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COLLOIDAL MOLYBDENUM COMPLEXES AND THEIR PREPARATION

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This invention concerns colloidal molybdenum complexes, their preparation, and improved lubricating oil compositions containing molybdenum complexes. The invention is particularly directed to the preparation of molybdenum complexes for use as antiwear additives for lubricating oils by a novel process that involves dispersion of an ether extract of a molybdenum compound in a dispersant material. This application is a continuation-in-part of application Serial No. 131,723, filed August 16, 1961, and abandoned after the filing of the present application.

It has been known for some time that molybdenum sulfide is a desirable additive for lubricating oils because of its ability to reduce friction and hence to minimize wear of the parts being lubricated. Although it is possible to prepare lubricating oil compositions containing molybdenum sulfide by grinding the material to exceedingly fine particle size and then dispersing it in lubricating oil, the dispersion is not completely stable and the particles of molybdenum sulfide tend to settle out. This settling may result because of an improperly formed colloid or it may be caused by changes occuring in the oil on standing or in use. There has been a need for more stable dispersions of molybdenum sulfide or, alternatively, a need for compositions exhibiting the wear-reducing properties of molybdenum sulfide but being free of the unstable nature of molybdenum sulfide dispersions.

While it has recently been found that colloidal dispersions of molybdenum sulfide can be prepared in situ in lubricating oils by reacting an aqueous solution of the molybdate with hydrogen sulfide in a lubricating oil medium containing a dispersant material and subsequently removing water, that process carried with it the limitation that in order to operate at high molybdenum levels more dispersant was necessary.

It has now been found that colloidal complexes having increased concentrations of molybdenum in proportion to the dispersant can be prepared in the following manner: an aqueous solution of a molybdenum compound as, for example, ammonium molybdate or molybdic acid in a mineral acid as, for example, 6 N aqueous HCl is prepared. This solution is then extracted with an ether, for example, ethyl ether, and then the ether solution is dispersed in an oil-soluble dispersant and the ether is subsequently removed. If the stripping gas used for removing the ether contains hydrogen sulfide, at least some molybdenum sulfide is formed in the product.

Not only does the process of this invention lead to higher molybdenum concentration levels, but it also enables wider versatility in the selection of dispersants that may be used; e.g., calcium compounds where barium compounds are objectionable; sulfonate detergents (nonlabile sulfur) or sulfur-free dispersants where active sulfur compounds (e.g. phosphosulfurized compounds) are objectionable. Alternatively, a high molybdenum concentration obtained in accordance with the present invention, even if the dispersant had certain drawbacks, would require a relatively small amount of the latter and would permit the concurrent use, in the finished lubricant, of a second, more desirable dispersant from the standpoint of

deleterious effects in use, even though the second dispersant might be less satisfactory for preparing the colloidal dispersion of molybdenum compounds in accordance with this invention, thus giving a highly satisfactory composition from every standpoint.

Any water-soluble compound of molybdenum wherein the molybdenum is present in the hexavalent state may be employed as the molybdenum source in the practice of this invention. Such compounds include molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, other alkali metal molybdates, and other molybdenum salts such as $MoOCl_4$, MoO_2Br_2, $Mo_2O_3Cl_6$, and $MoOF_4$. Molybdenum trioxide may be employed by dissolving it in aqueous ammonia followed by treatment with hydrochloric acid which in essence, converts the oxide to molybdic acid or ammonium molybdate.

The general procedure followed in practicing the invention is as follows. It is usually desirable to dissolve the molybdenum compound in the minimum amount of water necessary for complete solution, although the amount of water may range from 4 to 10 parts by weight per part of molybdenum compound. Then sufficient mineral acid, preferably aqueous HCl, is added to furnish a solution having a normality in the range of 4 to 8, preferably 5 to 7. If the acidity is greater than 7 N, there may be deleterious effects. For example, there is a tendency for excess chlorine to appear in the product if HCl has been used. If the acidity is below 5 N, the molybdenum utilization, i.e., the proportion of molybdenum in the product to the molybdenum used in the process, tends to be poor.

Preferably, the acidified solution is cooled to below 50° C. before the ether extraction to minimize evaporation losses. The required cooling would not be as great in a closed system. After a period of agitation for proper contact with the ether and then a period of settling for separation, the ether extract layer is added to a suitable dispersant. Contacting temperatures and mixing rates are controlled so as to prevent foaming problems. The ether is then removed by either (1) heat and vacuum, (2) heat and inert gas blowing, or (3) heat and H_2S blowing until a temperature of about 200° F. is reached followed by vacuum or inert gas blowing to remove excess H_2S. Nitrogen is a suitable inert gas and is relatively less expensive than other inert gases, e.g. helium. The procedure involving H_2S treating is preferred since this converts at least a portion of the product to colloidal molybdenum sulfide and ensures good antiwear properties. Extraction of the acidic solution of the molybdate is preferably conducted with ethyl ether. Other ethers may be used also. For example, tetrahydrofuran can also be employed when it is mixed with hexane to decrease its water solubility. Other ethers which are at least partially insoluble in water or which can be extracted from water, are also useful. Preferably, the ethers are those ranging from 3 to 8 total carbon atoms; more preferably, those having 4 to 6 total carbon atoms. Ethers having more than 8 total carbon atoms are not excluded.

