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SULPHUR OILS

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This invention relates to methods for making sulphur containing oils. More particularly, the invention is directed to methods for producing sulphurized oils, such as sulphurized pine oil especially adaptable for use as cutting and drawing oil bases.

Manufacture of sulphurized oils such as pine oil and use of the same as cutting and drawing oils have been previously proposed. Prior cutting and drawing oil bases of this general type have been such as to possess relatively low sulphur contents, generally in the neighborhood of around one to three percent sulphur. Furthermore, prior products known to us are unstable, and on standing become cloudy and deposit sulphur, thus lessening the sulphur content of the oil and reducing the compounding value. Attempts have been made to increase the sulphur content of such prior bases, i. e., by decreasing the amount of sulphur separating out of the oil, by subjecting the initial base oil to special treatment. However, in these instances, as far as known, it has not been possible to produce base oils containing as much as 10% sulphur.

One of the principal objects of the present invention is directed to provision of methods for preparing sulphurized oils, such as pine oil, of various relatively high sulphur content which are especially suitable for use as cutting and drawing oil bases and which are miscible in all proportions with other sulphur oil bases, and other mineral, animal and vegetable lubricant oils customarily used in the metal working art to dilute cutting oil bases. Another object of the invention lies in provision of methods for production of stable, heavy, viscous, high flash point oils which are clear and bright, non-corrosive and resist oxidation and do not deposit sulphur on standing.

In carrying out the process of the invention a quantity of a terpene oil, such as pine oil, is heated with variable quantities of elemental sulphur to incorporate sulphur with the oil, and any undissolved or unreacted sulphur is then preferably separated from the resultant mass. Such mass may be conveniently designated as an initial sulphurized oil. In accordance with the present invention it has been found that stable oils of high sulphur content may be produced and the objects of the invention attained by treating an initial sulphurized oil, under conditions hereinafter described, so as to remove sufficient quantity of unreacted or feebly combined terpene oil from the mass to render the oil stable with respect to sulphur deposition. It has been found that uncombined or feebly combined terpene oil may be removed from the mass by distilling the particular initial sulphurized oil at temperature less than that at which any substantial decomposition of such initial sulphurized oil takes place. It is preferred to distill the initial sulphurized oils at temperatures not substantially in excess of about 140° C. It has been found that the unreacted or feebly combined terpene oil may be removed from the initial sulphurized oils in several ways, for example by passing through a body of the oil a hot inert gas or by vacuum distillation. After such treatment, the residual oil left in the treating vessel is a stable oil of high sulphur content and constitutes the product of the process of the invention.

In carrying out the process of the invention in such a way as to produce stabilized oils having maximum sulphur contents, in order to make up an initial unstable sulphurized oil a charge of pine oil is introduced into a suitable heating vessel and a quantity of sulphur, for example not less than about 50% by weight of the oil, is added thereto. To obtain the best results when making stabilized oils of maximum sulphur contents, it is preferred to introduce into the heating vessel an excess of sulphur over that apparently combining with the oil. The mixture of oil and sulphur is then heated for a substantial period of time at temperatures of about or above the boiling temperature of the oil until it appears that no further incorporation of sulphur in the oil takes place. The boiling points of pine oils are understood to vary from about 185° C. to about 223° C. To secure the more desirable degree of incorporation of sulphur with the oil, it is preferred to heat the mass of sulphur and oil at temperatures appreciably above the initial boiling point of the oil. For example, satisfactory incorporation of sulphur with oil may be obtained when heating pine oil having a specific gravity of about 0.95 and an initial boiling point of about 185° C. with about 50% by weight of sulphur at about 210° C. for about 40 minutes. The temperature during the heating operation should preferably not exceed about 250° C. Heating time of around 30–40 minutes is usually satisfactory, although under some circumstances a shorter heating period may be employed or heating may be continued for say an hour. In the example mentioned, at the end of the 40 minute heating period, further incorporation of sulphur with the oil appears to cease. During heating of the mixture, a relatively small amount, say from 5 to 15% depending upon the heating

