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## STABILIZATION

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This invention relates to sulfur bearing lubricants. More particularly it relates to odor-stabilized lubricants comprising a sulfurized hydrocarbon oil and to processes for preventing or eliminating the evolution of foul or toxic odors from such lubricants.

Experience has shown that excellent lubricants useful in metal fabricating operations such as cutting, drawing, stamping and the like consist of blends of sulfurized hydrocarbon oils. These lubricants contain sulfur in loose chemical combination, true solution, or both, the sulfur contents varying in the range of about 1 to about 5% by weight, more or less. The normal viscosity range of these lubricants is about 50 to about 300 seconds Saybolt Universal at 100° F., although sulfurized lubricants of somewhat higher viscosity can be made and are sometimes used for specialized operations.

In spite of their excellent lubricating and cooling qualities in metal forming operations, sulfurized hydrocarbon oils suffer from the great disadvantage of odor development or evolution. Upon standing the sulfurized hydrocarbon lubricants evolve foul odors in the form of volatile sulfur compounds. The odor is due in large measure to hydrogen sulfide and also appears to be due in part to the evolution of volatile mercaptans from the sulfurized lubricants. This odor is unpleasant and toxic, constituting a highly undesirable attribute of the lubricant which renders it useless or unsalable.

Odor evolution from lubricants containing sulfurized hydrocarbon oils is readily detectable by mere olfactory examination. A much more satisfactory method of examination, which yields visual and reproducible records is as follows: A definite amount (usually 75 cc.) of the oil to be tested is added to 75 cc. of distilled water in a 500 cc. balloon flask. A paper which has been impregnated with a 20% aqueous solution of hydrated lead acetate and then dried is placed over the mouth of the flask and held in place by means of a glass chimney. The flask is then placed in a boiling water bath for 30 minutes. At the end of this period the lead acetate paper is removed and examined for signs of blackening. This test has proved satisfactory for comparative evaluation of different samples.

It is an object of this invention to confer odor stability on combinations of organic materials and sulfur which normally tend to evolve odor in the form of volatile sulfur compounds. Another object of this invention is to provide odor-stable lubricants comprising sulfurized hydrocarbon oils. Still another object of this invention is to prevent the deterioration of sulfurized hydrocarbon oils. A further object of this invention is to provide processes to prevent the evolution of sulfurous vapors from lubricants containing sulfur in loose chemical combination, physical solution or both.

We have discovered that odor development in sulfur bearing hydrocarbon oils normally tending to evolve volatile sulfur compounds can be inhibited by adding thereto small amounts of an alkylolamine capable of inhibiting such odor development. Suitable alkylolamines for this purpose include 2-amino-2-methyl-1-propranol; 2-aminobutanol; 2-amino-2-methyl-1,3 propanediol; 2-amino-2-ethyl-1,3-propanediol; monoethanol amine; diethanolamine and triethanolamine. Ordinarily, we prefer to use triethanolamine, diethanolamine and 2-amino-2-methyl-1-propanol. We particularly prefer to use triethanolamine. Our odor inhibitors may generally be used in proportions varying from about 0.025 to about 1% by volume in the sulfurized lubricants. The specific proportion of odor inhibitor used in any case will be dependent on the method of preparation of the sulfurized lubricant, the nature of the hydrocarbon oils used, the sulfur content of the libricant, the nature of the specific odor inhibitor chosen for use, its solubility in the particular sulfurized lubricant and the conditions under which the sulfurized lubricant is to be stored and used. Under specialized conditions more than 1% of the alkylolamine may be used.

The odor inhibitor may be added to the sulfurized lubricant at any stage of manufacture following sulfurization. It is preferable to incorporate the inhibitor into the sulfurized lubricant immediately following the sulfurization operation and in advance of the settling operation which usually follows thereafter in the manufacture of such lubricants. The odor inhibitor is not added to the reaction mixture undergoing sulfurization since the inhibitor is thereby converted to compounds which do not display the desired odor inhibiting properties. The odor inhibitors of this invention may also be applied to sulfurized lubricants which have already developed odor and will aid in fitting them for further use.

