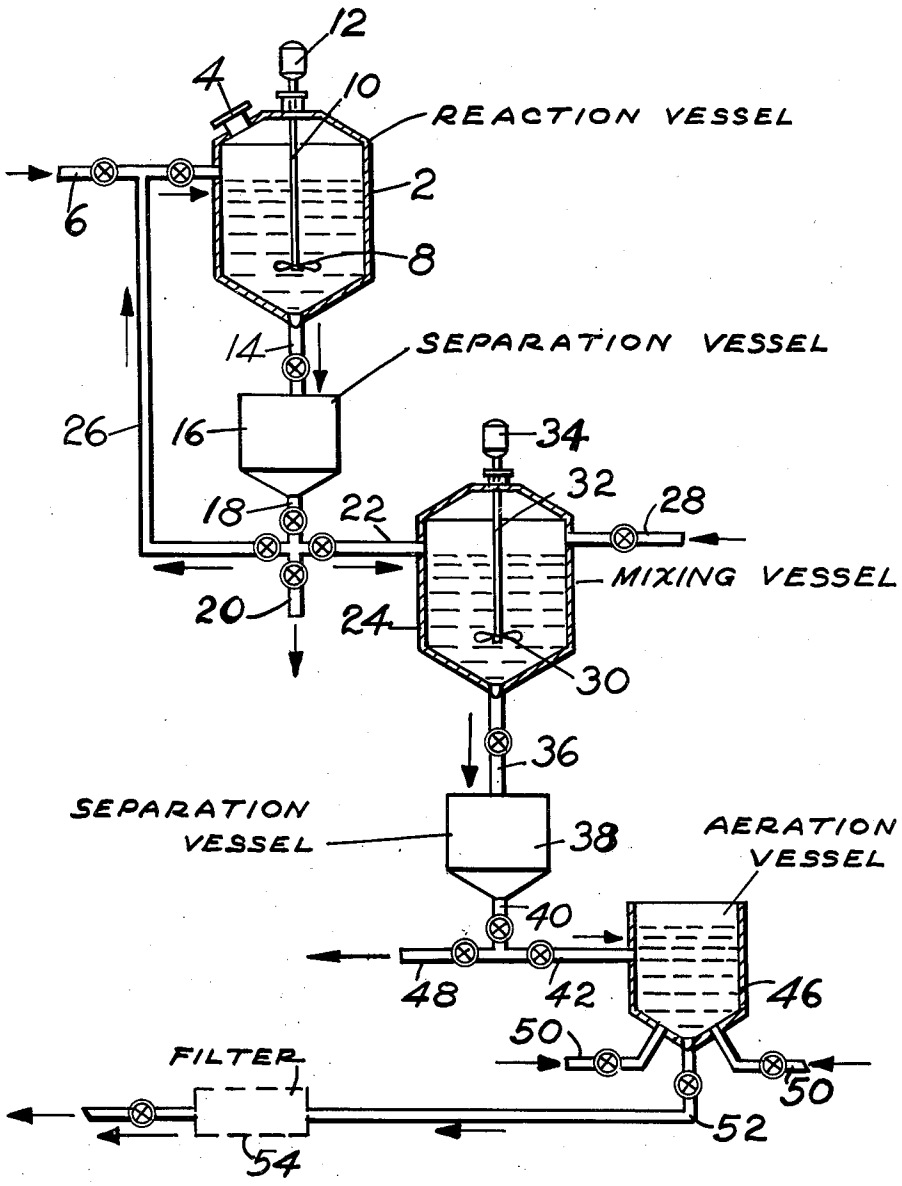
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PROCESS FOR THE FORMATION OF A SULFURIZED HALOGENATED ALIPHATIC HYDROCARBON

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## PROCESS FOR THE FORMATION OF A SULFURIZED HALOGENATED ALIPHATIC HYDROCARBON

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4 Claims. (Cl. 260—139)

1

This invention relates to lubricating oil additives. Particularly, it relates to an improved process for the manufacture of lubricating oil additives which have the characteristic of imparting desirable qualities to lubricating oils with which they are blended. More particularly, the invention relates to an improved process for the preparation of sulfurized halogenated aliphatic materials.

