Patented Aug. 5, 1947

2,425,085

UNITED STATES PATENT OFFICE

2,425,085

OIL PURIFYING SUBSTANCES AND METHOD OF MAKING THE SAME

Harold F. Dague, South Gate, Calif., assignor of one-half to William B. Collins, Los Angeles, Calif.

No Drawing. Application June 15, 1945, Serial No. 599,741

20 Claims. (Cl. 252—33.4)

1

This invention relates to compositions which have the effect of prolonging the useful life of lubricating oils with which they are associated and to a method of making such compositions. It is a general object of the present invention to provide a novel, highly efficient material or additive which produces a number of beneficial effects on mineral lubricating oils.

The material that I have provided is especially useful in connection with or for treating engine or machine oil, or the like, to counteract deterioration of the oil caused by high temperatures and high speed operations of engine or machine parts.

Another object of the present invention is to provide an additive for lubricating oil which produces a neutralizing, detergent, anti-oxidant, and carbon-flocculating effect. The additive that I have provided can be used with lubricating oil in an engine or the like to keep the oil clean and to materially add to its useful life.

A further object of the present invention is to provide an oil additive such as I have referred to which may be employed with highly beneficial effect by merely incorporating a small amount in the oil. The salutory effect on the additive that I have provided may be further increased by passing the treated oil through a filtering medium or porous substance to remove coagulated material from the oil.

It is a further object of my invention to provide a coagulating material or additive useful as an impregnant for or in an absorbent filter through which lubricating oil is caused to circulate. The invention further contemplates providing a particular filter medium with the additive to increase the effectiveness of the additive.

The various objects and features of my invention will be fully understood from the following detailed description of a typical preferred composition of my invention and a typical manner of carrying out the method of my invention.

I have found that the association of certain organic amines with oil-soluble salts of sulfonic acids has a beneficial effect upon the life or oxidation stability of petroleum lubricating oils. Further, as to the amines, the oil-soluble tertiary amines are more effective than other amines in association with the sulfonic acid salts. The beneficial effects gained by combining these two ingredients for use upon lubricating oil can be substantially increased by the inclusion of a hydrocarbon mixture which is commonly extracted from petroleum by furfural in the purification of various petroleum fractions ranging from kerosene or light spray oil to heavier lubricating oil and which I will term "furfural bottoms."

2

Furfural bottoms are commonly recognized as a substantially neutral mixture of higher molecular weight hydrocarbons of paraffinic, naphthenic, and aromatic structures, generally possessing a considerable degree of unsaturation. Asphaltenes may also be present in the extract. Furfural bottoms, of course, in practice are not pure hydrocarbons but contain a minor amount of other ingredients derived from the oil, such as naphthenic and other organic acids, phenols, sulphur compounds, nitrogen bases, and so on. In preparation of the furfural bottoms for my purpose, any sediment is taken out and they are neutralized if not already neutral. The furfural employed to effect the extraction is generally removed by vaporization. However, the presence of a residue of furfural in the mixture does not adversely affect its properties, and consequently no special effort need be made to effect its complete removal.

The furfural bottoms obtained from various individual petroleum fractions may usually be used interchangeably for carrying out the present invention, or if desired, the extracts resulting from the treatment of numerous separate fractions may be mixed together and used. For example, the furfural extracts resulting from the treatment of a spray oil fraction having a Saybolt Universal viscosity of 30 to 500 seconds at 100° F., as well as extracts obtained from treating lubricating oil stocks having a viscosity of 90 to 300 seconds at 130° F. or even a much more viscous fraction having, for instance, a viscosity of about 80 to 175 seconds at 210° F., have been employed effectively in carrying out my invention.

The oil-soluble organic amines of the present invention are characterized by being tertiary amines, that is, each of the three hydrogen atoms of a theoretical ammonia molecule are replaced by a hydrocarbon or substituted hydrocarbon radical such as butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, phenyl, xylyl, benzyl, tolyl, cresyl, naphthyl, etc., and their isomers (saturated and unsaturated, branched-chain and cyclic) and higher homologs as well as the corresponding hydroxyl derivatives. The three hydrocarbon or hydroxyl substituted radicals in each molecule may be the same or different. The presence of other substituents such as polar groups is not precluded. Generally alkylol amines having a minimum molecular weight of about 150 are us-

able, but those in the range of about 200 to 550 molecular weight are preferred.