In order to facilitate solution and/or dispersion of the odor inhibitor in the sulfurized lubricant it is desirable that it be added under conditions of vigorous agitation, produced, for example, by mechanical stirring or by the passage of gases such as dry steam or air through the contents

of the dissolution vessel. The odor inhibitor may be added at temperatures as high as about 300° F. but it is preferred to use temperatures below about 150° F. Sufficient quantities of the odor inhibitor may even be added at room temperature.

Specific applications of this invention to both dark and light colored cutting oils containing sulfurized hydrocarbon oils have proven singularly successful.

In order to illustrate this invention a specific embodiment as applied to a light colored or transparent sulfurized cutting oil will be described. Light colored sulfurized cutting oils are generally prepared by digesting hydrocarbon oils boiling in the lubricating oil boiling range with flowers of sulfur at temperatures in the range of about 260 to 320° F. at substantially atmospheric pressure for a period of time sufficient to produce an oil containing about 1 to 3% of sulfur by weight. More or less sulfur will be added to the base oil during the sulfurization step, depending upon its original sulfur content. Preferably, the finished oils will contain 2 to 3% of sulfur by weight. The normal viscosity range of these cutting oils is about 50 to about 200 seconds Saybolt Universal at 100° F. although somewhat higher viscosity products are sometimes prepared.

*Example 1*

A blend of 73.5% of an oil which we shall designate as "A" and 26.5% of an oil "B" was digested with 8 lbs. of sulfur per 100 gallons at about 300° F. and substantially atmospheric pressure to yield a product containing 2.4% sulfur. The viscosity of the product was 110 seconds Saybolt Universal at 100° F. Oils "A" and "B" had the following specifications:

| | Oil "A" | Oil "B" |
|---|---|---|
| Gravity, API | 24.7 | 24.7 |
| Viscosity at 100° F., seconds Saybolt Universal | 82 | 290 |
| Viscosity at 210° F., seconds Saybolt Universal | 36.5 | |
| Pour point, °F | −25 | −5 |
| Flash point, °F | 320 | 400 |
| Original sulfur, percent | 0.75–1.0 | 1.5 |

To the hot reaction mixture was added 2% of lard oil to clean up excess sulfur. After the sulfur clean-up had been effected the oil was allowed to cool to about 150° F. and 0.1% by volume of triethanolamine and 0.2% by volume of pine oil were added with thorough mechanical stirring. The oil was further cooled and passed to tanks where uncombined sulfur and other insoluble matter was separated by sedimentation. The product was a light colored cutting oil which proved extremely resistant to odor development in storage and use.

Our invention may also be applied with success to dark colored sulfurized cutting oils. These oils differ from light colored oils principally in sulfur content and color. In general they contain about 3 to 5% by weight of sulfur in loose chemical combination and/or physical solution. Sulfurization is generally carried out at a somewhat higher temperature than that employed in the sulfurization step used for the preparation of light colored cutting oils. Usually sulfurization may be effected in the temperature range 330 to 380° F. A specific example of the application of our invention to dark colored sulfurized cutting oils is as follows:

*Example 2*

A blend of 77% of an oil which we shall designate as "C" and 23% of an oil "D" was digested with 32 lbs. of sulfur per 100 gallons at about 340° F. for 12 hours under substantially atmospheric pressure to yield a product containing 3.7% sulfur. The viscosity of the product was 147 seconds Saybolt Universal at 100° F. Oils "C" and "D" had the following specifications:

| | Oil "C" | Oil "D" |
|---|---|---|
| Gravity, API | 24.7 | 20.9 |
| Viscosity at 100° F., seconds Saybolt Universal | 82 | 222 |
| Viscosity at 210° F., seconds Saybolt Universal | 36.5 | |
| Pour point, °F | −25 | −5 |
| Flash point, °F | 320 | 390 |
| Original sulfur, percent | .75–1.0 | 1.0 |

The hot reaction product was cooled to a temperature of 200° F. and blown with air for 45 minutes. At the end of this period the temperature had reached 150° F. and 0.1% by volume of triethanolamine was added with thorough mechanical stirring. The product was a dark colored cutting oil which proved extremely resistant to odor development in storage and use.