In U. S. Patent 2,124,598 issued July 26, 1938, there is disclosed a lubricating oil additive which is made by incorporating sulfur into halogenated aliphatic compounds. The additive materials disclosed in this patent have the desirable characteristics of imparting to a lubricating oil blend containing them resistance to extreme pressures under high rates of shear.

These lubricating oil additive materials have been made heretofore by combining with the desired halogenated aliphatic material, such as high molecular weight hydrocarbons, sulfur in the form of sodium hydrosulfide, elemental sulfur and the like. In general, the process has involved dissolving the halogenated material in a solvent such as an alcohol and admixing the sulfur-containing material therewith. After the desired period of time has elapsed and the sulfurization has reached the desired stage, the mixture is allowed to separate into its component layers by gravity separation. The top layer, being composed of the major proportion of the solvent, is withdrawn and recycled for reuse in the process. The bottom, or brine layer, is withdrawn and may be discarded, or approximately 10% of the alcohol is recovered by distillation.

The middle or product layer which contains the sulfurized halogenated hydrocarbon material also contains entrained or dissolved therein a minor proportion of the solvent along with extraneous matter such as reaction sludge, sediment and so forth. This entrained or dissolved solvent has normally been removed by a process of vacuum "stripping." Temperatures in the neighborhood of 200° F. to 255° F. are used at a vacuum of about 18 to 26 inches of mercury.

After the stripping step is completed and the entrained solvent has been removed the product is then passed through a filtering medium for removal of any extraneous material.

One of the major disadvantages of this process lies in the vacuum stripping step. In addition to being time consuming and requiring the utilization of expensive vacuum equipment, it has been found that the product after having been subjected to the stripping temperatures required for an extended period of time deteriorates slightly in its ability to impart the above mentioned desirable characteristics to the lubricating oil. Also the vacuum stripping has been done in the reactor vessel itself, thus tying up the vessel for an undesirably long period of time.

2

In the improved process which is the subject of this invention the above mentioned disadvantages are eliminated. The vacuum distillation step is completely done away with and substituted therefor is a process for the separation of the entrained or entrapped solvent by a simple selective solvation process. In this new procedure the product layer referred to above, that is, that layer containing the sulfurized halogenated hydrocarbon along with a minor amount of entrained solvent is admixed with a liquid in which the solvent used is soluble but in which the product is not soluble. It is to be understood, of course, that the particular liquid chosen will depend upon the particular solvent used in the reaction stage of the process. When the solvent used is an alcohol such as isopropyl alcohol the solubilizing liquid may be water.

The mixture of the product layer and the added liquid is agitated for a period of time sufficient to completely dissolve the solvent in the liquid and the mixture is then allowed to separate using a simple gravity separation. The top layer, which ordinarily will contain the dissolved solvent, is withdrawn and the bottom layer which contains the product, free from all but traces of entrained solvent, is airblown to remove traces of solubilizing liquid and solvent and is then passed through a filter medium for the removal of extraneous materials. If desired, a filtering agent such as diatomaceous earth may be added prior to the filtering step.

In the drawing there is illustrated an apparatus suitable for carrying out one embodiment of the invention. It is to be realized, of course, that the apparatus as shown is not limiting in any respect since other means of carrying out the process of this invention will be evident to those skilled in the art. In this particular embodiment a mixture of chlorinated wax and chlorinated kerosene is sulfurized using elemental sulfur and sodium hydrosulfide. Isopropyl alcohol is used as a solvent for the wax-kerosene mixture. The amounts of these constituents used will depend upon the product desired.

