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This invention relates to new compositions of matter useful as lubricating oil additives. More particularly, it relates to a new class of ashless dispersants and viscosity index improver additives, the process of preparing the same, and lubricating oil compositions containing such ashless dispersants.

It is generally considered that the chief source of engine operating difficulties as related to lubricants and lubrication is sludge deposits. The term "sludge" is used broadly to identify all types of engine deposits ranging from varnish or lacquer-like films to packed or hard carbon accumulations, as well as to the softer types of pasty or granular sludges. These deposits endanger the engine by causing disruption of oil circulation, by plugging of screens and passages, and by causing valve sticking and ring sticking. They also may lower the engine's efficiency by causing piston sticking in the cylinders, high oil consumption, loss of power and excessive detonation.

Operating conditions most conducive to sludge formation are the short haul, stop-start urban type. Engine idling, cold starting, engine warm-up, accelerating, coasting to a stop, or using the engine as a brake all increase sludge.

A large number of additives useful in controlling engine deposits are known. In the main, these compounds are metal salts of organic compounds. Oil solubility is attained by linking the metal salt substituent to a hydrocarbon group of sufficient size to render the compound oil solube. While these compounds have exhibited some dispersancy properties, they have for the most part, created a new problem. Such additive-treated motor oils usually have quite appreciable ash contents, and when such oils work up into the combustion chamber they leave inorganic residues upon ignition. These ash deposits are undesirable because they lower the efficiency of the engine by fouling spark plugs and valves and contribute to pre-ignition.

Good engine lubrication also requires an oil which will not thicken excessively at low temperatures nor thin out excessively at elevated temperatures, which means that oils of high viscosity index (VI) are to be preferred as engine lubricants. Such oils develop a minimum of friction and viscous drag at low temperatures, and accordingly allow easier engine starting in cold weather and more rapid flow and circulation during the warm-up period. At the elevated temperatures developed in running engines, high VI oils retain higher viscosities and thus provide better lubrication of hot engine parts and better sealing of piston rings to insure low oil consumption.

It is an object of this invention to provide a new class of compositions of matter. It is also an object of this invention to provide compositions which may be used as multi-functional additives in hydrocarbon oils. It is a further object to provide low molecular weight compositions useful as effective ashless dispersant additives in lubricating oils. It is another object to provide high molecular weight compositions useful as total VI improvers-dispersant combinations in lubricants. It is another object to provide intermediate molecular weight compositions useful as partial VI improver-dispersant combinations in lubricants. It is another object to provide a unique lubricating oil composition effective in low temperature automobile operation. It is another object to provide a process for the

preparation of new additives useful as dispersants and VI improver-dispersants. Other objects and advantages will be apparent as the discussion of the invention proceeds.

I have now discovered a process for the preparation of an ashless formulation that will leave no residue in the combustion chamber and will provide outstanding engine cleanliness at low operating temperatures. The compound is effective in both the form of a low molecular weight dispersant and in the form of a combination dispersant-VI improver for a multi-graded oil.

The preparation of the product of the process of the invention is accomplished by the reaction of a polymeric acylhalide and a polyamine or monoamine. The polymeric acylhalide is the reaction product of a polymeric olefin wtih an α-haloacetyl halide, preferably chloroacetyl chloride, under free radical conditions. Free radical conditions herein described can be either light catalyzed or catalyzed by use of the common free radical initiators such as peroxides, hydroperoxides, and azo compounds; a preferred initiator is di-tert-butyl peroxide. The polymeric acylhalide formed in the free radical reaction gives a reactive precursor which is then treated with a polyamine such as a polyalkylene amine, e.g. triethylene tetramine (TETA), tetraethylene pentamine (TEPA), ethylene diamine, pentaethylene hexamine (PEHA), or with a monoamine such as ammonia, mono-alkylamines, and di-alkylamines as well as compounds containing mercaptyl groups. By "polyalkylene amine" is meant those polyamines having the formula
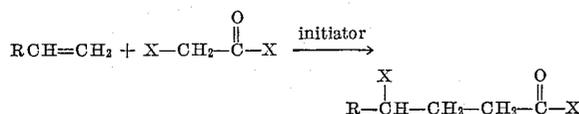
$$H_2N-\left(alkylene\text{-}N \atop \underset{R}{|}\right)_x-H$$
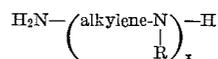
wherein x is an integer of from 2 to about 10, R is hydrogen or a lower alkyl hydrocarbon substituent and "alkylene" is a lower alkylene, i.e. divalent, open chain, hydrocarbon group having from 1 to 8 carbon atoms. Triethylene tetramine and tetraethylene pentamine are preferred.

