer from 0.05% to 10.0% by weight, based on the weight of the degraded copolymer, of the P_2S_5 reaction product of the barium salt of diisobutyl phenol sulfide.

11. A process according to claim 10 wherein said degradation is accomplished in the presence of a nitrogen blanket, said nitrogen blanket excluding air.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,239,501	Frolich et al.	Apr. 22, 1941
2,409,333	Wright et al.	Oct. 15, 1946
2,451,345	McNab et al.	Oct. 12, 1948