Referring now to the drawing, numeral 2 represents a reaction vessel suitable for carrying out the sulfurization of the halogenated hydrocarbon material. Through an opening such as port 4 the halogenated chlorowax-chloro kerosene mixture is added. However, any of the various chlorinated hydrocarbons such as chlorinated wax, chlorinated petrolatum, chlorinated kerosene, or mixtures of the above in any desired proportion may be added to the reaction vessel at this point. Also through port 4 the sulfurizing agent, elemental sulfur and sodium hydrosulfide is added. Sodium sulfide, or any of the polysulfides may be added to the reaction vessel at this point when it is desired to use these in-

gredients. Through valved line 6 the desired amount of isopropyl alcohol is added to the mixture in the reactor. Any of the lower alcohols, isopropyl alcohol usually being preferred, may be used.

The mixture in the reaction vessel is agitated for the desired period of time, usually 2 to 6 hours at reflux temperature, by means of an agitation device such as propeller 8 which is driven by shaft 10 and an electric motor 12. Suitable heating means such as a steam coil, not shown, may be used to raise the temperature of the ingredients in the reaction vessel to the desired level. Preferred temperatures will be within a range of from 160° F. to 180° F.

When the reaction between the sulfur compound and the halogenated hydrocarbon has proceeded to the desired point, the agitation is suspended and the contents of the reaction vessel are withdrawn through valved line 14 into a separation vessel 16. Here the mixture is allowed to separate by gravity separation. This usually requires from 15 minutes to 2 hours depending upon the constituents of the mixture. In the preferred embodiment, this separation will occur within from 15 minutes to 1 hour.

Three layers are formed on standing in separation vessel 16. The bottom layer which contains any of the excess sodium salt and any unused sulfur is withdrawn from vessel 16 through valved lines 18 and 20. Ordinarily this material is discarded. The middle or product layer which contains the sulfurized halogenated hydrocarbon material and a certain amount of the alcohol entrapped or dissolved is withdrawn through valved line 18 and introduced through valved line 22 into mixing vessel 24. The top layer, which contains the major proportion of the alcohol used is withdrawn through valved line 18 and recycled through valved line 26 for reuse in the reaction vessel.

To the product in mixing vessel 24 there is added through valved line 28 the desired amount of water. In other embodiments any liquid which will dissolve the entrained or entrapped solvent from the product may be used. A sufficient quantity of this liquid is added to insure that all of the entrained solvent will be dissolved.

By means of a suitable mixing device, such as propeller 30 driven by shaft 32 and electric motor 34, the desired amount of agitation is obtained. The temperature desired in mixing vessel may be obtained by means of a suitable heating device, such as a steam coil, not shown. Preferred temperatures are those between 70° F. and 150° F.

The mixture of water and product is agitated to insure complete solubilization of the alcohol which ordinarily will take from 15 minutes to 3 hours, depending upon type of agitation.

After the mixing is completed the contents of mixing vessel 24 are withdrawn through valved line 36 into separation vessel 38. Here gravity separation is allowed to occur again. The product layer freed from substantially all of the entrained solvent is removed through valved lines 40 and 42 and introduced into aeration vessel 46. The water layer containing dissolved therein substantially all of the alcohol which was entrapped by the product layer is removed through valved lines 40 and 48.

In aeration vessel 46 the product, which may contain a minor amount of entrapped water-alcohol mixture is blown with air which is introduced into the bottom of the aeration vessel through valved lines 50. The blowing with the air removes any of the entrapped liquid leaving the product free and clear except for minor amounts of extraneous materials such as reaction sludge, sediments, and the like.

The product is then withdrawn from aeration vessel 46 through valved line 52 and introduced into a filtering device as shown at 54. This filtering device may be any of the various filters known to the art such as a plate and frame press, and the like. If it is desired a filter aid such as diatomaceous earth may be added to the product in the aeration vessel to aid in the filtering operation.

This invention will be more completely described and more clearly explained by a reference to the following examples.

