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PROCESS FOR PREPARING SYNTHETIC OILS

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The present invention relates to the production of valuable lubricating oils, especially oils of low pour point and to methods for producing such products. Our invention will be fully understood from the following description of the products and their method of manufacture:

Lubricating oils obtained from petroleum and especially the higher grade lubricating oils contain waxy constituents and in consequence thereof are characterized by high pour points, that is to say, they become solid at relatively elevated temperatures, for example 30 or 40° F. or even 50 or 75° F., depending on the amount of wax present. It is the practice of refiners to remove a part or the whole of the wax so as to cause the oil to remain liquid to considerably lower temperatures, for example to 10° F. or even to 0 or lower, but this is an expensive operation and besides the wax is a desirable addition agent to the oil so that it is preferred not to remove it.

We have discovered a class of substances which when added to hydrocarbon oils improve their properties and when added to wax-containing oils even in small amounts cause the wax to crystallize in such a manner that the oil will remain fluid, and will pour at temperatures considerably below the normal pour points.

The substances which we have prepared are polymers of high molecular weight, soluble in oil and which do not undesirably affect the other properties of the oil. The polymers of a particular type produced in a special manner from certain raw materials form the basis of the present invention.

The raw materials are contained in the general class of organic materials which have relatively long straight hydrocarbon chains of, for example, 10 or 12 carbon atoms or more. They may be hydrocarbons and of these the hydrocarbons contained in paraffin wax are desirable since they are characterized by substantially straight chains. The normally liquid oils containing more than 10 or 12 carbon atoms are sometimes characterized by a marked branchy and/or cyclic structure and if so are undesirable for the present purposes.

It is not, however, necessary that the chains be fully saturated. Paraffin waxes are, indeed, the most satisfactory and they are generally fully saturated, but olefins of more than 10 carbon atoms arranged in a relatively long straight chain are equally desirable. The waxes are most desirable because of their cheapness, avail-

ability and the purity at which they may be obtained.

Hydrocarbons are not the only source of these desirable polymers and, in fact, they may be produced from any compounds selected from the class of the alcohols, esters, ethers, acids, ketones and the like which contain hydrocarbon groups of at least 10 carbon atoms in substantially straight chains. For example, stearic acid or its esters such as the methyl, ethyl or propyl steirates or oleic acid and its esters may be used; the alcohols above decyl, the corresponding aldehydes and ethers of such alcohols and related substances such as the ketones are also available. While we prefer the naturally occurring acids or esters because of their cheapness, materials produced synthetically or, which may be mixtures of many different compounds, or of compounds of the same type but of different number of carbon atoms, may be used with good results.

The method by which the above enumerated substances are treated to produce suitable polymers consists in the application thereto of high tension electric discharges. The process is carried out in the known manner under reduced pressure preferably below about 100 mm. absolute pressure but more elevated pressures about to atmospheric, say 650 mm. may be used, and provision is made for continuously maintaining this reduced pressure. An alternating current of 60 cycles per second, for example, may be used but it is far more desirable to have greater frequencies, say 10,000, 15,000 or even much higher. High voltages are also necessary, say 10,000 to 15,000 or higher, depending on the film of oil through which the current is to pass.

Any suitable apparatus as indicated above can be used for our purpose; and many types are well known. The temperature of the material should be sufficient to keep it in a fluid state and it may be caused to flow in a thin film over the electrodes or, to splash, foam or squirt over them in such a way as to subject the oil in thin films to the action of the high tension discharge. The electrodes may be placed in parallel, or in the form of plates which may be alternately dipped into and withdrawn from a bath of the material, or, they may be in the form of concentrically placed tubes or drums arranged in a horizontal direction and rocked about the horizontal axis through say 100 to 120 degrees or slowly rotated and in this way the oily material which may occupy something less than one-half of the annular space between the electrodes is

washed up over the inner and the outer tube in such a way as to leave a film exposed to the current. If desired, a small amount of gas, for instance nitrogen or hydrogen may be bubbled through the material undergoing treatment causing it to splash or foam. If desired, concentric electrodes may be used and rapidly rotated so as to cause the film of oil to form on the outer electrode where it is thrown by centrifugal force.