It is possible to employ extraction ratios as low as one part of ether per part by weight of molybdate or equivalent molybdenum compound. In general, however, the ether extraction step will involve the use of from about 10 to 40 parts of ether per part of molybdate or equivalent. The ratio of dispersant to molybdenum will depend largely on the basicity of the dispersant, because the latter should be sufficiently basic and should be used in sufficient quantity to neutralize the free acid in the ether extract. Also, the dispersant should be oil-soluble. Suitable dispersants include metal hydrocarbon sulfonates, metal carbonate sols, metal alkyl phenates, metal alkyl phenol sulfides, reaction products of metal oxides and/or metal hy-

droxides with phosphosulfurized hydrocarbons, and certain nonmetallic dispersants as described hereinafter. The preparation of the complex of the invention may be made in the presence of the dispersant per se but it is usually more convenient to conduct the preparation in an oil concentrate of the detergent or dispersant. Such concentrates usually contain from about 10 to about 80 wt. percent, preferably 20–60 wt. percent, of the dispersant in a lubricating oil. The lubricating oil may be either a mineral oil or a synthetic oil, the latter including diesters, complex esters, polysilicones, polyglycols and the like.

The sulfonates used as dispersants in practicing this invention are the oil-soluble alkaline earth metal salts of high molecular weight sulfonic acids obtained by the sulfonation of either natural or synthetic hydrocarbons. Sulfonic acids can be prepared by treating lubricating base stocks with concentrated or fuming sulfuric acid in a conventional manner to produce oil-soluble "mahogany" acids. These sulfonic acids generally have molecular weights in the range of about 300 to 700. Petroleum sulfonates are well known in the art. Suitable sulfonic acids can also be produced by sulfonating alkylated aromatic hydrocarbons such as benzene, toluene, and xylene alkylated with olefins or olefin polymers. For example, sulfonated didodecyl benzene may be used.

Specific examples of sulfonates suitable for practicing this invention include calcium petroleum sulfonates, barium petroleum sulfonates, calcium di-C_8 alkyl benzene sulfonate, barium di-C_9 alkyl benzene sulfonate and calcium C_{16} alkyl benzene sulfonate. The C_8 alkyl groups can be derived from dissobutylene, the C_9 alkyl groups can be obtained from tripropylene and the C_{16} alkyl group can be obtained from tetraisobutylene. It is preferred to use the so-called "high alkalinity" type of sulfonate, which is prepared by reacting metal base in excess of that required for simple neutralization of the sulfonic acid to form an alkaline product which can then be treated with carbon dioxide to reduce its free alkalinity and form a substantially neutral final product. It is believed that the high alkalinity sulfonates are primarily dispersions of metal carbonates in the neutral sulfonates.

Metal salts of alkyl phenols and of alkyl phenol sulfides are also well known in the art. Metal salts of alkyl phenols having straight-chain or branch-chain alkyl groups of from 5 to 20 carbon atoms are usually preferred, and the metal used to form the phenate is preferably an alkaline earth metal, e.g., calcium, barium, strontium, or magnesium, although other salts such as those of aluminum, sodium, cobalt, lead, chromium, or tin are sometimes used. A specific example is the barium salt of the alkylation product of phenol with tripropylene. Metal salts of the corresponding alkyl phenol sulfides may also be used. The latter are the thioethers and polysulfides of alkyl phenols, i.e., compounds in which the alkyl groups are joined by one or more divalent sulfur atoms. The alkyl phenols can be converted to phenol sulfides by reaction with sulfur dichloride. If sulfur monochloride is used, the resulting products are primarily alkyl phenol disulfides. Specific examples of the phenate sulfides include barium tertiary octyl phenol sulfide, calcium tertiary octyl phenol sulfide, barium-calcium nonyl phenol sulfide, barium tertiary amyl phenol sulfide, calcium dodecyl phenol sulfide, and barium nonyl phenol sulfide. Preferably, the metal phenols and metal phenol sulfides are of the high alkalinity type (i.e. of high metal content) prepared by reacting the metal salts with excess metal base.

