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## BENTONITE GREASES

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1

This invention relates to a new and improved lubricating composition. Particularly, the invention relates to a lubricating composition which comprises a synthetic oil thickened to a grease consistency with an organophilic bentonite. More particularly, the invention relates to a grease composition prepared by dispersing in a synthetic lubricating oil a complex reaction product formed by reacting a bentonitic type clay with an aliphatic amine salt.

The complex products formed by reacting bentonitic or montmorillonitic type clays with aliphatic amine salts are known in the art. Some of these compounds are described in U. S. Patent 2,033,856, issued to Smith, March 10, 1936. The swelling of these complexes in organic liquids and liquid mixtures has been observed and a mechanism advanced to account for the solvation phenomenon in an article by John W. Jordan in the Journal of Physical Colloid Chemistry, volume 53, number 2, February 1949, on pages 294–305 inclusive.

It has now been found and forms the subject of this invention that these organophilic bentonites when dispersed in a synthetic lubricating oil form valuable grease compositions having stable properties and excellent high dropping points.

It has been found that for the most part these organophilic bentonites, particularly those complexes formed by reacting an aliphatic amine salt with the bentonite, are dispersible in mineral lubricating oils only with extreme difficulty. However, when a synthetic lubricating oil which contains appreciable quantities of long chain alcohols are used these organophilic bentonites are easily dispersible and a very satisfactory grease composition results.

Although a great number of the synthetic lubricating oils are useful in manufacturing the greases of this invention the preferred embodiment contemplates the utilization of the synthetic oils obtained from the so-called "Oxo" process. This process may be described as the catalytic reaction of monoolefins with carbon monoxide and hydrogen. At temperatures of about 300° F. to 350° F. and under pressure of about 300 pounds per square inch in the presence of a catalyst an aldehyde is formed. This aldehyde is then hydrogenated to form a primary alcohol. The process was developed in Germany and was described in this country in U. S. Patent 2,327,066, issued to Roelen in 1943.

Depending upon the starting olefin various alcohols may be synthesized by this process. For example, a fraction primarily consisting of $C_7$ olefins which is isolated from the polymerization product of propylene, or a mixture of $C_3$ and $C_4$ monoolefins may be subjected to the "Oxo" process. The resulting alcohol mixture will be found

2

to have a major proportion of $C_8$ alcohol as well as a number of isomers. Other high molecular weight compounds are also found to be present.

From this reaction product, a major proportion of which is $C_8$ "Oxo" alcohol, the desired cuts are removed by distillation. For example, the $C_8$ "Oxo" alcohols are distilled off. The bottoms or residuum left after this distillation contains a large proportion of $C_9$ alcohols, higher boiling alcohols, acetals, esters, ethers and hydrocarbons. In a distillation step the $C_9$ "Oxo" alcohols along with any other low boiling materials may be removed. The residuum left from this second distillation step represents approximately 33% to 35% of the residue remaining after the $C_8$ "Oxo" alcohols are removed.

That proportion of the product of the "Oxo" process remaining after the $C_8$ "Oxo" alcohol and the $C_9$ "Oxo" alcohol cuts are removed, that is to say, that portion remaining after the product has been subjected to a temperature of 250° C., are hereinafter referred as to "Oxo" bottoms and constitute the preferred synthetic oil operable in this invention.

Although the above description is specifically directed to an "Oxo" process for the production of a major amount of $C_8$ "Oxo" alcohol, and the preferred embodiment of this invention contemplates the use of the bottoms from this particular process, the invention is not limited to the use of these particular bottoms. The synthetic oils or the residue remaining after distillation of the mixture of products obtained by subjecting a wide variety of olefins to the "Oxo" process are operable. For instance, any of the various olefins obtained by polymerizating mixtures of propylenes and butylenes may be subjected to the "Oxo" process and the bottoms from these processes may be used. In addition, the olefins obtained from the hydrocarbon synthesis reactions may be converted to "Oxo" alcohols and other products and these bottoms are operable in this invention.