The double bond-containing polymers useful in this free radical reaction may be mono-olefins, di-olefins and polyolefins and include polybutenes, polypropyleens, or copolymers such as isobutylene-isoprene, isobutylene-butadiene, cyclopentadiene-isobutylene. The suitable molecular weight range is approximately 300 to approximately 550,000. For the lower molecular weight dispersant, a suitable polymeric olefin is one having an average molecular weight of between approximately 300 and approximately 9,000, and advantageously between 300 and 2500. The polybutenes ranging in average molecular weight from about 450 to about 2000 are most advantageously utilized in the free radical reaction. A preferred polybutene is one with an average molecular weight of 1100 and a viscosity at 100° F. of 140,000 SSU and at 210° F. of 3000 SSU (hereinafter referred to as Polybutene A). Another preferred polybutene is one with an average molecular weight of 1800 and viscosity at 210° F. of 15,000 SSU (hereinafter referred to as Polybutene B). For the high molecular weight dispersont-VI improver it is advantageous to use a polymeric olefin having a molecular weight of between approximately 9000 and approximately 550,000. It is most advantageous to use a copolymer of isobutylene-butadiene with an average molecular weight of between approximately 30,000 to approximately 100,000. A preferred copolymer of isobutylene-butadiene is one with an average molecular weight of between 60,000 to 80,000 and a weight percent of butadiene of about 0.4 to about 2.0. Another preferable source of high molecular weight polymer is butyl rubber of average molecular weight of 450,-000 and an average mole percent unsaturation of 1.5–2.0. Two commercially available butyl rubbers marketed as Butyl Rubber 165 and 218 are suitable.

In most respects the reactions using the high molecular

weight copolymers are similar to those found with the low molecular weight olefins. One important difference which does occur, however, is the oxidative degradation of the very high molecular weight copolymers by the free radical initiator. This involves a cleavage of the internal double bonds. By such cleavage a polymer of molecular weight of approximately 450,000 may be degraded to a polymer of molecular weight of between 60,000 to 80,000. This is highly desirable.

There is evidence that the free radical reaction proceeds by way of addition of the haloacetyl halide compound to the double bonds of the polymer. The following mechanism conforms to this evidence:

$$RCH=CH_2 + X-CH_2-\overset{O}{\overset{\|}{C}}-X \xrightarrow{\text{initiator}}$$

$$R-\overset{X}{\overset{|}{C}H}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-X$$

wherein R is a hydrocarbon polymer or copolymer having a molecular weight of between 300 and 550,000, and X is a halide. This reaction is extremely versatile as shown by the fact that a very wide range of polymers of varying molecular weights and double bond contents may be successfully used in forming a precursor for the incorporation of polyamines or monoamines. Suitable polymers or copolymers have a molecular weight of between 300 and more than 80,000 (after the degradation effect described above).

Since the free radical addition step is an extremely short-chain reaction, the addition of the haloacetyl halide is strongly dependent on the amount of initiator used. It is desirable to use between 0.2 and 1 mole of initiator for every double bond per molecule of polymer. (Hereinafter the words "double bond," as used in mole ratios, are to be understood as meaning the double bond content per molecule of polymer. This method of expressing the mole ratios is used since the double bond content of the polymer, and not merely the number of moles of polymer, will influence the number of moles of reactants utilized.)

The amount of haloacetyl halide reactant necessary in the reaction depends upon the amount of the initiator used. Therefore, for a lower amount of initiator a higher quantity of haloacetyl halide is necessary. It is advantageous to use 2 to 20 moles of haloacetyl halide per mole of double bond. In addition, as the molecular weight of the polymer increases, it is desirable that the molar percent of the haloacetyl halide increase. The reaction, then, may proceed in a mole ratio of double bond:haloacetyl halide: free radical initiator of from about 1:20:0.2 to about 1:2:1. It is preferable to use 1 mole of initiator per mole of double bond. For a higher molecular weight polymer it is preferable to use 10 to 20 moles of haloacetyl halide per mole double bond, and for the lower molecular weight polymer it is preferred to use between 2 and 5 moles.