The reaction products of phosphosulfurized hydrocarbons with alkaline earth metal oxides or hydroxides can be prepared by first treating a hydrocarbon with the phosphorus sulfide and then reacting the product with an alkaline earth hydroxide or oxide, for example, barium hydroxide, preferably in the presence of an alkyl phenol

or an alkyl phenol sulfide and also preferably in the presence of carbon dioxide.

The phosphosulfurized hydrocarbons may be prepared by a reaction of a sulfide of phosphorus such as B_2S_5 with a suitable hydrocarbon material such as a terpene, a heavy petroleum fraction or a polyolefin. The olefin polymers that are employed have Staudinger molecular weights in the range of 500 to about 200,000 and contain from 2 to 6 carbon atoms per olefin monomer. Particularly preferred are the polybutenes having Staudinger molecular weights in the range of about 500 to about 200,000. Polymers of ethylene, propylene, butylene or isobutylene may be used, for example. The phosphosulfurized hydrocarbon can be prepared by reacting the hydrocarbon base stock with from 5 to 30 weight percent of a sulfide of phosphorus, and preferably with from 10 to 20 weight percent of phosphorus pentasulfide. The reaction is conducted under anhydrous conditions at temperatures from about 150 to about 600° F. for from about ½ to 15 hours. The preparation of phosphosulfurized hydrocarbons is more fully described in U.S. Patent 2,875,188.

Nonmetallic dispersants that may be employed in the present invention include the condensation products of alkenylsuccinic anhydrides and polyamines and the condensation products of alkenylsuccinic anhydrides, polyamines and carboxylic acids, said products having residual amino groups to impart basicity.

The preparation of reaction products of high molecular weight alkenylsuccinic anhydrides with various polyamine compounds is taught in U.S. Patents 3,024,195 and 3,024,237 and also in British Patent 922,831. The teaching in the U.S. patents referred to is that alkenylsuccinic anhydrides having alkenyl radicals derived from hydrocarbons of 400 to 3000 molecular weight can be reacted with amine derivatives of piperazine. The British patent referred to teaches that alkenylsuccinic anhydrides, as, for example, a polyisobutenylsuccinic anhydride, can be reacted with polyamines such as tetraethylene pentamine, diethylene triamine, triethylene tetramine, and the like.

The preparation of reaction products of alkenylsuccinic anhydrides with carboxylic acids and alkylene polyamines is disclosed and claimed in copending application Ser. No. 241,174 of Norman Tunkel et al., filed November 30, 1962. Briefly, those reaction products are prepared by the simultaneous reaction of about 0.5 to 1.5 mole proportions of a C_1 to C_{30} carboxylic acid, about 1 molar proportion of an alkylene polyamine, and about 1.0 to 1.5 molar proportions of an alkenylsuccinic anhydride wherein the alkenyl group contains in the range of from about 40 to about 250 carbon atoms, the reaction being effected by heating the reactants together until an oil-soluble product is obtained.

While the reactants, i.e. the alkenylsuccinic anhydride and the polyamino compound (and, when used, the carboxylic acid), upon simple mixing will interact to some extent, the products will generally be oil-insoluble. However, upon heating (e.g. to about 200–250° F.) the reaction mixture will become mineral-oil-soluble, and upon continued heating condensation reactions will begin to take place with the evolution of water. The evolved water can be readily removed by blowing nitrogen or other inert gas through the reaction mixture during the course of the reaction. The reaction may be carried out by heating the reactants for about 1 to 30 hours at 250 to 350° F. Preferred reaction conditions include heating for 6 to 20 hours at 275 to 300° F.

The preparation of an alkenylsuccinic anhydride is well known in the art and simply involves reacting maleic anhydride with an organic compound having an olefinic linkage. Generally, about equal molar proportions of maleic anhydride and the olefinic material are merely heated together.

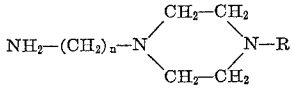
The hydrocarbon radicals may be either straight-chain

or branched chain and they may be either substituted, as for example, chlorinated or sulfurized, or they may be unsubstituted, and they will include aliphatic, acyclic and aromatic radicals. Preferably, the total number of carbon atoms in the hydrocarbon groups is within the range of from about 40 to 250, more preferably within the range of from about 50 to about 120. Particularly desirable for use, because of low cost and ready availability, are alkenyl groups obtained by reacting maleic anhydride with a polymer of a C_2 to C_5 monoolefin wherein the polymer has a molecular weight within the range of from about 300 to about 3000 or more. Especially useful products are obtained when the molecular weight range is from about 500 to about 1500. As specific examples, the alkenyl group may be derived from polypropylene or polyisobutylene, e.g., polyisobutylene of 780 molecular weight or of 1200 molecular weight.