temperature, of the pine oil is vaporized. The oil thus vaporized is condensed and recovered for use in a subsequent operation. Appreciable quantities of water, say 3–5% of the original pine oil used, are also found in the condensate. Following the heating operation, the resultant mass is allowed to cool preferably to around normal temperatures, to afford opportunity for suspended and unreacted sulphur to settle out. The sulphurized pine oil and the unreacted sulphur are then separated in any suitable way as by decantation or otherwise. When proceeding in accordance with this illustrative example, the initial sulphurized oil recovered at this stage may contain around 28% sulphur by weight.

In the preferred embodiment of the invention, the initial sulphurized oil is stabilized by passing hot inert gas through a body of the oil for a period of time sufficient to effect removal from the oil of substantially all the unreacted or feebly combined terpene oil contained in the mass.

In accordance with the preferred form of this phase of the invention, the initial sulphurized oil product is stabilized by passing through the mass a hot inert gas such as carbon dioxide, steam or nitrogen in quantity and for a period of time sufficient to remove substantially all of the unreacted or feebly combined terpene oil from the mass. It is preferred to subject the initial sulphurized oil to steam distillation to bring about removal of unreacted terpene, and for this purpose steam at temperatures preferably from about 100° C. to about 110° C. is introduced into the initial sulphurized oil by means of any satisfactory apparatus. If desired, steam at temperatures as high as 140° C. may be employed. In this modification of the invention, the distillation or inert gas treatment is continued until the oil in the still is substantially free of pine oil. Three successive overhead fractions showed 0.3%, 3.7%, and 4.9% sulphur respectively, and the sulphurized pine oil was steam distilled at temperature of about 108° C. for about three and a half hours until the last overhead fraction, having the 4.9% sulphur content, had a 26:1 water: oil condensate. The initial overhead fraction containing only 0.3% sulphur represented about 70% of the total oil distillate. The residual oil left in the still represents about 60% by volume of the initial sulphurized oil subjected to treatment, and constitutes the product of the process. In this example, the final oil contained about 43% sulphur by weight. It will be noted this value is substantially in excess of the 28% sulphur contained in the initial sulphurized pine oil. If desired, the stabilized oil may be further brightened by heating to say 60° C. and blowing with air. The vapors generated during the inert gas treatment procedure are condensed and recovered and utilized in a subsequent operation.

The principles of the invention may be applied to production of stabilized sulphurized pine oil having a sulphur content substantially less than in the above example. Such a stabilized oil may be produced by using a smaller amount of elemental sulphur, when making up the initial sulphurized oil, than the oil is capable of combining with and by then distilling the initial oil for such a period of time and to such an extent as to remove not necessarily all but at least a sufficient amount of the unreacted or feebly combined terpene oil to produce a final oil which is stable with respect to sulphur deposition. To illustrate, a pine oil having an initial boiling point of around 185° C. may be heated for about 40 minutes at 210° C. with about 19% by weight of elemental sulphur. During heating of the mixture about 14% by weight of the original pine oil may be vaporized and recovered in a suitable condenser. Following the heating operation, while the resultant mass is homogeneous and to all appearances contains no unreacted sulphur, if desired the mass may be allowed to cool to around normal temperature, and any sulphur incidentally settling out may be separated from the pine oil in any suitable way as by decantation or otherwise. When so proceeding, the initial sulphurized oil recovered at this stage may contain about 19% sulphur by weight. Such initial sulphurized pine oil may be then stabilized by subjecting the same to steam distillation. For this purpose steam at temperatures of about 108° C. may be introduced into the initial sulphurized oil by means of any satisfactory apparatus, and the steam distillation or inert gas treatment may be continued for about 70 minutes. The residual oil left in the still may represent about 64% by volume of the initial sulphurized pine oil subjected to treatment and constitutes the final product. In this example, the final oil is a stable, bright oil which does not deposit sulphur on cooling and standing and may contain about 28% sulphur by weight, may have a viscosity of 528 at 100° F. Saybolt Universal, specific gravity at 60° F. of 1.10, flash point 240° F., fire point 285° F., and a pour point below 15° F. When making a relatively low sulphur stabilized oil as just described, the time interval during which the initial sulphurized oil is subjected to distillation may vary in accordance with the nature of the oil. While it is not necessary to continue distillation until substantially all the unreacted or feebly combined terpene oil has been removed, distillation should be continued until a sufficient amount of the unreacted or feebly combined oil has been removed to render the product stable with respect to sulphur deposition, e. g. so that a sample on being cooled to about 0° C. does not deposit sulphur crystals.