The free radical addition of the haloacetyl halide takes place over a temperature range of 50° C. to 225° C. The exact temperature of the reaction is dependent upon the initiator and is chosen in such a manner as to provide the most efficient usage of the initiator over a reasonable length of time and which would allow for approximately 90% of the initiator to decompose. A suitable temperature range for the initiator, di-t-butyl peroxide is 125° C. to 170° C. The temperature range of 140°–155° C. and total reaction time of about 3 to 20 hours is preferred for this initiator. It is desirable that a portion-wise addition of initiator be made. From 5 to 10 portions may be added over a 2 to 5 hour period for the high molecular weight product and the total reaction time allowed for the adduct formation be between 3 and 6 hours. For the low molecular weight product, 2 additions of the initiator and a 20 hour total reflux period is advantageous with the above initiator.

In the polyamine addition step it is desirable, when reacting an amine with the haloacetyl halide-treated polymers, that the inverse addition of the reactants be followed. Thus, the haloacetyl halide adducts are added quite slowly to the amine. This technique prevents cross-linking, which leads to gels in high molecular weight polymers and affords mostly a one-ended type of product. The reaction temperature can vary from 25° C. to 175° C. It is preferred that the pot temperature be held between approximately 105° C. to approximately 175° C. so as to drive the reaction to imidazoline ring formation leaving only minor amounts of mono- and di-substituted amides in the finished product.

In the displacement reaction, it is desirable to use an excess of the amine (from 1 to 20 moles of amine to each double bond per molecule of polymeric olefin, preferably 2 to 10 moles) in order to take up the hydrogen halide given off during the reaction as well as to give a high yield of the one-ended product and prevent cross-linking. In most cases a major proportion of the unreacted amine and the amine-hydrogen halide salt settles out upon cooling leaving only small amounts of same dispersed throughout the reaction mixture. The dispersed amine and the salt may be removed by 20 percent methanol water wash followed by centrifugation.

Another method of removing the hydrogen halide is to treat the haloacetyl halide adduct with alcohol in order to form the ester. Treatment of this product with an amine at temperatures of from about 150° C. to about 175° C. would then afford the same type of active site giving the alcohol back as a reaction product.

The preparation of the reaction product of this invention is illustrated in the following examples:

EXAMPLE I

Preparation of low molecular weight dispersant

In a three-necked 5 liter flask was placed 900 grams (0.75 mole) of Polybutene A and 254 grams (2.25 moles) of chloroacetyl chloride in 2 liters of decane. The resulting solution was then refluxed (pot temperature 140–150° C.) and 90 grams (100 mole percent) of di-t-butyl peroxide added in 2 equal portions, 4 hours apart, with rapid stirring. The reflux period was extended an additional 16 hours, after which the excess chloroacetyl chloride was removed by atmospheric distillation. The resulting solution was then added slowly with rapid stirring to 361 grams (1.9 moles) of dried tetraethylene pentamine in 100 milliliters of refluxing decane. Upon completion of the addition, the mixture was refluxed another hour, cooled and added to approximately 5–8 liters of hexane. The resulting mixture was washed with 20 percent methanol-water solution (1 part wash to 3 parts final reaction mixture) and centrifuged. The organic layer was removed, 200 grams of 5W oil added and the hexane and decane solvents stripped under a vacuum (pot temperature 160° C. at 20 mm.). The final product weighed 1,088 grams and contained 81 percent polymer, representing 33 percent of the active ingredient. The basic nitrogen content by dialysis was 1.3 percent.