In small scale equipment it has been found desirable to continuously add heat to the material either by jacketing the vessel or by withdrawing a portion thereof, heating it, and returning it to the vessel so as to maintain the wax or other solid material in a freely flowing liquid state. If the oil is naturally liquid ordinary temperatures are permissible, but even in that case slightly elevated temperatures from, say 100° to 500° F. or more, are desirable to keep the polymer in a state of reduced viscosity. In larger scale equipment where radiation losses are necessarily lower, less heat is required but it is ordinarily desirable in any case to provide thermostatic jackets so as to keep the conditions substantially the same during the treatment.

The polymers which we desire to form have molecular weights well in excess of 600 and substances as high as 1000 to 2000 and perhaps higher have been found in the product. The lower polymers apparently do not possess the desired pour depressing properties but it is extremely difficult to separate fractions closely and to state with exactitude at just what point this action begins. It may be stated, however, that unpolymerized fractions of the original material, for example of paraffin wax may be removed from the heavier polymers by distillation and that the vaporized material generally possesses no pour inhibiting properties or, in any case, it is very weak and that the bottoms or residue concentrates the valuable or active material. The lighter fractions may be returned for retreatment in the same or in a successive treatment. The distillation should be conducted with fire and steam or with vacuum, and care should be taken to remove the lighter fractions without any substantial cracking of the residue.

While the "paraffinic material" by which we mean material containing relatively long hydrocarbon chains, whether the compound be a hydrocarbon or whether containing oxygen, may be used alone, it is permissible to add thereto a substance of a cyclic structure such as benzol or naphthalene, their hydrogenated or alkylated derivatives such as toluol, xylol and ethyl naphthalene. Hydroxylated aromatics such as the phenols and naphthols may be used for this purpose as well as the nitrated aromatics or the amino derivatives of the type of aniline, naphthylamine and the like. Even cyclic terpenes may be used. These materials are added in proportion of, say 10 to 14 or 20% of the paraffinic material and the condensation takes place in substantially the same manner as indicated above, but it is clear that the aromatic or cyclic material actually takes place in the combination.

The time of treatment varies according to the power input and consequently if that is low a time of, say 100 or 150 hours may be required, whereas if it is higher the work may be accomplished in 50 or 25 hours or even in less time. The amount of material to be used for our purposes may be generally described as in pour inhibiting proportions. If too much of the ma-

terial is used the pour inhibiting effect tends to diminish so that there is a decided optimum for pour depressing. The actual amount to be used, of course, also depends on the concentration of the active substance in the oily polymers. Ordinarily, if a good grade of polymer is produced 1% is sufficient, but in some instances as little as .1 to .5% may be sufficient, and in other cases 2 to 5% may be required. It is desirable, as indicated above, to concentrate the inhibitor to some extent and this is preferably done by distilling off the lower readily distillable fractions, for example, by vacuum distillation or by other suitable means. Where the agent is well concentrated the pour inhibiting effect may be obtained without substantial increase in viscosity.

As an example of the operation of the present process a good grade of paraffin wax having a melting point of 122° F. is subjected to an alternating current of 60 cycles, 13,000 volts, for a period of 150 hours. Temperature was carefully controlled at about 140° F. and a pressure of 15 mm. was maintained by means of a vacuum pump. The treating vessel consisted of a horizontally placed, jacketed tube of glass. Concentric therein is placed a small aluminum tube fitted with holes and in communication with the vacuum pump. The two tubes are carefully insulated from each other, and the melted paraffin wax is placed in the glass tube so as to just reach the level of the inner aluminum tube. These tubes are then rocked back and forth slowly on the central axis through an arc of about 130 degrees. The outer glass tube comprises one of the electrodes while the aluminum tube comprises the other.

