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DEMULSIFIABLE LUBRICANT COMPOSITIONS

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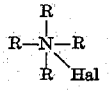
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This invention relates to improvements in lubricant compositions, and more particularly relates to compositions having improved demulsibility characteristics and to the method of preparing the same.

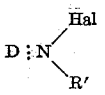
In many applications of lubricant compositions, such as gear lubricants, extreme pressure lubricants, etc., which contain one or more additives, such as soaps, organic halogenated compounds, sulfur-containing compounds, etc., to impart desired properties to such lubricants, the products become contaminated with water with the formation of relatively stable oil-in-water emulsions. If the lubricant composition does not readily demulsify or separate from the water, the use of such products as lubricants is materially decreased and must often be discarded.

It is an object of the present invention to provide a lubricant composition having improved demulsibility characteristics. Another object of the invention is to provide a compounded lubricant composition which will readily separate from water when contaminated with or emulsified with water. A still further object of the invention is to provide a lubricant composition which is resistant to the formation of oil-in-water emulsion, when used in the presence of water or when contaminated with water. Another object of the invention is to provide a method of improving the demulsibility characteristics of lubricant compositions. Other objects and advantages of the present invention will become apparent from the following description thereof.

In accordance with the present invention lubricant compositions having improved demulsibility characteristics are obtained by incorporating in such lubricants 0.002% to about 5%, and preferably from about 0.02% to about 1% of a quaternary ammonium compound having the general formula:



or



in which the R's represent the same or different alkyl, aralkyl, aryl groups or combinations thereof, Hal represents a halogen atom, such as chlorine, bromide, iodine, etc., D:N represents a heterocyclic compound, such as pyridine, and R' is an alkyl group of at least about 8 carbon atoms.

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In the above formula at least one R is an alkyl group having 1 to 3 carbon atoms, and at least one R is an alkyl group having at least 8 carbon atoms, and preferably 10 to 20 carbon atoms. Compounds formed by substituting one or more of the hydrocarbon substituents groups with a halogen, oxygen or sulfur are also suitable. Illustrative of specific compounds defined by the above formulas are the following:

Dodecylthiomethyl pyridinium chloride
Dimethyl-ditridecyl ammonium chloride
Triethyl-hexadecylthiomethyl ammonium chloride
Tributyl-tridecyloxymethyl ammonium chloride
Benzyl-dimethyl-dodecylthiomethyl ammonium chloride
Hexadecylthiomethyl pyridinium chloride
Benzyl-dimethyl-dodecylthiomethyl ammonium chloride
Triethyl-dodecylthiomethyl ammonium chloride
Benzyl-dimethyl - dodecyloxymethyl ammonium chloride
Methyldodecylbenzyltrimethyl ammonium chloride
Hexadecyl pyridinium bromide
Dimethyl-dilauryl ammonium bromide
Dimethyl-didecylthioethyl ammonium chloride
Methyl-diethyl-dodecylthioethyl ammonium iodide
Trimethyl - decylmethylaminoethyl ammonium bromide
Hexadecylthiomethyl pyridinium chloride

The lubricant composition in which the quaternary ammonium compounds of the type herein described find utility are those compositions which contain in addition to the viscous hydrocarbon lubricating oil, additives which tend to promote the formation of emulsions in the presence of water. Such additives are, for example, soaps of high molecular weight carboxylic acids, such as vegetable, animal and marine fats and fatty acids, halogen-containing and/or sulfur-containing and/or phosphorus-containing organic compounds, such as chlorinated hydrocarbons, sulfurized hydrocarbon oils, esters of acids of phosphorus, organic sulfides, sulfonates, naphthenates, etc. Such additives are usually employed in amounts of from about 0.25% to 15%, or more.

Illustrative of an application of the present invention is the lubrication of gears of heavy machinery in which, because of the high temperatures and pressures encountered, so-called extreme pressure gear lubricants are employed.

Such lubricants usually comprise viscous hydrocarbon oils and one or more extreme pressure (E. P.) agent, e. g., a chlorinated and/or sulfur-containing and/or phosphorus-containing organic compound. Examples of suitable additives are "Anglamol 85" and "Anglamol 88," which contain about 4.8% to 6.7% sulfur, 19–20% chlorine and about .3% phosphorus, marketed by Lubrizol Corporation, or "Santopoid 29" containing about 8.5% sulfur, 24% chlorine, and 0.56% phosphorus marketed by the Monsanto Chemical Company. An example is the equipment used in the rolling of metals. Frequently in the rolling of metals, water or water emulsions, known as "rolling solutions" are sprayed on the rolled sheet to loosen and wash away scale, act as coolant for the rolls and, in the case of "rolling solutions" to act as rust preventives. The water on "rolling solution" frequently contaminates the extreme pressure gear lubricant and emulsions are formed. Heretofore, such emulsions had to be stored in a quiescent state for sixteen to twenty-four hours or more to permit the stratification and separation of lubricant and water. In accordance with the present invention, the addition of small amounts of a quaternary ammonium compound of the type hereindescribed enables such emulsions to break and separate in a relatively short time, usually not more than one hour and in many cases in less than ten minutes; the time required for such emulsions to break and separate depending, of course, on the type of service and degree of oil and water mixing.