EXAMPLE II

To a refluxing solution of 300 grams (0.15 mole) of Polybutene B and 100 grams (0.89 mole) of chloroacetyl chloride in 2 liters of decane (pot temperature 150–155° C.) was added 70 grams (400 mole percent) of di-t-butyl peroxide (divided into 7–10 gram portions and added over half hour intervals). After the last addition, the solution was refluxed for 16 hours. Upon completion of the reflux period, the excess chloroacetyl chloride was removed by atmospheric distillation and 60 grams (0.45 mole) of oxo-octyl alcohol added. The solution was refluxed an additional 4 hours and then added to 86 grams (0.45 mole) of dry tetraethylene pentamine. Upon com-

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pletion of this addition, the solution was again refluxed another hour and then allowed to cool. The upper layer was decanted from the excess tetraethylene pentamine and added to 200 grams of 5W oil. The entire solution was then stripped yielding a bright product weighing 575 grams, containing 35 percent active ingredient with a basic nitrogen content by dialysis of 0.95 percent.

EXAMPLE III

To 400 grams of isobutylene-butadiene copolymer (intrinsic viscosity of 0.51, weight percent butadiene of 0.5) and 81 grams (0.7 mole) of chloroacetyl chloride and 1.5 liters of refluxing decane was added 12 grams (230 mole percent, 2 gram portions every half hour) of di-t-butyl peroxide. Upon completion of the addition, the solution was refluxed another hour after which the excess chloroacetyl chloride was removed by atmospheric distillation. The resulting solution was then added to 133 grams (0.7 mole) of dry tetraethylene pentamine, refluxed for an hour, cooled, decanted, and 3 liters of hexane added, along with 2000 grams of silica gel and 1000 grams of Celite. The entire mixture was rapidly stirred for 15 minutes, filtered, and a filtrate added to 300 grams of 5W oil. The solvent was removed by vacuum stripping giving 390 grams of a product containing 23 percent active ingredient and having a basic dialysis nitrogen content of 0.48 percent.

EXAMPLE IV

To refluxing solution of 400 grams of isobutylene-butadiene copolymer (intrinsic viscosity 0.67, weight percent butadiene 0.8) and 100 grams (0.89 mole) of chloroacetyl chloride in two liters of decane was added with rapid stirring. 12.5 grams (160 mole percent) of di-t-butyl peroxide was divided into 6 equal parts and added ½ hour apart. Upon completion of the addition, the solution was refluxed another hour after which the excess chloroacetyl chloride was removed by atmospheric distillation. The solution was then added slowly with rapid stirring to 151 grams (0.8 mole) of dry TEPA, refluxed for 2 hours, cooled, washed with 20 percent methanol-water, and centrifuged. The organic layer was removed and the polymer precipitated with methanol-acetone twice, added to 300 grams of 5W oil and the solvents removed on a steam plate. A bright, viscous product was obtained weighing 450 grams, containing 33 percent active ingredient with a percent basic N_2 of 0.51 by dialysis.

EXAMPLE V

A 400 grams sample of Butyl Rubber 218 (mole percent unsaturation 1.5–2.0) was dissolved and 3 liters of decane by use of heat and a high speed mixer. To this viscous solution was then added 150 grams (1.32 moles) of chloroacetyl chloride, the solution rapidly stirred and brought to reflux (pot temperature 155° C.) A total of 24.5 grams (130 mole percent) of di-t-butyl peroxide was added in 7 equal portions ½ hour apart. At the end of the addition period, the solution was refluxed another hour after which the excess chloroacetyl chloride was removed by atmospheric distillation. The resulting solution was then added slowly with stirring to 151 grams (0.8 mole) of dry TEPA followed by another hour reflux period. At the end of this reflux period the solution was cooled and 3 liters of hexane added. The entire mixture was then washed with 30 percent methanol-water and centrifuged. The organic layer was removed and the polymer was precipitated twice with methanol-acetone. The polymer was then redissolved in 1350 grams of 5W oil yielding 1700 grams of a dark, clear, viscous product, containing 0.29 percent basic N_2 by dialysis and 20 percent active ingredient.

The reaction product of this invention, when incorporated in a hydrocarbon oil of lubricating viscosity, exhibits exceptional dispersant qualities without leaving an ash residue in the engine. In addition to petroleum hydro-

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carbon sources, synthetic or other natural hydrocarbon oils may be used to provide the base oil. The reaction product above described will normally constitute from about 1 to 20 weight percent of the lubricant, but this percentage may be higher or lower. The percentage will usually depend upon the nature of the dispersant product, e.g. high molecular weight or low molecular weight; the use to which the lubricant will be put; and the use to which the additive will be put, e.g. no VI improvement, some VI improvement or total VI improvement. The preferable range of the lower molecular weight product in lubricating oil is from 3 to 5 weight percent, and for the higher molecular weight product, exhibiting total VI improvement, from 1 to 15 weight percent.

