Patented Apr. 18, 1939 2,155,204

UNITED STATES PATENT OFFICE

2,155,204

LUBRICANT

Carl F. Prutton, Cleveland Heights, Ohio, assignor, by mesne assignments, to The Lubri-Zol Development Corporation, Cleveland, Ohio, a corporation of Delaware

No Drawing. Application August 17, 1937, Serial No. 159,601

17 Claims. (Cl. 87—9)

This invention relates, as indicated, to improved lubricating compositions and more specifically to a new and improved addition agent for lubricating compositions generally; the method of producing such addition agent and the new and improved lubricating compositions resulting from the use of such addition agent.

This application is a continuation in part of my co-pending applications Ser. No. 111,111, filed November 16, 1936, now Patent No. 2,119,556 issued June 7, 1938, and Ser. No. 737,070, filed July 26, 1934.

In recent years there has been an increasing demand for improved lubricating compositions having improved characteristics which are not possessed by the usual plain mineral lubricating oils. Among the improved properties thus desired are extreme pressure characteristics, improved cold test, freedom from sludge, etc.

In general, it has been found that various types of halogenated organic compounds, when used as addition agents to mineral lubricating oils, produce the above-named improvements to a more pronounced degree than any other class of materials, particularly when properly selected and used in proper proportions.

The halogenated organic compounds which have been suggested for use as additions to lubricating compositions may be generally divided into two principal classes, i. e., compounds which have been very carefully chemically isolated, treated and stabilized, so that they are suitable for use under substantially all conditions and will not hydrolize and cause destructive corrosion even when subjected to high temperatures in the presence of substantial amounts of moisture.

The second class of halogenated organic compounds which have been employed are the halogenated complex petroleum derivatives whose principal appeal has been their low cost. Compounds falling within the last-named class, while admirably suited to provide extreme pressure lubricants for gears and the like are, however, unsuited for use in lubricants to be employed in the crankcases of internal combustion engines due to the fact that heretofore such materials have contained objectionable amounts of relatively unstable constituents.

A halogenated addition agent which is rather complex in its chemical structure, i. e., contains a rather wide variety of individual compounds, has, however, certain very desirable characteristics when used as an addition agent in that the wide variety of compounds present makes possible the securing of desired results of the various types previously enumerated and over a wide range of operating conditions such as temperature and pressure.

It is a principal object of my invention to provide an addition agent for lubricating compositions which is of a chemically complex nature and which has, however, been so stabilized that its use is now possible under certain types of conditions under which similar complex materials of the prior art were entirely unsuited, principally on account of their instability.

It is a further object of my invention to provide a method of producing the complex addition agent previously defined, which method is characterized by its simplicity and low cost of operation, so that the resultant addition agent is made available at relatively low cost.

It is a further object of my invention to provide an improved lubricating composition having as its principal constituent my improved halogenated complex addition agent.

Other objects of my invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail one approved combination of ingredients embodying my invention, such disclosed means constituting, however, but one of various forms in which the principle of the invention may be used.

This invention may be broadly stated as comprising the discovery that a new and improved stabilized halogenated complex organic addition agent for lubricating compositions may be satisfactorily and economically produced and that lubricating compositions containing the same have unexpected desirable properties.

The process of producing my improved addition agent may be briefly described as follows:— Any complex or heterogeneous mixture of organic compounds such as are found in mineral oil, mineral oil fractions such as scale wax, paraffin wax, etc., coal tar and wood distillates, is halogenated by the usual procedure well known to those familiar with the art until the composition contains from about 10% to about 60% of halogen.

The product immediately resulting from the halogenation step may be subjected to any of the well-known methods of removing the excess halogen, as well as certain of the more unstable of the halogen compounds, such processes comprising air blowing, treatment with an alkali, etc.

The product resulting from this preliminary stabilizing step will be found to contain various quantities of halogenated aromatic or aliphatic compounds, or both. In case both types of compounds are present the proportional relationship between the same will, of course, depend upon the composition of the starting material, the degree of halogenation and the particular preliminary stabilizing process such as air blowing or alkali treatment which has been employed.

Certain of the halogenated compounds present in this resultant heterogeneous mixture of halogenated constituents are, however, so unstable that while the composition may be admirably suited as an extreme pressure addition agent to lubricants useful in gear cases and the like, nevertheless such compounds are too unstable to permit their safe use under conditions such as those encountered in crankcases of internal combustion engines.