The aliphatic polyamine that is employed in preparing the reaction products of the present invention may be an alkylene polyamine fitting the following general formula:

$$NH_2(CH_2)_n—[NH(CH_2)_n]_m—NH_2$$

where n is 2 to 3 and m is a number from 0 to 10. Specific compounds coming within the formula include diethylene triamine, tetraethylene pentamine, dipropylene triamine, octaethylene nonamine, and tetrapropylene pentamine. N,N-di-(2-aminoethyl) ethylene diamine may also be used. Other aliphatic polyamino compounds that may be used are the N-aminoalkyl piperazines of the formula



wherein n is a number 1 to 3, and R is an amino-alkyl radical containing 1 to 3 carbon atoms, for example, N,N'-di-(2-aminoethyl) piperazine.

The use of mixtures of alkylene polyamines, mixtures of N-aminoalkyl piperazines, and mixtures of the alkylene polyamines with the N-aminoalkyl piperazines is also contemplated.

When preparing reaction products of the alkenylsuccinic anhydrides with the alkylene polyamines and/or the N-aminoalkyl piperazines, equimolar proportions of the alkenylsuccinic anhydride and the nitrogen-containing material are usually employed, although in some instances an excess of the anhydride or of the nitrogen compound can be used. Similarly, when preparing the reaction product of an alkenylsuccinic anhydride, a polyamine and a carboxylic acid, equimolar proportions of the three reactants are ordinarily used. However, variation in these relative proportions can be made, for example 1.0 to 1.5 moles of the anhydride and 1.0 to 1.5 moles of the carboxylic acid can be used per mole of polyamine.

The carboxylic acid component of the reaction mixture, when such is used, comprises a carboxylic acid of from 1 to 30 carbon atoms in an aliphatic hydrocarbon chain, which can be either branched or straight chain and either saturated or unsaturated. Both monocarboxylic acids and dicarboxylic acids are included. Preferably carboxylic acids having from 1 to 18 carbon atoms are used, including acetic acid, fumaric acid, adipic acid, lauric acid, oleic acid, linoleic acid and stearic acid.

The following examples serve to illustrate this invention.

EXAMPLE 1

An oil-soluble molybdenum complex can be prepared in accordance with this invention in the following manner: 1 part by weight of ammonium molybdate is mixed with 5 parts of water and an eqal volume of 12 normal HCl is added, thus giving a 6 normal solution. This solution is cooled to about 50° F. and extracted with 21.5 parts of ethyl ether. Separation into two layers is permitted and the ether laye ris then removed and stirred into 8 parts by weight of an oil-soluble disperant. The dispersion is then heated and stripped with gases to remove ether and water. Until a temperature of about 200° F. is attained, the stripping gas comprises hydrogen sulfide. Heating is continued until a temperature of about 350° F. is reached, nitrogen gas being used to strip ether and H_2S from the dispersions at temperatures above about 200° F. The product is then filtered.

While the preparation of the complexes may be done in a batch process, a continuous process may also be used wherein each of the steps will be conducted in a separate zone. The lower layer obtained during the separation step following the ether extraction step may be recycled to the step of mixing ammonium molybdate with water and HCl. Also, the ether that is removed during stripping can be scrubbed with NaOH for example to remove H_2S, and then be reused for further extraction.

The range of typical product analyses obtained in a number of runs using a high alkalinity calcium sulfonate as the dispersant is shown in Table I.

Table I

PRODUCT ANALYSIS WHERE DISPERSANT IS HIGH ALKALINITY CALCIUM SULFONATE

	Weight percent
Mo	5 to 6
S	1.4 to 3.4
Ca	10.5
CO_3	7.5 to 8.5
Cl	3.5 to 4.0

EXAMPLE 2

A phosphosulfurized hydrocarbon was prepared by reacting 100 parts by weight of a polybutene having an average Staudinger molecular weight of about 940 with 15 parts by weight of phosphorus pentasulfide for about 8 hours at 425–450° F., the mixture being stirred and blown with nitrogen during the reaction. The resulting phosphosulfurized polybutene analyzed about 3.5 wt. percent phosphorus and about 6.6 wt. percent sulfur. Its viscosity at about 210° F. was about 20,000 SSU.