While the above described reaction products can be suitably employed alone in the base oil, they are usually used in combination with other lubricant addition agents which impart various desirable characteristics to the base oil. Thus, although these reaction products exhibit a marked effectiveness in VI improvement and dispersancy, it may be necessary, depending upon the use of the lubricant, to incorporate other additives in the base oil, e.g. corrosion and rust inhibitors, pour point depressants, foam inhibitors, etc. Other lubricant addition agents can be used in combination with the additive of this invention.

A number of performance tests for evaluating the characteristics of lubricating oils were conducted. A test, made to determine the anti-sludge properties of the oil, is known as the Lincoln MS Test, Sequence V, developed by the Ford Motor Company. Briefly, the test consists of using the oil to be tested as a lubricating oil in a V–8 Lincoln engine under prescribed test conditions. Accordingly 5 quarts of oil are placed in the crankcase and the engine is started and run in accordance with the 4 hour cycle:

	Phase 1	Phase 2	Phase 3
Duration, min	45	[1] 2	75
Speed, r.p.m	500	2,500	2,500
Load, lbs	[2]	[3]	[3]
Temperature, ° F.:			
Water out	115–120	125–130	170–175
Oil Sump	120–125	175–180	205–210
A/F	9.5±0.5	15.5±0.5	15.5±0.5

[1] Hour. [2] No load. [3] 105 HP.

The four-hour cycle is reset a total of 48 times (192 hours running time. After each 16 hours of operation the engine is shut down for 8 hours. Two-ounce samples of oil are taken every 30 hours and the oil level is adjusted with fresh oil to a level of five quarts. Added oil is weighed. At the end of the test, the hot oil is drained, weighed and recorded. The engine is then disassembled and inspected for deposits of varnish and sludge among other observable results as set out in the table below. Engine components are examined visually and rated. All of the following ratings are considered perfect: 50 for total sludge and for total varnish; 0 percent for oil ring groove filling (ORGF) and oil screen clogging; and 10.0 for piston varnish. The following ratings are considered passing: 60 percent or lower for screen clogging; 50 percent or lower for ring plugging; 26 or higher for total sludge; and 7 or higher for piston varnish.

The following results may be considered under 3 headings:

Class I.—Low molecular weight (under 2500) dispersant—no VI improvement;

Class II.—Intermediate molecular weight (between 2500 and 30,000) dispersant—some VI improvement (supplemented with small amounts of VI improver); and

Class III.—High molecular weight (above 30,000) dispersant—total VI improver combination.

CLASS I

Sample	Formulation		Base Oil	Rating				
	Additive	Wt. Percent active ingredient in base oil		Total Sludge	Total Varnish	Percent ORGF	Percent Oil Screen	Piston Varnish
1	Reaction product of Example I.	1.0	Multi-graded premium oil	37	43	0	0	9.0
2	___do___	1.5	___do___	48	43	0	1	9.0
3	___do___	1.5	Extended drain oil	45	35	0	0	8.0
4	A current commercial dispersant.	1.6	Multi-graded premium oil	35	35	0		8.0
5	___do___	2.4	___do___	45	40	0		8.0

CLASS II

	Reaction product of Example 3.	2.0	Multi-graded oil	47	39	19	2	8.5
7	A current commercial product.*	1.0	___do___	20	32	98	50	6.0

CLASS III

8	Reaction product of Example 4.	2.0	Premium oil	45	45	9.4	10	10.0
9	Reaction product of Example 5.	2.0	___do___	45	44	13	1	8.6
10	A current commercial product.*	1.0	___do___	20	32	98	50	6.0

*The additive used in Samples 7 and 10 is the most comparable commercial dispersant-VI improver combination available. However, due to differences in structure of these products with the products of this invention, a true weight percentage comparison is impossible. To use more than 1.0 percent active ingredient would be detrimental to the VI improvement properties necessary for a properly multi-graded oil composition. Therefore, a 2.0 weight percent activity of this commercial product would cause the oil to fall outside the acceptable viscosity range for multi-graded oils and would not appreciably change the ratings.