The composition containing a heterogeneous mixture of halogenated compounds prepared in the previously described or any other conventional process, is next treated with anhydrous aluminum chloride or equivalent agent according to conventional practice in the well-known Friedel-Crafts or similar condensation reaction. It is preferred, however, that the reaction be carried on to the extent that only the more unstable of the halogenated compounds react, either with one another, or with other compounds present in the composition. During the reaction, therefore, preferably only a minor amount of the combined halogen present in the original halogenated material is removed. The less stable halogenated compounds, if aliphatic, may become attached as alkyl side chains to aromatic compounds, or if of other types, condense with, or react with the same or other compounds present. Certain halogenated aliphatic compounds will also be condensed with or combine with the same or other aliphatic compounds to form relatively stable products. The final product, depending upon the amount of unstable halogenated compounds originally present and the extent to which the reaction has been carried out, will contain certain proportions of the reaction products, halogenated alkyl or aromatic compounds or both, and also certain proportions of the more stable halogenated compounds originally present.

This treatment with an agent such as $AlCl_3$ will promote the condensation of halogenated aromatic with halogenated aliphatic compounds, and is also more or less effective in causing the condensation of halogenated cyclic compounds (as typified by halogenated cyclohexane) with halogenated aliphatic compounds, and halogenated aliphatic compounds with other halogenated aliphatic compounds. Since the condensation is most efficient when occurring between halogenated aromatic and halogenated aliphatic compounds, it may on occasion, be desirable to add up to about 20% of halogenated aromatic compounds to insure the combination of substantially all of the relatively unstable halogenated aliphatic constituents.

The aluminous sludge resulting from the Friedel-Crafts reaction is then removed according to conventional practice, such as by diluting the mixture with a light hydrocarbon solvent to promote settling and then distilling off the solvent.

The resultant composition which comprises the new composition of matter according to my invention, will, when the starting material has been a petroleum derivative, contain minor amounts of more or less halogenated alkylated aromatic compounds and their derivatives and major proportions of relatively stable halogenated aliphatic compounds.

Inasmuch as the addition agent thus prepared is to be used most generally in a mineral lubricating oil or grease, a certain amount of care should be exercised in selecting the starting material so that the resultant composition, after halogenation and after the Friedel-Crafts reaction, will be soluble in or miscible with mineral oil and have a sufficiently high boiling point or low vapor pressure that it will not be volatilized at the temperatures encountered during its contemplated use. For example, the resultant composition to be used as an addition agent should have a vapor pressure less than atmospheric at a temperature of 140° and preferably at a temperature of 170°.

If certain of the addition agents thus prepared are found to be of such a heavy consistency as not to be readily dissolved in or miscible with mineral oil, a mutual solvent may be employed for the purpose of facilitating the preparation of the final composition.

The new addition agent prepared in accordance with the process which comprises one of the phases of this invention may be added to any suitable lubricating composition base, the one most generally used being mineral lubricating oil. When mineral lubricating oil is used as the base, my new and improved addition agent may be added to the mineral oil base in various percentages from about .1% to about 20% depending upon the particular use for which the final composition is designed. For use under conditions where high temperatures and extreme pressures are encountered, such as in crankcase lubricants, from about .1% to about 10%, and preferably from about .25% to about 3.5% of the addition agents may be added to mineral oil. It is also within the contemplation of my invention to employ my improved addition agent in conjunction with certain other oils which may be generally classified as non-mineral oils and which include animal oils, vegetable oils, etc., used either as the lubricating oil base or likewise as an addition agent to a mineral lubricating oil base.

My new and improved addition agent, when added to lubricating oil bases of the character previously described, will be found to desirably improve the extreme pressure characteristics of the resultant composition. In certain instances, the addition agent will also lower the cold test of such composition, and/or generally improve the sludging characteristics of the composition. All of the halogen compounds present in the heterogeneous mixture are more or less effective in affording extreme pressure characteristics. Certain types of halogenated alkylated aromatic compounds in the heterogeneous mixture are particularly effective to improve the cold test of the lubricating composition since only small percentages of such compounds are usually required in order to markedly improve this property of a mineral lubricating oil. The presence of a wide variety of halogenated compounds in the heterogeneous mixture is particularly advantageous in that the improved properties of the lubricating composition containing such heterogeneous mixture as an addition agent extend over a wider range of operating condition than that usually secured by the addition of a single compound.