It will be seen therefore that the process of the invention is such as to make possible manufacture of stable sulphurized oils having, within certain limits any desired sulphur content.

As indicated, stabilization of the initial sulphurized oil may be effected by distillation under relatively high vacuum. Such operation may be carried out in any suitable type of still equipped with means to subject the oil undergoing treatment to high vacuum and to remove overhead distillate from the still. Heating of the mass may be brought about by externally heating the still and/or by means of steam injected into the mass in the still. In one example, an initial unstable sulphurized pine oil containing 27.5% sulphur by weight was distilled under a vacuum of about 28.75 inches of mercury, the maximum temperature during distillation being about 137° C. In this example, the overhead distillate amounting to about 35% by weight of the initial sulphurized pine oil contained about 2.8% sulphur. The residual stabilized pine oil left in the still comprised about 60% by weight of the initial sulphurized pine oil and contained about 44.7% sulphur by weight.

The nature of the reactions taking place in the present process, both in the initial heating of the sulphur and pine oil and in the subsequent stabilizing treatment stage, are not completely understood. Since the initial sulphurized oil obtained

after removal of the unreacted sulphur is apparently homogeneous, it appears that all of the oil and sulphur are part of a probably unstable combination. The fact that a large amount of pine oil, containing from little to no sulphur, is recovered as distillate from the stabilizing treatment would seem to indicate that during such treatment unstably combined or unreacted pine oil is separated from the mass. Whatever the reactions involved may be, it will be observed that the sulphur content of the product is higher than that of the initial sulphurized oil before the same is subjected to treatment, which in addition to stabilizing and raising the sulphur content of the oil removes foul smelling and corrosive reaction products such as hydrogen sulphide and other sulphur compounds, and also removes light oils which if present would tend to lower the flash point of the product. The product oils are stable reddish oils, remain bright on standing, and do not deposit elemental sulphur at reduced or room temperatures. The oils show no tendency to oxidize on long standing or exposure to air, and are quite viscous and heavy bodied, and of high flash point. High viscosity of the oil presents the advantage that it is unnecessary to add heavy bodied mineral oil to produce a cutting and drawing oil base of the required viscosity.

The sulphurized oil bases described are miscible in all proportions with other sulphur oils, and with other vegetable, animal and mineral lubricant oils such as are customarily used in the metal working art to dilute cutting oil bases.

The sulphurized pine oil bases described are especially adaptable for blending with sulphur oil bases derived from acid sludge formed by sulphuric acid treatment of petroleum oils. Such acid sludge sulphur oil bases may be obtained for example as follows: Acid sludge may be decomposed by heating in known way to produce a gas mixture comprising sulphur dioxide, water vapor, and sulphur containing hydrocarbon oil vapors, together with solid carbonaceous residue. The gas mixture is cooled to about normal temperatures to condense the water and oil vapors and separate the same from the sulphur dioxide gas, and the water and sulphur bearing oil may be separated by decantation or otherwise. For the purpose of removing coke and other solid foreign matter, the sulphur oil may be distilled and two fractions recovered, one containing oils boiling up to about 350° C., and the other containing oils boiling between about 350° F. and 650° F. The oils obtained in this way are high sulphur oils suitable for cutting oil bases. The higher boiling fraction is the preferred oil on account of the higher flash point. An oil of this type has a low viscosity, about 32 to 34 Saybolt at 100° F., and may contain for example 20% sulphur. As above indicated, the heavy bodied sulphurized pine oil of the invention has a high viscosity and high sulphur content, and for this reason may be advantageously blended with the acid sludge high sulphur oil mentioned to impart thereto any desired viscosity which may be required in a cutting oil base, without decreasing, but in many cases increasing, the sulphur content of the acid sludge sulphur oil. The blends obtained in this way are miscible in all proportions with other sulphur oils, and with mineral, animal and vegetable oils used in the metal working art to dilute cutting oil bases.