A mixture of 60 parts of chlorinated kerosene (41.0% chlorine) and 40 parts of chlorinated wax (34% chlorine based on 100 pts.) was reacted with 3.2 parts of elemental sulfur and 58.5 parts of 25% aqueous sodium hydrosulfide in the presence of 105 parts of isopropyl alcohol as a solvent. After 3 hours at 176° F. the reaction mixture was allowed to separate into three layers.

Four 500 milliliter portions of the middle or product layer were taken. One portion was subjected to a vacuum distillation step. The distillation was carried out at a temperature between 215° F. and 220° F. for one half hour at 26 inches of mercury. An inspection of the product after the distillation was completed showed that it was free of alcohol. This sample was labeled Example IV.

The remaining three portions of the product, Examples I, II and III, were each agitated with 125 milliliters of water until the alcohol was completely dissolved. The mixtures were then allowed to separate and the product layers withdrawn from the water layers. The separated product layers were then blown with air to remove any residual water-alcohol solution.

The temperatures of the water washing and air blowing steps with the settling time and the blowing time are given in Table I below:

TABLE I

| Example | Water Washing | | Air Blowing | |
|---|---|---|---|---|
| | Temp. | Settling Time | Temp. | Time |
| | ° F. | hrs. | ° F. | hrs. |
| I | 70 | 3 | 70 | 2½ |
| II | 100 | 3 | 100 | 2½ |
| III | 125 | 3 | 125 | 2½ |

The four examples treated as detailed above were then tested for per cent chlorine, per cent sulfur and viscosity at 210° F. Results are shown in Table II below:

TABLE II

*Inspection test data*

| Example | Percent Chlorine | Percent Sulfur | Percent Gravity | Viscosity (S. U. S. at 210° F.) |
|---|---|---|---|---|
| I | 30.5 | 5.9 | 17.9 | 61.0 |
| II | 30.6 | 5.9 | 17.9 | 61.2 |
| III | 30.6 | 6.0 | 18.0 | 61.2 |
| IV [1] | 33.5 | 5.8 | 17.8 | 61.7 |

[1] This sample of product was vacuum distilled at a temperature of 215°-220° F. for one-half under 26 inches of mercury to remove excess isopropyl alcohol.

The data in Table II above shows that there is no differentiation in the final products of the two processes as regards to the per cent chlorine, per cent sulfur, and viscosity at 210° F., all tests agreeing within experimental error.

The materials of Examples I through IV were then tested as to their solubility in different base oils. In all cases 10% by weight of the material was blended with the test oil. The results of these solubility tests are shown in Table III:

TABLE III

*Solubility tests (10% blend of material in test oils)*

| Example | Oil A [1] (100° F.) | | Oil B [2] (100° F.) | |
|---|---|---|---|---|
| | after 1 hr. | after 24 hrs. | after 1 hr. | after 24 hrs. |
| I | clear | cloud | clear | clear. |
| II | do | do | do | Do. |
| III | sl. cloud | do | do | Do. |
| IV [3] | cloud | do | do | Do. |

[1] Oil A=a paraffinic aviation oil having a viscosity at 210° F. of 76-84 S. U. S. and a viscosity index of 100.

[2] Oil B=50% of a propane deasphalted phenol treated residuum from Panhandle Crude having a viscosity of 210° F. of 160-170 S. U. S. and a viscosity index of 90 with 50% of a treated and filtered paraffinic distillate having a viscosity at 100° F. of 285-295 S. U. S. and a viscosity index of 72.

[3] This sample of product was vacuum distilled at a temperature of 215°-220° F. for one-half hour under 26 inches of mercury to remove excess isopropyl alcohol.

That the additive material manufactured according to the process of this invention is equally potent with that material made by the old process is conclusively pointed out by the data given in Table IV.

