

## UNITED STATES PATENT OFFICE

2,398,271

## COMPOSITION OF MATTER

John C. Zimmer, Union, and Arnold J. Morway,  
Clark Township, Union County, N. J., assignors  
to Standard Oil Development Company, a cor-  
poration of Delaware

No Drawing. Application January 1, 1943,  
Serial No. 471,019

2 Claims. (Cl. 252-45)

The present invention relates to the field of lubricants and lubricating agents and more particularly to sulfurized material derived through the sulfurization of polymers obtained by the clay treatment of steam cracked petroleum distillates.

It is quite well known that mineral lubricating oils do not provide adequate lubrication or service for many types of industrial uses and many different expedients have been resorted to, some quite successfully, in an attempt to increase or fortify the lubricating quality or characteristics of mineral lubricating oil for those extreme conditions where straight mineral lubricating oil has been found to be inadequate. It has long been known that the presence of sulfur, particularly when the sulfur is in the combined form, will increase the lubricity or lubricating quality of a mineral lubricating oil and generally speaking the extent of such improvement is in direct proportion to the amount of sulfur present. It does not follow however that the mere addition of sulfur will suffice for it has been found that the form or condition in which the sulfur is present is a determining factor and that the sulfur must be present in a combined but active form. Sulfur does not combine directly with mineral lubricating oil very readily and therefore other expedients must be utilized to get the sulfur into the oil. One of these expedients is to react the sulfur with a material with which the sulfur readily combines and to dissolve the resulting reaction product in the mineral lubricating oil. The successfulness of this method is limited by either one or more of several factors; either the material will not react or absorb sufficient sulfur to adequately fortify the mineral lubricating oil when dissolved therein, the material contains a high percentage of sulfur but is insoluble in mineral oil or the material is unstable in oil solution, breaking down, on standing, in the form of a sludge or sediment. The polymers resulting from the clay treatment of thermally cracked petroleum oil distillates where the cracking is conducted in the absence of steam and cracking coal tars have been suggested as possible materials to be sulfurized to yield a mineral lubricating oil improving agent. The former of these materials does not absorb an effective amount of sulfur while the latter is objection-

able for the reason that the lubricating oil blends made therefrom deposit an oil-insoluble sludge on standing.

It is an object of the present invention to form a sulfurized material which contains a high percentage of sulfur, is soluble in mineral lubricating oil and when blended with mineral lubricating oil will not break down on standing in the form of a sludge or sediment. Other objects will be apparent to those skilled in the art upon reading the following description.

It has now been found that the polymers resulting from the clay treatment of steam cracked petroleum oil distillates readily absorb sulfur forming a product which is oil soluble, contains a high percentage of sulfur and is an effective additive for blending with mineral lubricating oil to form a sulfurized cutting oil or an extreme pressure lubricant. It is believed that the efficacy of these particular polymers is attributable to their high diolefin content which ranges from 20 to 35 expressed as diene numbers. This is equivalent to substantially one diolefin linkage per molecule. The unsaturated diolefin-containing polymers are obtained from vapor or liquid phase clay treatment of petroleum distillates which have been cracked at high temperatures, 800° F.-1500° F., in the presence of steam. They are viscous oils, having viscosities ranging from 500 seconds Saybolt at 100° F. upward, but for the purposes of this invention it is preferred to use those polymers whose viscosities fall within the range of 500 seconds at 180° F. to 300 seconds Saybolt at 210° F. These unsaturated polymers are characterized by their low A. P. I. gravity and ability to react and combine with large quantities of sulfur supplied either as elementary sulfur, sulfur halides or other sulfur-bearing reagents. Quantities of sulfur ranging from 10-40%, can be combined with these unsaturated diolefin-containing hydrocarbons, but it is preferred to sulfurize them to the extent of from 15-30%.

As an example: a satisfactory polymer was obtained by treating a steam cracked gasoline with fresh No. 1 burned Attapulugus clay (30-60 mesh) in an eight gallon tower operated adiabatically. Initial conditions were 375° F. clay temperature, 100 lbs. gauge pressure, and 0.25 v./v./hour feed rate. For the purpose of ready comparison inspection data on this type of poly-

mer as compared with the polymer obtained by clay treating a thermally cracked gasoline, which was cracked in the absence of steam, appear in the following table.