It is a significant and noteworthy fact that the tertiary amines are far superior to either the corresponding primary or secondary amines in the combination that I have provided, and of the tertiary amines the oil-soluble ones are more effective than the water-soluble members. For example, tri-normal-butyl amine greatly outperforms tri-ethanol amine, and tri-normal-amyl amine gives even better results. Likewise, the amines themselves are more effective than the corresponding amine soaps or esters. However, they have not been previously considered suitable for oil additives due to the fact that when even as little as .013% of the oil-soluble amine gets into lubricating oil, it causes lacquering in an engine in which the oil is used. In the material that I have provided combining amines and sulfonic acid salts with furfural bottoms, this lacquering effect is not noticeable until upward of 2.5% is used.

The sulfonic acid salts that I use are typified by the sulfonated or sulfated reaction products resulting from the well known treatment of petroleum, and in particular of lubricating oil fractions, with concentrated sulfuric acid. They are in general relatively high molecular weight paraffinic, naphthenic, and aromatic sulfonates (depending upon the particular constitution of the crude oil from which they are obtained). Analogous sulfonates may be derived by treating individual hydrocarbons or mixtures of hydrocarbons which do not necessarily originate from petroleum, for example, toluene, naphthalenes, shale oil, and the like. The oil-soluble petroleum sulfonates are commonly known as mahogany acids, and since such substances are well known articles of commerce, it will not be necessary to describe them further here.

For the present purposes, it is the oil-soluble salts or soaps of the sulfonic acids that are employed. Preferably the metallic salts are used, such as the alkaline earth salts, calcium, barium, strontium, and magnesium, or the alkali metal salts, sodium, potassium, and lithium. However, other polyvalent metallic salts as well as non-metallic (e. g. ammonium) salts may be employed.

By providing an association of the sulfonic acid salts with the above illustrated oil-soluble tertiary amines I produce an oil additive that gives a desirable coagulating effect upon impurities such as decomposition products formed, for example, in lubricating oil during engine operation. In carrying my invention further I multiply the coagulating effect gained by the association of the two ingredients just mentioned about three to six times by the introduction of furfural bottoms into the material. The presence of the furfural bottoms in the composition greatly increases the life and activity of the composition and facilitates coagulation, so that decreased gumming is evidenced for an appreciably longer period of time. It will thus be appreciated that the incorporation or combining of the three ingredients mentioned results in an additive which has a salutary effect upon a lubricating oil. The material may be added to oil in use in an engine or the like, or it may be used in salvaging used oil which has been taken from internal combustion engines or other sources. Amounts of the material on the order of .003% to 1% weight are effective in the average case.

Ordinarily when my additive is used it is desirable to remove the resulting coagulated particles from the oil as they are formed. This may be done by the use of a suitable filtering device. In fact one of the primary objects of my invention is to provide a coagulating agent effective to transform oil decomposition products and other impurities from their usually colloidal state into a form in which they may be readily removed from the oil by filtration without interrupting the employment of the oil as a lubricant. In this connection, any of the well known filtering media or porous percolation substances may be used, such as cloth, paper, cotton linters, wood pulp, steel wool, sawdust, and the like. Such a filter may be advantageously formed with a cartridge of filter material which can be installed in the oil circulating line or system so that after having absorbed a quantity of coagulated colloidal particles and/or other deleterious materials it can be removed and replaced by a clean cartridge.

The beneficial effect of the additive that I have provided is improved or augmented by employing the additive with a filtering medium such as an absorbent clay or fuller's earth. Whether this is due to some obscure chemical reaction with the porous play or merely to the particular adaptability or physical attraction of its surface structure is not at present known. Such absorbent filtering clay or fuller's earth is well known in commerce, the most satisfactory varieties for my purpose being obtained from deposits in Georgia, Florida and California.