The viscous hydrocarbon oil can be any hydrocarbon oil, e. g. petroleum oil, having a Saybolt Universal viscosity within the range of from about 80 seconds at 100° F. to about 500 seconds at 210° F. The oil can be a distillate or residuum oil or mixtures thereof. The oil may or may not be a solvent-extracted oil. There can also be blended with the hydrocarbon oil asphaltic materials such as heavy residuums or blown or oxidized residuums. The choice of the oil used will be largely determined by the nature of the service for which the lubricant is designed.

The following examples are illustrative of types of lubricant compositions for which the present invention is adapted. These examples are given solely by way of illustration and are not intended to be indicative of the scope of the invention.

Example I

	Per cent	
Organic E. P. agent	0.5	–15
Asphalt	0.0	–10
Hydrocarbon lubricating oil	75	–99.5
Quaternary ammonium compound [1]	0.002–	5.0

Example II

	Per cent
Chlorinated hydrocarbon	7.0
Oxidized MC asphalt [2]	4.6
Petroleum oil	89.3
Dilauryldimethyl ammonium bromide	0.1

[1] Of the type hereinabove described.
[2] Preferably an oxidized asphalt from residuum, having melting points within the range of about 60° F. to 100° F., which have been oxidized by air blowing or other suitable means to increase the melting points by an increment of from about 80° F. to about 200° F.

Example III

	Per cent
E. P. agent [1]	8.75
Oxidized MC asphalt	5.0
Petroleum oil	86.15
Dilauryldimethyl ammonium bromide	0.1

Example IV

	Per cent
Sulfurized sperm oil	22
Chlorinated paraffin wax containing 40% chlorine	2.75
Lead naphthenate	4.10
Dilauryldimethyl ammonium bromide	0.10
Petroleum oil (S. U. S. at 210° F.–95)	71.05

Example V

	Per cent
Dibenzyldisulfide	2.50
Chlorinated paraffin wax	7.5
Dimethyldodecylbenzyl ammonium chloride	0.075
Petroleum oil	89.925

The effectiveness of the quaternary ammonium compounds of the type herein described in improving the demulsibility characteristics of lubricant compositions is demonstrated by the data in the following table. These data were obtained in the following manner:

An extreme pressure gear lubricant consisting essentially of:

	Per cent
E. P. agent [1]	8.75
MC oxidized asphalt (ASTM penetration at 77° F. 30–40; softening point ring and ball method 175–185° F.)	5.0
Solvent-extracted SAE 10 base stock	17.25
Solvent-extracted SAE 50 base stock	31.0
Bright stock	38.0

[1] Chlorine, sulfur, and phosphorus-containing organic compound.

after being emulsified with water in the manner described below, showed substantially no water separation after standing sixteen hours at 130° F. In order to demonstrate the effectiveness of the quaternary compounds in breaking and/or preventing such emulsions, small amounts of such materials were added to the above base formulations and demulsibility determined by the following test:

Fifty-three cubic centimeters of distilled water and twenty-seven cubic centimeters of the lubricant were placed in a clean 100 cc. graduate. The graduate and contents were placed in a 130° F. water bath and permitted to remain therein for fifteen minutes. After this period the graduate was placed in a Herschel apparatus (Day's Handbook of Petroleum Industry, vol. 1, page 701) and stirred at the standard speed, about 1500 R. P. M. for five minutes. The stirrer was then stopped, the paddle lifted and cleaned into the graduate. The graduate and contents were placed in the 130° F. water bath and observed as to the volume of water separated by the end of five minutes and at the end of a one hour period. A series of tests were made on the above base lubricant and the base lubricant containing 0.1% each of the following quaternary ammonium compounds:

Sample 1—Control (no quaternary ammonium compound)
Sample 2—Dilauryldimethyl ammonium bromide
Sample 3—Dimethyldodecyl benzyl ammonium chloride
Sample 4—Dodecylthiomethyl pyridinium chloride
Sample 5—Dimethylditridecyl ammonium chloride