TABLE I  
Inspection of polymers from vapor phase cracked petroleum distillates

|                           | Cracked with steam |          | Cracked without steam |
|---------------------------|--------------------|----------|-----------------------|
|                           | Sample A           | Sample B |                       |
| Treating temperature..... | 400                | 400      | 400                   |
| Gravity, A. P. I. ....    | 10.6               | 13.7     | 16                    |
| Flash open cup, °F. ....  | 305                | 240      | 200                   |
| Saybolt vis./100° F. .... | 8,040              | 1,266    | 200                   |
| Saybolt vis./210° F. .... | 116                | 66       | ---                   |
| Iodine number.....        | 119                | 207      | 200                   |
| Bromine number.....       | 120                | ---      | ---                   |
| Diene number.....         | 24.8               | 21.1     | 11.6                  |

According to the present invention the polymerized material produced by the vapor phase clay treatment of steam cracked petroleum distillate is sulfurized by heating the polymer with a sulfurizing agent such as flowers of sulfur or sulfur chloride to a temperature of 300° to 400° F. and stirred at that temperature for a period of 30 minutes to 3 hours, then cooled after which it is ready for blending with a mineral lubricating oil to give a sulfurized cutting oil or an extreme pressure lubricant. For blending purposes about 5 to 30 parts by weight of the sulfurized material is used with 95 to 70 parts by weight of mineral lubricating oil, although the preferred blend is 90 parts by weight of mineral lubricating oil to 10 parts by weight of the sulfurized material.

Although a wide range of lubricating oils may be employed as the base for the improved lubricant composition, in general the base oil comprises an oil having a viscosity at 100° F. in the range of about 100 seconds at 100° F. to 200 seconds at 210° F., an A. P. I. gravity of 20 to 28, and a flash point above 300° F. The polymer may have a viscosity between 500 and 10,000 at 100° F. and a viscosity of 8,000 at that temperature is preferred.

The invention will be more specifically understood by the following illustrative examples:

#### EXAMPLE I

200 parts of polymer (diene number 24.8) were mixed with 20 parts of flowers of sulfur, all parts by weight, placed in a kettle equipped with a stirrer and heated while stirring to 320° F. After stirring for about 30 minutes, 20 more parts of flowers of sulfur were added, the temperature raised to 330° F. and the stirring was continued at this temperature for an additional 30 minutes. 20 parts of sulfur monochloride were then added, the temperature being maintained at 330° F., and after 20 minutes of continued heating and stir-

ring the material was allowed to cool. After cooling, the material formed a hard resinous mass, containing 27% of sulfur, which was soluble in mineral lubricating oil. 10 parts by weight of the resinous material was then blended with 90 parts by weight of a highly refined Coastal lubricating oil of 40 vis. at 210° F., heating slightly to hasten solution and was found to carry 15 weights gradual loading and 11 weights shock loading on the Almen machine. On standing the blend showed no evidence of stratification or sulfur separation.

#### EXAMPLE II

100 parts of polymer (diene number 24.8) and 15 parts of flowers of sulfur, all parts by weight, were heated and stirred for 3 hours at a temperature of 320-340° F. On cooling the material formed a soft tacky resinous mass containing 15% of sulfur. The resinous mass was readily soluble in petroleum lubricating oil, and the solution showed no sulfur separation after standing. A 10% blend of this resinous material in a 40 vis. Coastal lubricating oil withstood 15 weights gradual loading and 11 weights shock loading on the Almen machine.

The sulfurized bases prepared from the steam cracked polymers herein described may be added to mineral oil with or without the addition of chlorinated products fatty oil phosphorous derivatives, metal soaps, etc. to prepare extreme pressure lubricants, greases, cutting oils and similar products of high load-carrying capacity. The sulfurized polymer oils may also be used in motor and engine crankcase oils to minimize or eliminate corrosion of bearings such as those made from copper-lead, lead-cadmium, silver or cadmium-nickel. In this connection the sulfurized polymers may be employed with amine, phenol, phenolic ether or other effective antioxidants. They may also be employed with metal soaps, metallic derivatives of phenols, alcohols, phenol sulfides, xanthates, mercaptan disulfides, thioethers, phosphorous compounds such as employed as detergents, anti-oxidants and bearing corrosion inhibitors in Diesel and other engine oils.

What is claimed is:

1. The method of making a sulfurized lubricating oil additive which consists in heating a polymer having a viscosity of 500 to 10,000 at 100° F. obtained by the vapor phase clay treatment of steam cracked petroleum distillates with a sulfurizing agent at a temperature between 300°-400° F. for from 30 minutes to 3 hours.

2. The method of making a sulfurized lubricating oil additive which consists in heating a polymer having a viscosity of 8000 at 100° F. obtained by contacting a steam cracked petroleum distillate with Attapulugus clay in the vapor phase at about 400° F. with sulfur at a temperature of 320-340° F. for 3 hours.

JOHN C. ZIMMER.  
ARNOLD J. MORWAY.