A solution of 115 parts by weight of the phosphosulfurized polybutene prepared as above was made in 112 parts by weight of a refined mineral lubricating oil having a viscosity of 150 SSU at 100° F. To the mineral oil solution was added 273 parts by weight of a nonyl phenol having an average molecular weight of 248. The nonyl phenol was prepared by alkylation of phenol with tripropylene and comprised about 60–65% monononyl phenol and about 35–40% of dinonyl phenol. The mixture of alkyl phenol, mineral oil and phosphosulfurized polybutene was treated with barium hydroxide pentahydrate and carbon dioxide at a temperature of about 250–260° F. for 6–8 hours. The amounts of barium hydroxide and carbon dioxide used were selected to furnish a weight ratio of barium to phenolic hydroxyl group of about 12 to 1 and a weight ratio of barium to CO_2 of about 4 to 1. Then 339 parts by weight of the resulting product, 101 parts of additional phosphosulfurized polybutene, and 60 parts of additional mineral lubricating oil of the same viscosity were reacted for an additional 2 hours at 300° F. and then stripped with nitrogen to remove residual hydrogen sulfide. The product was then filtered. The filtered product, which is hereinafter referred to as dispersant A, had the following weight percent composition:

	Percent
Phosphosulfurized polyisobutene	27.0
Alkyl phenol (248 average molecular wt.)	11.7
Barium oxide	10.6
Carbon dioxide	2.5
Mineral oil	48.2

EXAMPLE 3

A dispersant concentrate was prepared in the following manner. A blend of 19.8 parts by weight of the phospho-

sulfurized polybutene of Example 2, 6.5 parts by weight of nonyl phenol, 1.6 parts by weight of ammonium sulfonate of about 450 mol. wt. and 41.7 parts by weight of a neutral mineral oil of 150 SSU viscosity at 100° F. was prepared. To this was added at a temperature in the range of 100–130° F., 4.4 parts by weight of commercial ammonium hydroxide of 29% NH_3 content. Then 1 part by weight of water and 16 parts by weight of calcium hydroxide were added at a temperature of 120–150° F., followed by 9 parts by weight of CO_2 added over a period of 3–4 hours at a temperature in the range of 145–160° F. The mixture was then dehydrated by heating to a final temperature of about 370° F. and then filtered. The filtered product, which is hereinafter referred to as dispersant B, had the following weight percent composition:

Ca	9.0
CO_3	12.0
Phosphosulfurized hydrocarbon	22.5
Nonyl phenol	7.4
Neutral mineral oil	47.4
Ammonium sulfonate	1.7

EXAMPLE 4

This example shows that a countercurrent ether extraction process can be used to obtain more highly concentrated ether solutions so that still larger concentrations of molybdenum may be introduced into the given dispersant. The same quantity of ether was used to extract three successive aqueous solutions. As shown in Table II, the successive extraction of the aqueous solution resulted in additional recovery of molybdenum. The total recovery in three extractions with successive portions of 250 cc. of ether was 76%. Indications are that a countercurrent extraction process could cut the ether requirement in half.

Table II

ETHER EXTRACTION OF MOLYBDIC ACID SOLUTION

Aqueous Solution: 50 grm. ammonium molybdate in 500 ml. of 6N HCl (Contains 27.18 gm. Mo).

Ether Extractions: 250 cc. each portion.

Aqueous Solution	Ether Used to Extract	Grams Mo in Ether—			Percent of Orig.
		Before	After	Enrichment	
No. 1 Fresh	No. 1 Fresh	0.0	10.15	10.15	38
No. 1 Used Once	No. 2 Fresh	0.0	7.27	7.27	27
No. 1 Used Twice	No. 3 Fresh	0.0	3.10	3.10	11
Total from No. 1 Aqueous Solution		0.0	20.52	20.52	76
No. 2 Fresh	No. 2 Used Once	7.27	13.68	6.41	24
No. 2 Used Once	No. 3 Used Once	3.10	10.30	7.20	27
Total from No. 2 Aqueous Solution		10.37	23.98	13.61	51
No. 3 Fresh	No. 3 Used Twice	10.30	15.53	5.23	20

EXAMPLE 5

Using the general procedure outlined in Example 1, molybdenum complexes were prepared using various dispersant concentrates, including a high alkalinity calcium sulfonate, a high alkalinity barium sulfonate, and the dispersant A of Example 2. In each case the reactants were employed in the ratio of one part ammonium molybdate, 10 parts of 6 normal HCl, and 20 parts of dispersant concentrate, and (in the first two cases) 30 parts of ethyl ether (all parts are by weight). In the preparation using dispersant A, only 18 parts of ether were used, employing three successive extractions of 6 parts each. The high alkalinity calcium sulfonate was a commercially available synthetic sulfonate available from the Bryton Chemical Company under the name "Bryton C–300." It was a 46% concentrate in mineral oil of a calcium sulfonate of about 420 molecular weight containing 11.4% calcium and 16% carbonate as CO_3, and had a total base number of 319 (i.e. an alkalinity equivalent to 319 mg. KOH/gram). The high alkalinity barium sulfonate was also a commercial product available from Enjay Chemical Company as Paranox 30. It was a 45% concentrate in mineral oil and analyzed about 14.5% barium and had a total base number of 59.