The approximate composition of the residuum boiling above 250° C. is as follows:

85.0% $C_{12}$ "Oxo" alcohols and higher alcohols
5.0% $C_{13}$+ acetals
5.0% $C_{14}$+ esters of mixed alcohols and the mixed acids
5.0% high molecular weight ethers and hydrocarbon

Inspection tests on this residuum show:

| | |
|---|---|
| Flash point | over 350° F. |
| Pour point | —55° F. |
| S. S. U. viscosity at 100° F. | 68.3 |

Of the organophilic bentonitic materials operable in this invention it is preferred to use the complexes formed by reacting bentonite with an aliphatic amine salt in which the aliphatic con-

tributed portion of the amine has a carbon chain length of from 10 to 18 carbon atoms. Either the primary aliphatic amine salt or the quaternary ammonium salt may be used. In the case of the latter salt the aliphatic groups may be either alike or different, the total number of carbon atoms, however, must be within the range of from 10 to 18 carbon atoms.

These organophilic bentonites are normally prepared by adding to a water dispersion of the bentonite the desired aliphatic amine salt. These salts are normally prepared by reacting the aliphatic amine with the desired acid. Acetic and hydrochloric acid represent the desired salt forming acids.

In general, the amounts of the organophilic bentonites and the synthetic oil used for the formulation for the greases of this invention are not critical so long as desired stable grease structure is obtained. However, for most purposes a grease formed of from 10% to 25% of the organophilic bentonite with 90% to 75% of the synthetic oil results in greases having optimum stability characteristics and outstanding structure.

As was mentioned above the formation of the grease composition involves a dispersion of the organophilic bentonite in the synthetic oil. This dispersion is advantageously accomplished by a milling process. This milling step may be accomplished by any of the conventional milling procedures familiar to the art such as a rolling mill, colloid mill, Lancaster disperser, Manton-Gaulin homogenizer, etc., as long as sufficient shearing action is obtained to give satisfactory dispersion.

This invention will be further explained by examination of the following examples.

*Example I*

15% by weight of a complex formed by reacting bentonite with a quaternary aliphatic amine salt was admixed with 85% by weight of "Oxo" bottoms by stirring cold in a grease kettle or other type mixer. The dispersion was thoroughly accomplished by milling the mixture on a 3-roll mill with only one pass of the material through the mill. A solid grease composition resulted which gave the following inspection tests:

| | |
|---|---|
| Penetration, unworked | 300 mm./10. |
| Penetration, worked (60 strokes). | 310 mm./10. |
| Penetration, worked (1000 strokes) (fine hole worker). | 315 mm./10. |
| Dropping point | 500° F.+. |
| Solubility | Insoluble in boiling water. |

*Example* II

20% by weight of a complex formed by reactin a quaternary aliphatic amine salt with bentonite was dispersed in 80% of an Oxo bottoms synthetic oil in a manner similar to that described in Example I above. Inspection tests on this grease composition gave the following results:

| | |
|---|---|
| Penetration, unworked | 250 mm./10. |
| Penetration, worked (60 strokes). | 260 mm./10. |
| Penetration, worked (1000 (1000 strokes) (fine hole worker). | 270 mm./10. |
| Dropping point | 500° F.+. |
| Solubility | Insoluble in boiling water. |

It has been found that the complex formed by reacting the bentonitic materials with a primary aliphatic amine salt are especially difficult to disperse in organic mineral hydrocarbon oils. However, by first dispersing this complex in a minor amount of a synthetic oil which contains an appreciable quantity of long chain high molecular weight alcohols the resulting dispersion may be further dispersed in a mineral oil resulting in a satisfactory grease composition. This will be further explained by reference to the following example.

*Example III*

15% by weight of a complex formed by reacting bentonite with a primary aliphatic amine salt was admixed with 8½% by weight of "Oxo" bottoms. The dispersion thus formed was passed through a standard laboratory colloid mill with 76.5% by weight of an acid-treated naphthenic distillate having a viscosity at 210° F. of 55 S. U. S. The resulting grease composition was subjected to the standard ASTM tests and gave the following results:

| | |
|---|---|
| Penetration, unworked | 290 mm./10. |
| Penetration, worked (60 strokes). | 310 mm./10. |
| Penetration, worked (1000 strokes) (fine hole worker). | 325 mm./10. |
| Dropping point | 500° F.+. |
| Solubility | Insoluble in boiling water. |

To test the oxidation resistance characteristics of the grease compositions of this invention a grease similar to that of Example I was made incorporating therein 0.5% by weight of phenyl alpha naphthylamine. This grease composition was subjected to the Norma-Hoffman Bomb Oxidation Test and gave excellent results. Operating at 210° F. and 110 pounds per square inch initial oxidation pressure drop was 5 pounds per square inch in 150 hours.