It is to be understood that other and similar

complex organic mixtures, as above described, may be similarly treated with satisfactory results in producing similar addition agents. Likewise catalysts other than aluminum chloride, such as $AlBr_3$, $FeCl_3$, $ZnCl_2$, etc., which are effective in promoting Friedel-Crafts reaction, may be utilized, although the former is preferred.

The amount of catalyst to be used may be from about 1/10% to about 10% based on the amount of chlorinated material and in the case of aluminum chloride may preferably be from ½ to 2%. The reaction may be carried out at temperatures up to about 100° C., but preferably, in most cases, below 100° C., say 20° to 50° C.

The reaction generally should require from about ¼ to 2 hours and usually for best results only from ½ to 1 hour is required

The reaction may be carried on by adding the catalyst directly to the chlorinated material or the chlorinated material plus an additional amount of aromatic compounds; or it may also be carried out in the presence of a solvent which may be inert or which may be the aromatic compound itself as, for example, benzene.

As an example of the reaction carried out in the absence of a solvent:

3 parts of aluminum chloride were added to 400 parts of chlorinated paraffin wax containing 36.4% of chlorine and the mixture heated to a temperature of 75° C. for one-half hour. The mixture was then cooled to room temperature, an equal amount of benzene added and the aluminum sludge removed by washing with dilute hydrochloric acid and then with water. The benzene was then removed by vacuum distillation. The final product contained 32.0% of chlorine.

The stability of the material can be determined by heating in an iron container at a temperature of about 110° C. until there is evidence of decomposition. The original product under these conditions was stable for ½ hr. and the stabilized product for more than 2½ hours.

As an example of the reaction carried on in the presence of the solvent, as well as in the presence of added aromatic compounds:

300 parts of chlorinated wax were diluted with 200 parts of benzene and treated with 2¼ parts of aluminum chloride at about 25° C. About the same improvement in stability resulted from this treatment. In this case part of the material remained emulsified in the wash water and was removed from the final product. Analysis showed that the part removed had a relatively low chlorine content so that the final product had a higher chlorine content than the original.

As will be seen from the data given for the first example above, the amount of chlorine removed by the reaction was less than 10% of the total chlorine in the original material.

In other cases, a marked improvement in stability was obtained by the removal of less than 5% of the total chlorine originally present.

In general, when stabilizing chlorinated complex organic compounds such as are found in mineral oil, mineral oil fractions, coal tar and wood distillates, the amount of condensing catalyst added or the extent to which the condensation reaction is carried out in order to effect the desired stabilization of the product when the original material contains from about 10 to about 60% of halogen will be such as to remove during the condensation from a fraction of a percent to about 20% of the chlorine content of the material being stabilized.

The following is an example of the improvement in stability effected by treatment with aluminum chloride:

A chlorinated petroleum wax containing approximately 40% chlorine, which had been prepared and purified in the usual way and placed in an oven was maintained at a temperature of 110° to 115° C. At the end of approximately thirty minutes certain of the constituents of the material began to decompose as evidenced by a noticeable change in color of the composition accompanied by evolution of hydrogen chloride gas. The same material, after being treated with aluminum chloride in accordance with this invention, was subjected to the same test. No decomposition of any of the constituents was noted until after about five and one-half hours.

Throughout the foregoing description the various compounds referred to have been identified as halogenated compounds. Of the various halogens, chlorine is preferred, principally on account of its low cost and the relative ease by which it may be handled as compared with certain other halogens.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the materials employed in carrying out the process, provided the ingredient or ingredients stated in any of the following claims or the equivalent of such stated ingredient or ingredients be employed.

I, therefore, particularly point out and distinctly claim as my invention:—

1. As a new composition of matter, a halogenated complex mixture of organic compounds of the types found in petroleum oils and in which the less stable compounds have been converted by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

2. As a new composition of matter, a halogenated naturally occurring complex mixture of organic compounds of the types found in petroleum oils, coal tar and wood distillates and in which mixture subsequent to halogenation the less stable compounds have been converted by treatment with a condensing-agent of the type represented by anhydrous $AlCl_3$.