Each of the molybdenum complexes obtained was a clear product. The molybdenum contents of each of the products are given in Table II. The presence of molybdenum utilization given in the table was calculated in each case from the ratio of actual molybdenum found to the total amount of molybdenum that could theoretically be incorporated in each of the products.

Table III

Dispersant	Percent Mo Product	Percent Mo Utilized
High Calcium Sulfonate	2.19	81
High Barium Sulfonate	2.12	78
Disperant A	2.21	82

EXAMPLE 6

Again using the general procedure outlined in Example 1, a molybdenum complex was prepared by extracting a solution of 90 parts by weight of ammonium molybdate in 900 parts of 6 normal HCl with 2700 parts of ethyl ether and then adding the ether extract to 500 parts of the dispersant B of Example 3. The filtered product had a molybdenum content of 6.78%.

EXAMPLE 7

To a solution of 5 grams of ammonium molybdate (2.75 grams Mo) in 25 milliliters of water, 25 ml. of 12 N hydrochloric acid was added. The resulting clear solution was cooled to about 10° C., after which 25 ml. of water, 25 ml. of tetrahydrofuran and 25 ml. of hexane were added. The mixture was agitated and then allowed to stand, causing the separation of an upper layer consisting largely of tetrahydrofuran and hexane. It was determined that this layer contained 0.53 gram of molybdenum.

A second extraction of the aqueous layer with 25 ml. of tetrahydrofuran and 25 ml. of hexane yielded a top solvent layer which was found to contain 0.04 gram of molybdenum. A third extraction with the same quantities of each solvent as in the second extraction gave three layers. The top layer weighed 32.3 grams and contained 0.81 gram Mo, while the middle layer weighed 2 grams and contained 0.16 gram of molybdenum.

By mixing the four solvent layers thus obtained it was possible to form a homogeneous solution containing 1.38 grams of molybdenum, or 50 percent of the molybdenum

in the original aqueous solution. The blend of solvent layers was soluble in the dispersant A of Example 2 and could thus be processed further with H_2S and nitrogen as in Example 1.

EXAMPLE 8

Employing the general procedure outlined in Example 1, molybdenum complexes were prepared using as the dispersant a concentrate containing 21 weight percent of a calcium petroleum sulfonate. The concentrate had a total base number of 283 and analyzed 11.5 weight percent calcium and 13.6 weight percent CO_3. It was obtained as a commercial product known as Lubrizol 56. Three preparations were made using the proportions of ingredients given in Table IV. The molybdenum contents of the products and the molybdenum utilization data are also given in Table IV. It is seen that more molybdenum can be incorporated as the ratio of dispersant to ammonium molybdate is increased.

Table IV

	Preparation		
	A	B	C
Reactants, Parts by Weight:			
Lubrizol 56	100	100	100
Ammonium Molybdate	5	10	15
6 N HCl	50	100	150
Ether Used in Extraction	150	300	450
Molybdenum Content of Product, Wt. Percent	2.11	3.91	6.8
Molybdenum Utilization, Percent	78	72	72

EXAMPLE 9

Additional preparations were made in the manner of Example 1, i.e., extracting an acidified solution of ammonium molybdate with ether, adding the ether extract to a dispersant and then stripping the ether from the mixture with gases. In one of these preparations no H_2S was used, but nitrogen blowing was continued throughout the stripping operation. As in Example 8, the dispersant was Lubrizol 56. The proportions of reactants and of ether used in extraction are given in Table V, along with the molybdenum contents of the filtered products.

Table V

	Preparation		
	D	E	F*
Reactants, Parts by Weight:			
Lubrizol 56	200	200	200
Ammonium Molybdate	25	35	25
6 Normal HCl	250	350	250
Extraction Ether	750	1,050	750
Molybdenum Content of Product, Wt. Percent	6.1	7.11	5.23

*Prepared without hydrogen sulfide blowing.

EXAMPLE 10

A mixture of 180 pounds (0.180 pound mole) of polyisobutylene of about 800 molecular weight and 22.5 lbs. (0.230 pound mole) of maleic anhydride was heated for 24 hours at 450° F. under a nitrogen blanket to form polyisobutenylsuccinic anhydride. The product was found to have a saponification number of 86.6 mg. KOH/gm. of reaction mixture. A light mineral lubricating oil having a viscosity of 150 SUS at 100° F. was added as a diluent in sufficient quantity to result in a solution containing 75 wt. percent of the polyisobutenylsuccinic anhydride. Then 30 p.p.m. of Dow Corning 60,000 cs. polymethyl silicone was added as an antifoamant. Next, 17.22 lbs. (0.091 pound mole) of tetraethylene pentamine and 5.46 lbs. (0.091 pound mole) of acetic acid were added. The reaction mixture was then heated at 300° F. for 10.5 hours while nitrogen was blown through it until no more water came off. The reaction product concentrate, after filtration, contained 2.22 wt. percent nitrogen based on the total product, i.e. the actual reaction product and oil diluent. The concentrate had a base number of about 24.