After about 150 hours the reaction product is removed and it is topped under vacuum to remove the unchanged wax or, at least the greater portion thereof, together with lower polymers. The residual liquid comprising 53% of the original wax is an oily material with the following inspection:

Gravity-----	31.8° A. P. I.	
Viscosity-----	3800 seconds Saybolt at 100° F.	
Viscosity-----	349 seconds Saybolt at 210° F.	
Flash-----	600° F.	
Pour-----	70° F.	
Color-----	1½ Robinson	
Carbon-----	.65%	

When this material is added in concentration of 1% to an oil of about 50 seconds Saybolt viscosity at 210° F. and having the normal pour point of 30° F., it is observed that the oil will pour at temperatures down to 5° F. There is no substantial change in the other properties of the oil except for a slight increase in viscosity.

In another experiment the paraffin wax was treated in an ozonizer of the usual form for 48 hours. The temperature was slightly above the melting point of the wax and a pressure of about 100 mm. was maintained. An electric current alternating at a rate of 2,000 cycles per second was used and the potential difference between the two electrodes was about 10,000 volts. When the reaction product was withdrawn it was found that about 30% of the wax was unreacted and could be removed from the heavy oil by distillation. The remaining product had a viscosity of 1500 seconds Saybolt at 210° F. and when added in the proportion of 1% to the oil of the type used in Example 1 with a normal pour point of 35° F., it was found to be depressed to -15° F.

While it is preferred to electrically treat wax

which has been separated from an oil, the wax can be polymerized while dissolved in a suitable oil stock such as a lubricating oil or a hydrogenated lubricating oil. The oil in such case is polymerized to some extent as will be appreciated and the product although rich in wax has a low pour point due to the presence of the inhibitor produced in situ. This product can be used as an inhibitor and added to other oils such as natural waxy oils or to hydrogenated or synthetic oils, or may be used as a lubricant as such.

This application is a continuation-in-part of application Serial No. 623,814, filed July 21, 1932.

Our invention is not to be limited by any theory of the mechanism of electrical condensation, nor of pour reduction, but only to the following claims in which we wish to claim all novelty inherent in the invention.

We claim:

1. Process for preparing improved polymerization and condensation products of high molecular weight, soluble in lubricating oils and having the characteristic of lowering the pour point of waxy lubricating oils when added thereto in small amounts, comprising subjecting a mixture consisting essentially of paraffine wax and about 10% to 20% of an aromatic compound, in liquid phase, to an electric glow discharge of an intensity and for a period sufficient to effect substantial copolymerization of the paraffine wax and the aromatic compound.

2. Process according to claim 1 in which the said mixture contains about 10 to 20% of naphthalene.

3. Process according to claim 1 in which the

said mixture contains about 10 to 20% of a phenol.

4. Process according to claim 1, in which the said aromatic compound comprises an amine.

5. Process for preparing improved polymerization and condensation products of high molecular weight, soluble in lubricating oils, and having the characteristic of improving lubricating oils when added thereto in small amounts, comprising subjecting a mixture consisting essentially of a saturated aliphatic compound having at least 10 carbon atoms in a straight chain and of a hydroxy aromatic compound admixed in a proportion of at least about 10% of said saturated aliphatic compound, in liquid phase, to a silent electric discharge of an intensity and for a period sufficient to effect substantial copolymerization of the saturated aliphatic compound and the hydroxy aromatic compound.

6. Process for electrically polymerizing an aromatic compound to a product of high molecular weight and soluble in lubricating oils which comprises subjecting the aromatic compound admixed with paraffinic hydrocarbons containing at least 10 carbon atoms per molecule the said mixture containing the said aromatic compound in a proportion of at least about 10% of said paraffinic hydrocarbons, in liquid phase, to silent electric discharges of an intensity and for a period sufficient to effect substantial copolymerization of aromatic and paraffinic hydrocarbon molecules.

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