10% by weight of the product was blended with test Oil C and was subjected to the tests as reported below:

TABLE IV

*Inspection tests (10% of material blended in Oil C)* [1]

| Example | Copper Strip Corrosion (after 1 hr. at) | | SAE Machine (Scale Pounds) | Evaporation Loss (100 hrs. at 300° F.) | Viscosity Loss (S. U. S.) (100 hrs. at 300° F.) |
|---|---|---|---|---|---|
| | 212° F. | 300° F. | | | |
| | | | | *percent* | |
| I | Pass | Pass | 340 | 2.5 | 14.0 |
| IV [2] | do | do | 332 | 1.7 | 12.8 |

[1] Oil C=69% of a steam refined cylinder stock from a Pennsylvania Crude having a viscosity at 210° F. of 210-225 S. U. S. with 31% of a treated paraffin distillate having a viscosity at 210° F. of 285-295 S. U. S. and a viscosity index of 72.

[2] This sample of product was vacuum distilled at a temperature of 215°-220° F. for one-half hour under 26 inches of mercury to remove excess isopropyl alcohol.

To summarize briefly, this invention involves an improved process for the formation of sulfurized halogenated hydrocarbon materials. In the process an expensive time-consuming vacuum stripping step is eliminated and substituted therefor is a simple procedure for accomplishing the same end, that is, removing any entrained solvent by dissolving the entrained solvent with a liquid in which it is soluble, separating the liquid-solvent mixture, and removing any minor amount of the liquid from the product by blowing with air.



What is claimed is:

1. A process for the formation of a sulfurized halogenated aliphatic hydrocarbon which comprises subjecting a mixture of chlorinated wax and chlorinated kerosene to the action of elemental sulfur and sodium hydrosulfide in the presence of an alcohol as a solvent in a reaction zone, allowing the reaction to proceed for the desired period of time, permitting the reaction mixture to separate into three layers, discarding the bottom brine layer, recycling the top alcohol layer to the reaction, removing the middle product layer to a mixing zone and adding thereto water, mixing said product and said added water for until the alcohol entrained with said product is dissolved, allowing said mixture to separate into two layers, a top layer and a bottom product layer, removing the top layer from said mixing zone, removing the bottom product layer to a second mixing zone, blowing the removed product layer with a gas to remove any residual solubilizing agent and solvent, removing the blown product to a filtering zone, and filtering said product to remove extraneous material.

2. A process according to claim 1 wherein the solvent used is isopropyl alcohol.

3. A process according to claim 1 where the gas used is air.

4. A process for the formation of a sulfurized halogenated aliphatic hydrocarbon having the characteristic of imparting desirable extreme pressure resisting properties to a lubricating oil with which it is blended which comprises subjecting a mixture of chlorinated wax and chlorinated kerosene to the action of elemental sulfur and sodium hydrosulfide for from 2 to 6 hours in a reaction zone heated to a temperature of from 160° F. to 180° F. in the presence of isopropyl alcohol as a solvent, withdrawing the product into a settling zone, allowing the product to separate into three layers, discarding the bottom brine layer, recycling the top alcohol layer to the reaction zone, removing the middle product layer to a mixing zone and adding thereto 5 to 25 parts of water, raising the temperature of said mixing zone to one within the range of from 70° F. to 150° F., agitating the product in said mixing zone for from ¼ to 3 hours, withdrawing the mixture into a second separation zone, allowing the mixture to separate into two layers, a top water-alcohol layer and a bottom product layer, withdrawing said top water-alcohol layer from said separation zone, introducing said bottom product layer into a separate mixing zone, blowing said product in said second mixing zone with air heated to a temperature within a range of from room temperature to 200° F. for from 1 to 5 hours in said second mixing zone to remove any residual water, removing the blown product to a filtering zone, and filtering said blown product to remove extraneous material.

NICHOLAS M. SCHNEIDER.
RAYMOND M. DEAN.

## REFERENCES CITED

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

UNITED STATES PATENTS


| Number | Name | Date |
|---|---|---|
| 2,124,598 | Turner | July 26, 1938 |
| 2,192,700 | Turner | July 26, 1938 |