EXAMPLE 11

Using the general procedure of Example 1, a molybdenum complex is prepared by extracting a solution of 20 parts of ammonium molybdate in 200 parts of 6 N hydrochloric acid with 500 parts of ethyl ether and adding the extract to 100 parts of the dispersant concentrate of Example 10.

EXAMPLE 12

Compositions were prepared using as the base oil a high viscosity index SAE 10W–30 motor oil, containing a copolymeric type viscosity index improver and a detergent inhibitor comprising a stabilized colloidal barium carbonatephenate complex. One composition contained 2 weight percent of the additive D of Example 9, and a second composition contained 0.14 weight percent of additive E of Example 9, giving respective molybdenum contents of 0.12 weight percent and 0.01 weight percent in the two compositions. Each of the compositions also contained as an antioxidant 0.5 weight percent of a phosphosulfurized terpene marketed commercially as Santolube 394C. A third composition consisted of the base oil plus 0.9 wt. percent of a zinc dialkyl dithiophosphate in which the alkyl groups were derived from a mixture of 35% butyl and 65% amyl alcohols. Each of these compositions was separately tested in the Volkswagen Valve Train Wear Test.

In this test, the Volkswagen engine is lubricated with the oil in question and the engine is run for a period of 100 hours using the following electronically controlled operating cycle, which is continuously repeated for the duration of the test:

(a) Five minutes at 600±25 r.p.m., no load
(b) Ten minutes at 1200±r.p.m., no load
(c) Shut down for one minute.

The oil temperature during the test is the temperature normally reached by the oil during engine operation; i.e. no attempt is made to hold the oil temperature at a controlled level.

The wear on each tappet is measured and the wear for the 8 tappets is averaged. If more than one run in made with the same oil, the results for all runs are averaged. The oil is considered to have failed the test if wear exceeds 10×10^{-4} inch on any tappet.

The results obtained in the tests are given in Table VI. It will be seen that the wear was at a satisfactory level, in each instance where a molybdenum complex of the invention was used and that in no instance did the wear on any one tappet exceed the permissible 10×10^{-4} inch. Contrasted with this the well-known antiwear additive, zinc dialkyl dithiophosphate gave 4 to 7 times as much wear and that the wear on some of the individual tappets was quite high. A run made on a base oil similar to that used in the compositions tested, but differing only in that it contained a slightly greater concentration of the detergent-inhibitor gave an average tappet wear of 3.5×10^{-4} inch, with a range of 0–22.

Table VI

	Tappet Wear Inches$\times10^{-4}$		
	Mo Wt. percent	Avg.	Range
Oil Plus Additive D	0.12	0.81	0–5
Oil Plus Additive E	0.01	1.62	0–4
Oil Plus 0.9% Zinc Dialkyl Dithiophosphate	----------	5.5	0–64

EXAMPLE 13

Using as the base oil a refined mineral lubricating oil of SAE 30 viscosity grade compounded with 3.5 weight percent of dispersant A of Example 2 and 0.5 weight percent of the phosphosulfurized terpene antioxidant known as Santolube 394–C, blends were made with additive E of Example 9 and with the additive of Example 6, in each case using sufficient of the additive to furnish 0.025 weight percent of molybdenum in the composition.

Each of these blends was tested in the well-known, 4-ball wear testing machine. The test was conducted as follows. The test lubricant was placed in the cup of the machine and heated to 150° C. The test cup contains 3 steel balls which are fixed in position by a screw cap. A fourth steel ball, held in a chuck, is pressed against the 3 lower balls with a force of 10 kilograms and is rotated at 1800 r.p.m. for a period of 10 minutes. At the end of the test, the amount of wear is determined by measuring the diameter of the wear scar on each of the balls and averaging the results.

The results obtained in the 4-ball wear test with each of the above blends, as well as with the base oil, are given in Table VII. It will be seen that there was less wear with either blend than with the base oil.

Table VII

Oil blend:	4-ball wear, mm.
Base oil	0.449
Oil plus Additive E	0.366
Oil plus Additive of Example 6	0.249

The lubricating oils to which the antiwear agents of the present invention may be added include not only mineral lubricating oils but various synthetic oils. The mineral lubricating oils may be of any preferred type including those derived from the ordinary paraffinic, naphthenic, asphaltic or mixed base mineral crude oils by suitable refining methods. Synthetic hydrocarbon lubricating oils may also be employed. Other synthetic oils include dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, and complex esters as, for example, the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid.