Sample 6—Triethylhexadecylthiomethyl ammonium chloride

Sample 7—Benzyldimethyldodecylthiomethyl ammonium chloride

Sample 8—Hexadecylthiomethyl pyridinium chloride

Sample 9—Triethyldodecylthiomethyl ammonium chloride

Sample 10—Benzyldimethyldodecyloxymethyl ammonium chloride

Additive Identification	Additive Concentration	cc. Water Separation at 130° F.	
		After 5 min.	After 1 hour
	Percent		
1	None	None	None
2	0.0075	20	21
	0.0375	16	52
	0.075	3	52
	0.150	6	51
3	0.0075	19	19
	0.0375	25	41
	0.075	23	27
	0.150	10	25
4	0.003	19	19
	0.015	21	22
	0.030	27	30
	0.060	44	51
5	0.0036	20	20
	0.0180	19	20
	0.036	14	48
	0.72	11	51
6	0.004	11	11
	0.020	19	20
	0.040	24	25
	0.080	22	24
7	0.003	20	20
	0.015	20	22
	0.030	21	23
	0.060	21	23
8	0.0037	22	22
	0.0185	22	22
	0.037	26	34
	0.074	28	45
9	0.0023	19	19
	0.0115	20	21
	0.023	21	22
	0.046	43	47
10	0.0035	17	16
	0.0175	20	20
	0.035	22	28
	0.07	16	35

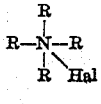
As demonstrated by the above data, the addition of small amounts of quaternary ammonium compounds of the type herein described effectively promote the demulsification of oil-in-water emulsions.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

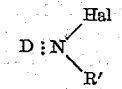
While the present invention has been described by reference to preferred embodiments thereof, the same have been given by way of illustration only and are not limitations of the invention, which includes within its scope such modifications and variations as come within the scope of the appended claims.

I claim—

1. A lubricant composition comprising essentially a major proportion of a hydrocarbon oil of from about 0.5% to about 15% of an organic extreme pressure agent containing an element selected from the group consisting of chlorine, sulfur, phosphorus, and mixtures thereof and normally susceptible to the formation of oil-in-water emulsions in the presence of water, from 0% to about 10% of an asphalt, and from about 0.005% to about 1% of a compound selected from the group consisting of a quaternary compound having the general formula:



in which the R's represent radicals selected from the group consisting of alkyl, aralkyl, aryl radicals and mixtures thereof, of which at least one R is an alkyl group of 1 to 3 carbon atoms, and at least one R is an alkyl group having at least 8 carbon atoms, and Hal is an halogen atom, and a quaternary compound having the general formula:



in which D:N is a heterocyclic compound, R′ is an alkyl group of at least 8 carbon atoms, and Hal is an halogen atom.

2. A lubricant composition as described in claim 1 in which the quaternary ammonium compound is dilauryldimethyl ammonium bromide.

3. A lubricant composition as described in claim 1 in which the quaternary ammonium compound is dimethyldodecylbenzyl ammonium chloride.

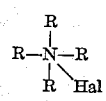
4. A lubricant composition as described in claim 1 in which the quaternary ammonium compound is dodecylthiomethyl pyridinium chloride.

5. A lubricant composition as described in claim 1 in which the quaternary ammonium compound is triethyldodecylthiomethyl ammonium chloride.

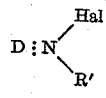
6. A lubricant composition as described in claim 1 in which the organic extreme pressure agent is a phosphorus-sulfur-chlorine-containing hydrocarbon.

7. A lubricant composition comprising essentially a major proportion of petroleum oil, about 8.75% of a phosphorus-chlorine and sulfur-containing organic extreme pressure agent normally susceptible to the formation of oil-in-water emulsions in the presence of water, about 5% of an oxidized asphalt, and from about 0.02% to about 1% of dilauryldimethyl ammonium bromide.

8. The method of imparting demulsibility characteristics to a lubricant composition normally susceptible to the formation of oil-in-water emulsions in the presence of water, which composition comprises essentially a major proportion of a hydrocarbon oil, from about 0.5% to about 15% of an organic extreme pressure agent containing an element selected from the group consisting of chlorine, sulfur, phosphorus and mixtures thereof, and from about 5% to 10% of an asphalt, which comprises incorporating in said lubricant composition from about 0.002% to about 5% of a compound selected from the group consisting of a quaternary compound having the general formula:



in which the R's represent the radicals selected from the group consisting of alkyl, aralkyl, aryl radicals and mixtures thereof, of which at least one R is an alkyl group of 1 to 3 carbon atoms, and at least one R is an alkyl group having at least 8 carbon atoms, and Hal is an halogen atom, and a quaternary compound having the general formula:



in which D:N is a heterocyclic compound, R' is an alkyl group of at least 8 carbon atoms, and Hal is an halogen atom.

9. The method of claim 8 in which the quaternary ammonium compound is dilauryldimethyl ammonium bromide.

10. The method of claim 8 in which the quaternary ammonium compound is dimethyldodecylbenzyl ammonium chloride.

11. The method of claim 8 in which the quaternary ammonium compound is dodecylthiomethyl pyridinium chloride.

12. The method of claim 8 in which the quaternary ammonium compound is triethyldodecylthiomethyl ammonium chloride.

13. The method of claim 8 in which the organic extreme pressure agent is a phosphorus-sulfur- and chlorine-containing hydrocarbon.

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