According to my invention the three components or ingredients of the present coagulant are transformed or combined into a substantially homogeneous state by first heating together the amine and sulfonic acid salt at a temperature of about 120° to 150° F. for a period on the order of a half hour during which time the mass is agitated. Optionally, the temperature may go as high as about 200° F. without ill effect. The furfural bottoms are then stirred into the initial mixture and the temperature maintained for approximately another half hour.

In general, relative proportions, by weight, of the three ingredients are in the range of about 30% to 50% furfural bottoms, about 35% to 55% oil-soluble tertiary organic amines, and about 5% to 25% sulfonic acid salt. If the components vary much outside of these ranges, stratification or phase separation occurs when the mixture is allowed to cool and stand. An optimal ratio for the three components is about 4:4.5:1.5 (by weight) in the order given.

Without wishing to be committed to any particular theory of reaction, it seems to me at present likely that the effectiveness of my material is due at least in part to a reaction between the unsaturated components of the furfural extract and the decomposition products or impurities formed in lubricating oil. The furfural bottoms may also reduce the surface tension or produce a wetting-out action on carbon particles in the oil. The coagulation of such products is then promoted by the oil-soluble tertiary amines which possess a high degree of polarity and at least some of which have probably combined with the furfural bottoms in the homogenizing process described above.

The sulfonic acid salt functions in the nature of a detergent and may also form some of a complex with the furfural extract and the amine. In addition, association of the three components is believed effective in holding the amine in the oil at temperatures at which it would otherwise be driven off or decomposed. Apart from the co-

agulating phenomenon, this latter effect is also important in retaining the amines in the oil for the purpose of neutralizing acids which are formed in the oil particularly at high engine operating temperatures.

As a further illustration of my invention, approximately three parts by weight of tri-normal-butyl amine were mixed with one part of calcium salt of petroleum sulfonic acids by agitating the two at a temperature of about 120° to 150° F. for about half an hour. A mixture of extracts resulting from furfural treatment of both light and heavy petroleum fractions was then stirred into the hot mixture and the heating continued for another half hour. Upon cooling, the composition possessed the formula:

	Per cent by weight
Furfural bottoms	40
Tri-normal-butyl amine	43.7
Calcium sulfonate	16.3

This mixture was incorporated in absorbent clay in the amount of five grams for a filter pack of 70 cubic inches. This pack, when installed in the oil circulation system of an automobile was found capable of maintaining a volume of two gallons of oil entirely clean for a period in excess of 8000 miles of normal driving. In contrast, a clay filter pack of the same size and construction but without my material kept the same volume of oil clean for only 3000 miles.

It is to be understood that the exact proportions and specific examples set out herein are given by way of illustration only and no limitation of my invention is to be inferred except as defined in the following claims.

Having described only a typical preferred form of the materials that I have provided and typical manner of carrying out my method, I do not wish to be limited or restricted to the specific details herein set forth, but wish to reserve to myself any variations or modifications that may appear to those skilled in the art and fall within the scope of the following claims.

Having described my invention, I claim:

1. A composition of the character described comprising about 35% to 55% by weight of an oil-soluble tertiary organic amine, about 5% to 25% by weight of an oil-soluble sulfonic acid salt and about 30% to 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted from petroleum with furfural.

2. A composition of the character described comprising about 35% to 55% of an oil-soluble tertiary organic amine, about 5% to 25% by weight of an oil-soluble sulfonic acid salt, and about 30% to 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted from petroleum with furfural; and an absorbent clay.

3. A composition of the character described comprising about 35% to 55% by weight of an oil-soluble tertiary organic amine, about 5% to 25% by weight of an oil-soluble sulfonic acid salt, and between about 30% and 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted with furfural from a petroleum fraction having a Saybolt Universal viscosity of about 30 to 50 seconds at 100° F.

4. A composition of the character described comprising between about 35% and 55% by weight of an oil-soluble tertiary organic amine, between about 5% and 25% by weight of an oil-soluble sulfonic acid salt, and between about 30% and 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted with furfural from a petroleum fraction having a Saybolt Universal viscosity of about 90 to 300 seconds at 130° F.

