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PROCESS FOR MANUFACTURE OF
IMPROVED LUBRICATING OILSRobert W. Henry, Bartlesville, Okla., assignor to
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This invention relates to lubricating oil and more particularly to a process of making an improved lubricating oil.

It has long been known that the presence of sulfur in some forms in lubricating oils is beneficial in reducing wear, reducing oxidation in the presence of metals by inhibiting the catalytic action of such metals, and in reducing corrosion, especially corrosion of certain bearing metal alloys such as copper-lead, cadmium-silver, cadmium-nickel, etc. However, lubricating oil distillates from high sulfur bearing crude oils ordinarily are of the low viscosity index, so-called naphthenic, type which are relatively unsuited to many high duty engine services. The industry has attempted to manufacture high viscosity index oils from such naphthenic or coastal type distillates, as by solvent extraction, but in such case excessive extraction is necessary with consequent very low yields and high cost, and the resulting oils exhibit undesirable properties due to the excessive extraction. These undesirable properties include lack of stability to oxidation, lack of desired film strength, and tendency to corrosiveness, due to removal, in the excessive extraction, of natural inhibitors to oxidation and corrosion, and of components contributing to high film strength. These desirable inhibiting and high film strength components which are removed to an objectionable degree by the excessiveness required in the extraction in order to give the desired increase in viscosity index may or may not be of the sulfur bearing type.

Also, attempts have been made to secure the advantages of presence of certain sulfur compounds in lubricating oils by heating the finished refined oils with elemental sulfur whereby a very little sulfur goes into permanent solution and a larger amount reacts chemically with the oil, the resulting compounds being soluble in the oil. In this chemical reaction, numerous diverse and complex sulfur compounds tend to form in the lubricant, with formation and evolution of hydrogen sulfide. Control of this reaction to give a uniform product having the desired properties without also adding deleterious properties has been found to be impossible, and the product contains undesirable sulfur compounds in an excessive amount.

Another method of securing the desirable properties accompanying the presence of certain sulfur compounds is to add a synthetic organic sulfur compound to the refined lubricating oil. This method involves the objections that the cost of such desirable synthetic sulfur compounds is ex-

cessively high and moreover the results are not entirely satisfactory.

The principal object of the present invention is to provide a process enabling attainment of the advantages of sulfur containing lubricating oil of high viscosity index without the presence of deleterious sulfur compounds and decomposition products.

Another object is to provide a novel process of preparing an improved lubricating oil from a high viscosity index mixed base lubricating oil stock of extremely low sulfur content.

Another object is to prepare a lubricating oil of improved characteristics from an Oklahoma City type lubricating oil stock.

Another object is to prepare an improved sulfur-containing lubricating oil in improved yield from a mixed base stock.

Another object is to provide a process of introducing sulfur in desirable combined form into a mixed base crude in an extremely efficient manner involving a minimum loss of sulfur in the form of hydrogen sulfide and in the form of undesirable sulfur compounds which must be removed from the oil and disposed of.

Numerous other objects will hereinafter appear.

In proceeding in accordance with my invention, I may add sulfur to an unrefined lubricating oil stock of high viscosity index, i. e., at least 75, but of low sulfur content, i. e., not more than 0.3 per cent by weight of sulfur, by mixing with the unrefined oil elemental sulfur and mildly heating. The heating is controlled so as to put all or substantially all of the added sulfur, amounting to from about 0.5 per cent to about 4.0 per cent by weight of sulfur based on the weight of the stock, into the raw oil in combined form without excessive formation of deleterious products and without evolution of hydrogen sulfide or appreciable formation thereof. To this end the temperature should be at least 200° F. and less than 250° F., a temperature of 240° F. being preferred. The combination of the oil stock and the sulfur may be in a separate step, or in conjunction with a step in the usual refining process, for example in a pipe-coil heater preliminary to solvent extraction.

The resulting raw stock containing the combined sulfur is then refined by solvent extraction. It has been found that the commercial selective extraction solvents, such as phenol, cresol, furfural, beta dichloroethyl ether, nitrobenzene, aniline, liquid sulfur dioxide preferably in conjunction with benzene, etc., remove only the deleterious sulfur compounds, together with any de-

composition products, along with the components which would normally be removed by such solvents when applied to the unrefined oil stock which had not been treated with sulfur in the manner just described. The solvent extraction leaves the desirable sulfur compounds in the raffinate oil.

Thus a high viscosity index lubricating oil having the advantages of desired sulfur content without the disadvantages of the presence of undesirable unstable, complex sulfur compound of the more reactive type, is formed.

Preferably the solvent used in the extraction step of my process is polar, since it has been found that extraction with a polar solvent removes the more polar sulfur compounds, leaving in the raffinate the relatively non-polar sulfur compound. Examples of the more polar solvents which are preferred are phenol, cresol, furfural, nitrobenzene, aniline, liquid sulfur dioxide, nitromethane, and the like. While the exact composition and structural configuration of the desirable sulfur compounds introduced into the stock by my process is not known, they are known to be relatively non-polar and are believed to be of the sulfur-in-the-ring type with long paraffin chains also attached to the ring. These compounds impart to the refined oil the properties of high film strength, increased stability to oxidation, and decreased corrosive tendency.