Although the antiwear additives of this invention are primarily intended for use in lubricating oils designed for automotive crankcases, they may also be employed in other hydrocarbon oil compositions including turbine oils, various industrial oils, hydraulic fluids, transmission fluids and the like.

The oil compositions may contain other additives such as detergents, sludge dispersers, viscosity index improvers, e.g. polymethacrylates, polybutenes, etc., antioxidants such as phenyl-alpha-naphthylamine, alkyl phenols, bis phenols and the like, pour point depressants, dyes, and other additives for improving the properties of the compositions.

The additives of this invention are particularly applicable for use in lubricating oil compositions containing viscosity index improvers and detergent-inhibitors. The function of the latter is to prevent or minimize sludge formation as well as to hold in suspension sludge that may be formed in crankcase oils under conditions of low speed, low temperature operation, as in stop-and-go driving. In performing their function as sludge inhibitors and sludge dispersers, the detergent-inhibitors keep the wearing surfaces particularly clean and, for this reason, contribute to a higher degree of wear then would occur if no detergent-inhibitor were present. This problem of wear with high detergency oils shows up particularly in the valve train of automotive engines and, especially, in the valve lifter mechanism, where pressures as high as 50,000 to 100,000 p.s.i. can exist between the valve lifter and its actuating cam. The additives of the present invention are particularly effective for reducing wear in this region of the engine when it is lubricated with a high detergency motor oil.

Concentrates containing from about 2 to about 8 weight percent of molybdenum and from about 10 to about 80 weight percent of surfactant (on an active ingredient basis) in oil are readily prepared by the techniques of this invention. These concentrates can then be added to lubricant compositions to supply in the finished lubricants from about 0.01 to about 2 weight percent of molybdenum. In fluid lubricants the upper range of molybdenum concentration will seldom exceed 1 weight percent or so, while in grease formulations sufficient of the additive may be used to furnish as much as 2 weight percent of molybdenum.

It is to be understood that the examples presented herein are intended to be merely illustrative of the invention and not as limiting it in any manner; nor is the invention to be limited by any theory regarding its operability. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. A process for preparing a stable colloidal complex containing molybdenum which comprises the steps of preparing an acidic aqueous solution of a compound of molybdenum selected from the class consisting of molybdic acid and the halogen, ammonium, and alkali metal salts thereof, said solution having been acidified with a mineral acid to an acidity within the range of from 4 N to 8 N, extracting said acidic solution with a hydrocarbon ether of from 3 to 8 carbon atoms, dispersing the resultant extract in an oil-soluble dispersant having sufficient basicity to neutralize the free acidity of said extract, and then removing ether from the dispersion.

2. A colloidal complex prepared by the process of claim 1.

3. Process as defined by claim 1 wherein said oil-soluble dispersant is employed as an oil solution.

4. Process as defined by claim 1 wherein said ether removal is effected by heating the dispersion and blowing the same with a gas selected from the group consisting of inert gases and hydrogen sulfide.

5. Process as defined by claim 1 wherein said molybdenum compound is molybdic acid.

6. Process as defined by claim 1 wherein said molybdenum compound is ammonium molybdate.

7. Process as defined by claim 1 wherein said molybdenum compound is an alkali metal molybdate.

8. Process as defined by claim 1 wherein said dispersant comprises a high alkalinity metal salt of a hydrocarbon sulfonic acid having a molecular weight in the range of 300 to 700.

9. Process as defined by claim 1 wherein said dispersant comprises the reaction product of a phosphosulfurized hydrocarbon with a basic substance selected from the group consisting of alkaline earth metal oxides and alkaline earth metal hydroxides.

10. Process as defined by claim 1 wherein said dispersant comprises a condenstion product of an alkenyl-succinic anhydride and an aliphatic polyamine, wherein said alkenyl-succinic anhydride has alkenyl groups totaling in the range of from about 40 to 250 carbon atoms.

11. Process as defined by claim 1 wherein said dispersant comprises a condensation product of an alkenyl-succinic anhydride, an aliphatic polyamine, and a C_1 to C_{30} carboxylic acid, said alkenyl succinic anhydride having alkenyl groups totaling in the range of from about 40 to 250 carbon atoms.

12. An additive concentrate for lubricating compositions consisting essentially of a lubricating oil into which has been incorporated from about 10 to about 80 weight percent of an oil-soluble dispersant and from about 2 to about 8 weight percent of molybdenum in the form of a colloidal complex prepared by the process of claim 1.

13. A lubricating composition comprising a major proportion of a lubricating oil and from about 0.01 to about 2 weight percent of molybdenum in the form of a colloidal complex prepared by the process of claim 1.

14. Lubricating composition as defined by claim 13 wherein said ether has been removed from the dispersion by stripping the dispersion with the aid of hydrogen sulfide.

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