While our invention has been described in connection with certain preferred embodiments, it is to be understood that these are submitted by way of illustration and not by way of limitation. It is to be understood that our invention is broadly applicable to the odor stabilization of any combination of sulfur and an organic material which normally tends to evolve volatile sulfur compounds.

It is apparent that this invention supplies a novel and useful means by which odor evolution in unstable sulfur bearing hydrocarbon oils may be readily inhibited. Further, it will be appreciated that this invention provides novel compositions of matter which are highly useful as metal forming lubricants and at the same time do not constitute a health hazard to the operators using the same.

We claim:

1. A composition of matter comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development and an alkylolamine chosen from the group consisting of 2-amino-2-methyl-1-propanol; 2-aminobutanol; 2-amino-2-methyl-1, 3-propanediol; 2-amino-2-ethyl-1, 3-propanediol; monoethanolamine, diethanolamine and triethanolamine, said alkylolamine being present in sufficient amount substantially to inhibit said odor development.

2. A composition of matter comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development and about 0.025 to about 1% of an alkylolamine chosen from the group consisting of 2-amino-2-methyl-1-propanol, 2-aminobutanol, 2-amino-2-methyl-1, 3-propanediol, 2-amino-2-ethyl-1, 3-propanediol, monoethanolamine, diethanolamine and triethanolamine.

3. A composition of matter comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development and triethanolamine in sufficient amount substantially to inhibit said odor development.

4. A composition of matter comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development and diethanolamine in sufficient amount substantially to inhibit said odor development.

5. A composition of matter comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development and 2-amino-2-methyl-1-propanol in sufficient amount substantially to inhibit said odor development.

6. A metal fabricating lubricant comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development, said lubricant having a viscosity in the range of about 50 to about 300 seconds Saybolt Universal at 100° F. and a sulfur content of about 1 to about 5% and about 0.025 to about 1% of an alkylolamine chosen from the group consisting of 2-amino-2-methyl-1-propanol; 2-aminobutanol; 2-amino-2-methyl-1, 3-propanediol; 2-amino-2-ethyl-1, 3-propanediol; monoethanolamine, diethanolamine, and triethanolamine.

7. A metal fabricating lubricant comprising a sulfurized hydrocarbon oil containing substantially no corrosive halogen compound and being normally susceptible to odor development, said lubricant having a viscosity in the range of about 50 to about 300 seconds Saybolt Universal at 100° F. and a sulfur content of about 1 to about 5% and about 0.025 to about 1.0% of triethanolamine.

8. A process for inhibiting odor evolution in a sulfurized hydrocarbon cutting oil normally susceptible to odor evolution comprising adding to said cutting oil by means of vigorous agitation at a temperature below about 300° F. an alkylolamine chosen from the group consisting of 2-amino-2-methyl-1-propanol; 2-aminobutanol; 2-amino-2-methyl-1, 3-propanediol; 2-amino-2-ethyl-1, 3-propanediol; monoethanolamine, diethanolamine and triethanolamine in quantity sufficient substantially to inhibit said odor evolution.

9. A process for inhibiting odor evolution in a sulfurized cutting oil normally susceptible to odor evolution comprising adding triethanolamine to said cutting oil by means of vigorous agitation at a temperature below about 300° F.

10. A process for inhibiting odor evolution in a sulfurized cutting oil normally susceptible to odor evolution comprising adding diethanolamine to said cutting oil by means of vigorous agitation at a temperature below about 300° F.

11. A process for inhibiting odor evolution in a sulfurized cutting oil normally susceptible to odor evolution comprising adding 2-amino-2-methyl-1-propanol to said cutting oil by means of vigorous agitation at a temperature below about 300° F.

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