Although the invention is particularly applicable to pine oil, other terpenes such as turpentine, pinene, terpineol, polymerized pine oil and mixtures of the same may be used in place of pine oil.

In the appended claims stabilization of the oil with respect to sulphur is intended to define a condition in which substantially no sulphur separates out of the oil on standing.

We claim:

1. The method for making sulphurized oil which comprises heating sulphur and a terpene oil at temperature sufficiently high to effect incorporation of sulphur with the oil but at temperature not substantially in excess of 250° C., distilling the resultant oil mass at temperature less than that at which substantial decomposition of the oil mass takes place, and recovering the oil residue, said distillation operation being continued for a time interval until such a sufficient amount of substance comprising unreacted and feebly combined oil has been removed that substantially no sulphur separates out of said oil residue on standing.

2. The method of claim 1 in which the distillation operation is carried out at temperature not substantially in excess of 140° C.

3. The method for making sulphurized oil which comprises heating sulphur and a terpene oil at temperature sufficiently high to effect incorporation of sulphur with the oil but at temperature not substantially in excess of 250° C., passing through the resultant oil mass inert gas at temperature sufficiently high to effect removal from the mass of at least some of the constituents thereof and at temperature less than that at which substantial decomposition of the oil mass takes place, and recovering the oil residue, said gas passage being continued for a time interval until substantially no sulphur separates out of said oil residue on standing.

4. The method of claim 3 in which the inert gas is steam.

5. The method for making sulphurized oil which comprises heating sulphur and a terpene oil at temperature sufficiently high to effect incorporation of sulphur with the oil but at temperature not substantially in excess of 250° C., separating unreacted sulphur from the resultant oil mass, passing steam through the oil mass, and recovering the oil residue, said steam passage being continued for a time interval until substantially no sulphur separates out of said oil residue on standing.

6. The method for making sulphurized oil which comprises heating a terpene oil and sulphur in excess of that apparently combining with the oil at temperature above the initial boiling temperature of the oil but at temperature not subtantially in excess of 250° C., cooling the oil mass and permitting sulphur to settle, separating settled sulphur from the mass, passing through the oil mass inert gas at temperature not less than about 100° C. and not substantially in excess of 140° C., and recovering the oil residue, said gas passage being continued for a time interval until substantially no sulphur separates out of said oil residue on standing.

7. The method for making sulphurized oil which comprises heating sulphur and a terpene oil at temperature sufficiently high to effect incorporation of sulphur with the oil but at temperature not substantially in excess of 250° C., distilling the resultant oil mass at reduced pressure and at temperature less than that at which substantial decomposition of the oil mass takes place, and recovering the oil residue, said distilla-

tion operation being continued for a time interval until substantially no sulphur separates out of said oil residue on standing.

8. The method for making sulphurized oil which comprises heating sulphur and a terpene oil at temperature sufficiently high to effect incorporation of sulphur with the oil but at temperature not substantially in excess of 250° C., separating unreacted sulphur from the resultant oil mass, distilling the oil mass under high vacuum and at temperature not substantially in excess of 140° C., and recovering the oil residue, said distillation operation being continued for a time interval until substantially no sulphur separates out of said oil residue on standing.

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