3. As a new composition of matter a stabilized complex mixture of organic compounds, which mixture includes substantial amounts of halogenated alkylated cyclic compounds and relatively stable halogenated aliphatic compounds, prepared by halogenating a naturally occurring complex mixture of organic compounds of the types found in petroleum oils and then eliminating the instability of certain of the components by treatment with a condensing agent of the type best represented by anhydrous $AlCl_3$.

4. A composition of matter for use as an addition agent to mineral lubricating oils comprising a naturally occurring complex mixture of organic compounds of the types found in petroleum oils and which mixture has been halogenated and then stabilized by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

5. The method of producing an improved addition agent for lubricating compositions which comprises halogenating complex mixtures of organic compounds of the types found in petroleum oils, coal tar and wood distillates, and then treating such halogenated mixtures with a condensing agent of the type represented by anhydrous $AlCl_3$.

6. A lubricating composition comprising a major proportion of mineral lubricating oil and

less than 20% based on the amount of such mineral oil of a halogenated naturally occurring complex mixture of organic compounds which has been stabilized by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

7. A lubricating composition comprising a major proportion of mineral oil and a minor proportion of a halogenated naturally occurring complex mixture of petroleum derivatives, which mixture has been stabilized by treatment with a condensing agent of the type best represented by anhydrous $AlCl_3$.

8. A method of producing stabilized lubricating compositions which comprises halogenating a complex mixture of organic compounds of the types found in petroleum oils and then effecting a Friedel-Crafts reaction between the halogenated aromatic compounds and the halogenated aliphatic compounds with the aid of $AlCl_3$ and then separating from the $AlCl_3$ and any other solids leaving halogenated alkylated aromatic compounds as a major constituent in the resulting composition, which is then added to a mineral lubricating oil base.

9. As a new composition of matter, a chlorinated complex mixture of organic compounds of the types found in petroleum oils and in which the less stable compounds have been converted by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

10. As a new composition of matter, a chlorinated naturally occurring complex mixture of organic compounds of the types found in petroleum oils, coal tar and wood distillates and in which mixture subsequent to chlorination the less stable compounds have been converted by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

11. As a new composition of matter a stabilized complex mixture of organic compounds, which mixture includes substantial amounts of chlorinated alkylated cyclic compounds and relatively stable chlorinated aliphatic compounds, prepared by chlorinating a naturally occurring complex mixture of organic compounds of the types found in petroleum oils and then eliminating the instability of certain of the components by treatment with a condensing agent of the type best represented by anhydrous $AlCl_3$.

12. A composition of matter for use as an addition agent to mineral lubricating oils comprising a naturally occurring complex mixture of organic compounds of the types found in petroleum oils and which mixture has been chlorinated and then stabilized by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

13. The method of producing an improved addition agent for lubricating compositions which comprises chlorinated complex mixtures of organic compounds of the types found in petroleum oils, coal tar and wood distillates, and then treating such chlorinated mixtures with a condensing agent of the type represented by anhydrous $AlCl_3$.

14. A lubricating composition comprising a major proportion of mineral lubricating oil and less than 20% based on the amount of such mineral oil of a chlorinated naturally occurring complex mixture of organic compounds which has been stabilized by treatment with a condensing agent of the type represented by anhydrous $AlCl_3$.

15. A lubricating composition comprising a major proportion of mineral oil and a minor proportion of a chlorinated naturally occurring complex mixture of petroleum derivatives, which mixture has been stabilized by treatment with a condensing agent of the type best represented by anhydrous $AlCl_3$.

16. A method of producing stabilized lubricating compositions which comprises chlorinating a complex mixture of organic compounds of the types found in petroleum oils and then effecting a Friedel-Crafts reaction between the chlorinated aromatic compounds and the chlorinated aliphatic compounds with the aid of $AlCl_3$ and then separating from the $AlCl_3$ and any other solids leaving chlorinated alkylated aromatic compounds as a major constituent in the resulting composition, which is then added to a mineral lubricating oil base.

17. A method of producing stabilized lubricating compositions which comprises halogenating a complex mixture of organic compounds of the types found in petroleum oils and then effecting a condensing reaction between the halogenated compounds with the aid of a re-agent such as $AlCl_3$ and then separating from the re-agent such as $AlCl_3$ and any other solids leaving halogenated alkylated aromatic compounds as a major constituent in the resulting composition, which is then added to a mineral lubricating oil base.

CARL F. PRUTTON.