5. A composition of the character described comprising between 35% and 55% by weight of an oil-soluble tertiary organic amine, between 5% and 25% by weight of an oil-soluble sulfonic acid salt, and between 30% and 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted with furfural from a petroleum fraction having a Saybolt Universal viscosity of about 80 to 175 seconds at 210° F.

6. The composition of claim 1 whereby the amine component comprises an oil-soluble, tertiary alkylol amine.

7. The composition of claim 1 wherein the amine component comprises tri-normal-butyl amine.

8. The composition of claim 1 wherein the amine component comprises tri-normal-amyl amine.

9. The composition of claim 1 wherein the sulfonic acid salt component comprises an oil-soluble alkaline earth sulfonate.

10. The composition of claim 1 wherein the sulfonic acid salt component comprises an oil-soluble alkali metal sulfonate.

11. The composition of claim 1 wherein the sulfonic acid salt component comprises an oil-soluble calcium sulfonate.

12. The composition of claim 1 wherein the petroleum extract, amine and sulfonic acid salt are present in an approximate weight ratio of 4:4.5:1.5.

13. A composition useful for purifying used lubricating oil, which composition comprises a mass of porous filtering medium having intimately admixed therewith a composition comprising between about 35% and 55% by weight of an oil-soluble tertiary organic amine, between about 5% and 25% by weight of an oil-soluble sulfonic acid salt and between about 30% and 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted from petroleum with furfural.

14. A mineral lubricating oil containing an additive comprising between about 35% and 55% by weight of an oil-soluble tertiary organic amine, between about 5% and 25% of an oil-soluble sulfonic acid salt and between about 30% and 50% by weight of a substantially neutral, predominantly hydrocarbon mixture extracted from petroleum with furfural, said mixture being present in amount sufficient to coagulate decomposition products of the oil.

15. A composition useful for purifying used lubricating oil, which composition comprises about 35% to 55% weight of an oil-soluble tertiary organic amine, about 5% to 25% weight of an oil-soluble sulfonic acid salt, and about 30% to 50% weight of furfural bottoms.

16. A composition of the character described comprising: an oil-soluble tertiary organic amine, an oil-soluble sulfonic acid salt, and a substantially neutral, predominantly hydrocarbon mixture extracted from petroleum with furfural, said amine, sulfonic acid salt and furfural extract being present in an approximate weight ratio of 4.5:1.5:4.

17. A method of preparing a purifying composition for the treatment of lubricating oils which comprises: combining 1 part of an oil-soluble sulfonic acid salt with from 1.4 to 11 parts by weight of a soluble, tertiary organic amine at a temperature of between about 120° F. and 200°

F. until a homogeneous phase results, and then incorporating furfural bottoms while maintaining said temperature until a substantially homogeneous composition results, said furfural bottoms being added in quantity to constitute between about 30% and 50% by weight of the total composition.

18. A method of the character stated in claim 17, wherein the furfural bottom comprise a substantially neutral, predominantly hydrocarbon mixture extracted with furfural from a petroleum fraction having a Saybolt Universal viscosity of about 30 to 50 seconds at 100° F.

19. A method of the character stated in claim 17, wherein the furfural bottoms comprise a substantially neutral, predominantly hydrocarbon mixture extracted with furfural from a petroleum fraction having a Saybolt Universal viscosity of about 90 to 300 seconds at 130° F.

20. A method of the character stated in claim 17, wherein the tertiary amine is an oil-soluble tertiary alkylol amine.

HAROLD F. DAGUE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,633,941	Hey	June 28, 1927
1,747,987	Reddish	Feb. 18, 1930
2,262,926	Edgar et al.	Nov. 18, 1941
2,303,546	Greger	Dec. 1, 1942
2,300,555	De Groote et al.	Nov. 3, 1942
2,321,884	Allan	June 15, 1943
2,343,435	Wells et al.	Mar. 7, 1944
2,343,436	Wells et al.	Mar. 7, 1944
2,363,504	De Groote et al.	Nov. 28, 1944