My invention is particularly applicable to lubricating oil stock typified by that derived from Oklahoma City crude oil. Such unrefined stock has a viscosity index of 75-80 and a sulfur content of from 0.2 per cent to 0.3 per cent by weight. However my invention is also applicable to unrefined stocks of even higher V. I. and even lower sulfur content such as stocks derived from Pennsylvania crude, which are greatly benefited by treatment in accordance with the present invention. In general unrefined stocks from Pennsylvania crude have a V. I. of at least 100 and a sulfur content of less than 0.05 per cent.

By employing a low temperature in effecting reaction with the sulfur, my process avoids the formation of objectionable hydrogen sulfide which involves inefficient utilization of sulfur and interferes with the subsequent selective solvent extraction. Use of a low temperature also makes my process economical and prevents undue decomposition and side reactions.

My process enables a very efficient utilization of the added sulfur, allowing at least 80 per cent and generally more of the added sulfur to remain in the finished oil in the form of desirable sulfur compounds. In other words, the deleterious sulfur compounds removable in the solvent refining step are not formed in the heating step in amount corresponding to more than about 20 per cent of the added sulfur. Thus it is not necessary to employ an excess of sulfur, although such an excess may of course be initially added if it be desired, the unreacted sulfur being removed either by settling and filtration, centrifuging, or the like after the heating step, or by the solvent used in the extraction step. The use of from about 0.625 per cent to about 5.0 per cent of initially added sulfur, with complete combination, and with 20 per cent removal in the extraction step, or 80 per cent utilization, introduces the desired 0.5 to 4.0 per cent into the oil.

In addition to effecting improved utilization of sulfur, my process enables the attainment of a very high yield of refined oil based on the original stock. This yield may be above 90 per cent

and frequently above 95 per cent by volume based on the volume of the original deasphalted, dewaxed, but otherwise unrefined, stock. The possibility of such high yields may be attributed to the very high V. I. of the original stock, to the relatively high percentage of desirable sulfur compounds formed in the process, and to the flexibility of control of the process. If desired, however, the process may be so carried out that lower yields are obtained, higher yields being sacrificed for other considerations. It will of course be understood that the actual yield will additionally depend upon a variety of controllable factors in the solvent extraction step, among which are the solvent employed, ratio of solvent to the reaction product from the heating step, temperature of extraction, length of contact, mode of effecting extraction, etc.

Example

A deasphalted dewaxed Oklahoma City lubricating oil stock having a V. I. of 80 and a sulfur content of 0.27 per cent was admixed with 1 per cent of its weight of sulfur. The mixture was heated to 240° F. for three hours when all of the sulfur had combined with the oil. The treated stock was then cooled to 140° F. and extracted in a continuous countercurrent tower with 300 per cent by volume of furfural. The raffinate had a viscosity index of 81 and a sulfur content of 0.83 per cent. It exhibited much higher film strength, resistance to oxidation, and freedom from corrosiveness than the untreated raw stock solvent extracted in the same manner. The yield of the raffinate was 96% based on the volume of the original raw stock.

From the foregoing it will be seen that the process of the present invention provides a convenient and economical method of preparing improved lubricating oil from relatively high viscosity index stock which is very low in natural sulfur and of relatively paraffinic type, i. e., either the more paraffinic of the Mid-Continent stocks or the highly paraffinic Pennsylvania stocks. It will further be seen that the process involves relatively little waste or loss of sulfur, the small amount of sulfur employed serving to very effectively improve the characteristics of the treated oil by simultaneously effecting introduction of desirable sulfur compounds into the oil and the formation and removal of the undesirable sulfur compounds from the oil. Another advantage is the excellent yield of very high quality motor oil made possible by the present invention. Another advantage is the low cost of the process. In addition by eliminating the necessity for employing fatty oils the process effects further economies. Yet other advantages are the elimination of the formation of hydrogen sulfide, and the use of low temperatures in the sulfurizing step. Numerous other advantages will appear to those skilled in the arts.

It will be understood that numerous changes may be made without departing from the spirit of my invention which is to be taken as limited only by the appended claims. For example, the heating step may be conducted under elevated pressures if desired.

I claim:

1. The process of refining a Mid-Continent lubricating oil stock having a viscosity index of at least 75 and a sulfur content below approximately 0.3% by weight which comprises incorporating into the oil stock approximately 0.625% to 5% by weight of elementary sulfur, heating the re-

sulting mixture to a temperature between the approximate limits of 200° to 250° F. for a sufficient length of time as to cause substantially all of the added sulfur to combine with the oil stock without appreciable formation of hydrogen sulfide, and solvent extracting the so treated oil to remove any deleterious sulfur compounds and other undesirable components and leave a refined lubricating oil stock containing sulfur in the form of desirable sulfur compounds and comprising at least 95% by volume of the original oil stock, the extract containing not more than 20% of the added sulfur in the form of said deleterious sulfur compounds.

2. The process of refining an Oklahoma City unrefined lubricating oil stock having a viscosity index of at least 75 and a sulfur content below approximately 0.3% by weight which comprises

incorporating into said oil stock approximately 0.625% to 5% by weight of elementary sulfur, heating the resulting mixture to a temperature of approximately 240° F. for a sufficient length of time as to cause substantially all of the added sulfur to combine with the oil stock without appreciable formation of hydrogen sulfide, and solvent extracting the so treated oil to remove any deleterious sulfur compounds and other undesirable components and leave a refined lubricating oil stock containing sulfur in the form of desirable sulfur compounds and comprising at least 95% by volume of the original oil stock, the extract containing not more than 20% of the added sulfur in the form of said deleterious sulfur compounds.

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