It is significant to note that in most cases a considerably smaller quantity of the reaction product of this invention was used to obtain results comparable to or better than a typical commercially available product now being used. While the commercially available dispersants are somewhat effective, as regards to dispersancy, it is necessary to incorporate with them an additional VI improver for multi-graded oils. This is not necessary when using my high molecular weight composition inasmuch as it exhibits excellent VI improvement. Furthermore, only a small amount of VI improver is necessary when using an intermediate molecular weight product of this invention. The following indicates the effectiveness of the high molecular product of Example V as a viscosity index improver:

Additive	Product of Example V	Commercial VI Improver
Wt. Percent Active Ingredient in Base Oil	2.0	2.0
Base Oil	50–50 5W–10W	50–50 5W–10W
Kinematic Viscosity, 210° F. SSU	64.1	62.7
VI ASTM D–567–53	137	130

A further illustration of the usefulness of this invention is provided by an examination of the results of sludge spot dispersancy test. In this test oil formulations already tested under control tests at various levels of dispersancy in a standard engine detergency-dispersancy test are employed as source of "in engine" produced sludge. A composite of these used formulations is made and thoroughly mixed. A weighed amount of used oil composite and a weighed amount of the detergency candidate are combined and heated to 300° F. Thereafter this mixture is added to an equal volume of fresh unused, unformulated SAE 20 oil also at 300° F. The resultant mixture is held at 300° F. for two hours. Thereafter, while thoroughly stirring the hot mixture of fresh oil, used oil and detergency candidate, duplicate drop (from capillary pipette) portions are placed on blotting paper. The blotting paper so treated is permitted to stand for 12 to 16 hours. There are two concentric circles where each three drop deposit is made. The inner circle is black and the outer annulus is somewhat clear. For each of the duplicate spot tests the diameter's measurements are made by measuring the spot

diameter twice: two directions at right angles to each other. The outer circle diameters are taken in the same way. Thus for each set of duplicate spot tests, four diameter ratios are obtained. The average of the four ratios of diameter of spot to diameter of large oil ring multiplied by 100 is called SDT number. The SDT number relates semi-quantitatively to degree of sludge dispersancy of the candidate tested. This does not mean that SDT number data can be used to predict the total sludge value rating which will be obtained in a Lincoln Sequency V engine test but when used with a control spot test (no fresh detergent) and compared with known high detergency additives tested at the same time the relative order of the SDT numbers are indicative of performance to be expected from actual Lincoln Sequence V tests. SDT number values of 60 to 80 for detergency candidates are indicative of likely success in attaining a passing total sludge value rating and not that a particular total sludge value rating will be achieved for any particular SDT number value in the 60 to 80 range.

Compound:	SDT rating

Sample X.—Polybutene A—chloroacetyl chloride—TETA ___ 73

Sample Y.—Polybutene A—chloroacetyl chloride—PEHA ___ 83

Sample Z.—Polybutene B—chloroacetyl chloride—TEPA ___ 81

Unless otherwise stated, the percentages stated herein and in the claims are weight percentages.

While I have described my invention by reference to specific embodiments thereof, the same are given by way of illustration. Modifications and variations will be apparent from my description of those skilled in the art.

I claim:

1. A process for the preparation of a lubricant oil soluble product from a polyalkylene amine having the formula

$$H_2N-\left(\text{alkylene-N}_{\underset{R}{|}}\right)_x-H$$
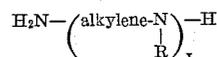
wherein x is an integer from 2 to about 10, R is hydrogen

or lower alkyl and alkylene is lower alkylene of from 1 to 8 carbon atoms, a polyolefin and an α-haloacetyl halide which comprises first reacting at 50° to 225° C. an α-haloacetyl halide with a polymeric olefin having a molecular weight in the range of from about 300 to 550,000 in the presence of a free radical initiator and then adding said free radical initiated reaction product slowly to said polyalkylene amine at 25 to 175° C.

2. The process of claim 1 wherein the α-haloacetyl halide is α-chloroacetyl chloride and the polyalkylene amine is tetraethylene pentamine.

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