Although in the preferred embodiment of this invention the dispersant is a synthetic oil obtained from the "Oxo" process it is also within the concept of this invention to use as the dispersant other synthetic oils. Long chain esters, esters of dibasic acids for example sebacates, adipates, and the like, polymers of cracked wax, alkylated aromatics, polyglycols, copolymers of such materials as diolefins with other saturates, and other synthetic lubricants known to the art are operable in this invention. Of particular utility among these may be mentioned a fluid copolymer of low molecular weight obtained by copolymerizing conjugated diolefins with a minor proportion of an unsaturated comonomer. The fluid copolymer preferred is a low molecular weight butadiene-acrylonitrile product which is liquid at temperatures as low as +20° F. to —70° F. This copolymer per se and a preferred method of preparation are described in detail in copending application Serial No. 637,782, now Patent No. 2,500,983, filed December 28, 1945.

An excellent smooth adhesive grease preparation was manufactured using a copolymer of butadiene and acrylonitrile in which about 76% by weight of butadiene was copolymerized with about 25% by weight of acrylonitrile in accordance with the procedure described in the above mentioned application.

15% by weight of a quaternary aliphatic amine salt of bentonite was admixed with 85% by weight

of the copolymer of butadiene and acrylonitrile by stirring in a grease kettle or other type mixer. Dispersion was thoroughly accomplished by milling on a 3-roll paint mill. The yellow adhesive grease obtained was found to be insoluble in motor gasoline and petroleum naphthas and gave an ASTM penetration of 215 mm./10 unworked and a worked penetration (1000 strokes using the fine hole worker plate) of 220 mm./10. These penetration tests data show the loss of only 5 mm./10 after working which indicates excellent structural stability.

The grease compositions of this invention may include any of the conventional additive materials such as tackiness agents, viscosity index improvers, anti-corrosion agents, oxidation inhibitors, extreme pressure agents and the like.

In summation, this invention comprises the manufacture of a new and useful grease composition by dispersing in a synthetic oil obtained from the "Oxo" process an organophilic bentonite complex formed by reacting bentonite with the salt of a long chain aliphatic amine. Either the primary aliphatic amine or the quaternary aliphatic amine may be used to obtain the salt to react with the bentonite. If the quaternary amine is used the aliphatic groups may be the same or different. The preferred embodiment contemplates the use of hydrochloric or acetic acid to form the salt with the aliphatic amine.

What is claimed is:

1. A lubricating composition consisting essentially of a synthetic lubricating oil thickened to a grease consistency with a complex formed by reacting bentonite with an aliphatic amine salt, said synthetic lubricating oil being the residue remaining after distillation at about 250° C. of the mixture of products obtained by subjecting a $C_7$ monoolefin to the action of carbon monoxide and hydrogen in the "Oxo" process.

2. A lubricating composition consisting essentially of a synthetic lubricating oil thickened to a grease consistency with about 10% to 25% by weight of a complex formed by reacting bentonite with a hydrochloric acid salt of a primary aliphatic amine, said synthetic lubricating oil being the residue remaining after distillation at about 250° C. of the mixture of products obtained by subjecting a $C_7$ monoolefin to the action of carbon monoxide and hydrogen in the "Oxo" process.



3. A lubricating composition consisting essentially of a synthetic lubricating oil thickened to a grease consistency with about 15% to 25% by weight of a complex formed by reacting bentonite with a quaternary aliphatic amine salt, said synthetic lubricating oil being the residue remaining after distillation at about 250° C. of the mixture of products obtained by subjecting a $C_7$ monoolefin to the action of carbon monoxide and hydrogen in the "Oxo" process.

4. A process for the formation of a new and useful lubricating composition which comprises milling for the desired period of time a mixture of about 10% to 25% by weight of a complex formed by reacting bentonite with an aliphatic amine salt with about 90% to 75% by weight of a synthetic lubricating oil, said synthetic lubricating oil being the residue remaining after distillation at about 250° C. of the mixture of products obtained by subjecting a $C_7$ monoolefin to the action of carbon monoxide and hydrogen in the "Oxo" process.

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## REFERENCES CITED

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

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 2,033,856 | Smith | Mar. 10, 1936 |
| 2,248,636 | Marsden | July 8, 1941 |
| 2,260,625 | Kistler | Oct. 28, 1941 |
| 2,467,148 | Morway | Apr. 12, 1949 |
| 2,531,440 | Jordan | Nov. 28, 1950 |