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SULPHURIZED PETROLEUM CUTTING OILS

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This invention relates to sulphurized petroleum cutting oils; and it comprises a process of making from petroleum oils a stable sulphurized oil base of high sulphur content from which a lubricating and cooling oil may be compounded for use in machining metal parts and in cutting metal objects in general, said process comprising heating a petroleum distillate containing unsaturated hydrocarbons with relatively large amounts of elemental sulphur until the sulphur disappears as such and distilling the sulphurized oil at a moderate temperature so as to remove unsulphurized hydrocarbons; and it further comprises a sulphurized oil base of low viscosity used for the preparation of cutting oils and composed of a stable liquid union of unsaturated petroleum hydrocarbons and sulphur in a proportion from 15 to 40 per cent of the whole; all as more fully hereinafter set forth and as claimed.

Cutting oils, that is, oils used for lubricating machine tools in the cutting of metals of all kinds, have become important in connection with the use of high speed machine tools. It is an achieved object of the present invention to provide a cutting oil made from petroleum and having the lubricating action in the cutting of metals which has been long recognized as advantageous in lard oil, sperm oil and the like; to make a satisfactory cutting oil from petroleum.

In metal cutting work, lard oil has been the standard lubricant. It possesses the property of wetting and sticking to the metal and thus lubricating the cutting tool and the cut metal. The lubricating and cooling action results in better cutting work and in prolonging the use of the cutting tool without dulling or breaking. Other fatty oils of animal and vegetable origin have been used as cutting oils in place of lard oil. Mineral lubricating oils generally do not give as good results as the fatty oils. It is desirable to be able to make satisfactory cutting oils from mineral oils, such as petroleum, and this has been the subject of much research.

Attempts have been made to produce cutting oils from petroleum bases by treating petroleum in various ways, such as chlorination and sulphurization to form oily or greasy bases from which cutting oils can be formed by dilution or compounding with lighter oils. The sulphurized mineral oils heretofore made are deficient as regards lubricating and cooling action in cutting work and the chlorinated petroleum oils have the serious disadvantage of decomposing during use with evolution of corrosive gases containing HCl.

Sulphurized petroleum cutting oils have been made in the form of emulsions of sulphur in oil. The tendency of these emulsions to break has not been entirely overcome and separation of sulphur from the emulsions has been a common disadvantage. In making sulphurized petroleum bases in which sulphur is held in chemical combination with the petroleum hydrocarbons, the proportion of sulphur held in combination has been small and use of these bases with compounding oils has been necessarily limited by their low sulphur content.

In the present invention I have succeeded in forming a stable liquid union of petroleum hydrocarbons and sulphur in proportions such that the sulphur content of the sulphurized base is high enough to permit mixture of the sulphurized base with low grade oils in dilutions of the order of 10 or 20 to 1 or even higher, without separation of sulphur and without loss of the adhesive or wetting properties of the diluted base. I have found that ordinary cracked distillates containing the usual amounts of unsaturated hydrocarbons can be combined with elemental sulphur in amounts such as to form stable liquid compounds containing from 15 to 40 per cent sulphur. The combination is effected by heating the cracked distillate with powdered sulphur to moderate temperatures above the melting point of sulphur until the added sulphur disappears and by distilling off unsulphurized hydrocarbons to leave a sulphurized residue. I have found that digesting a cracked distillate with sulphur at temperatures rising from around 200° to about 300° F. and not exceeding 350° F. during 4 to 5 hours results in combination with the oil of as much as 17 per cent by weight of sulphur, depending to a considerable extent upon the proportion of unsaturated hydrocarbons in the original distillate. I have further found that reduction by distillation of this sulphurized oil at temperatures not exceeding 305° F. by about 65 per cent, results in a loss of less than one per cent of the added sulphur, leaving a reduced liquid residue containing sulphur in stable combination in a proportion as high as

about 40 per cent of the total residue. It is also found that the reduced residue remains stable and homogeneous, losing upon continued standing substantially no sulphur as such. The distillate separated from the sulphurized unsaturated hydrocarbons contains less than 1 per cent sulphur and is available for the usual purification treatments to produce a marketable gasoline. This purified gasoline is substantially free from unsaturates and stabilized against oxidation and gum formation.

The heating digestion of the cracked distillate with sulphur is most advantageously carried out at atmospheric pressure in a still provided with a reflux condenser. The temperature is automatically regulated by the boiling point of the liquid mixture which slowly rises as the digestion proceeds. However, satisfactory sulphurization can be effected by heating under increased pressure with a gradually increasing temperature and separation of a low boiling oil fraction. Temperatures below 300° F. maintained for several hours effect a stable combination of unsaturates with sulphur.

The exact composition of the sulphur compounds formed by the digestion of unsaturated hydrocarbons with elemental sulphur can not be stated. It appears probable that stable hydrocarbon sulphids are formed. The residue after separation of the unsulphurized low boiling distillate remains stable and homogeneous. For use as a cutting oil it is or may be diluted with the common neutral refined oils. I have found that the sulphurized liquid residue made as described to contain 40 per cent sulphur, and diluted in 10 to 20 parts of neutral oil to a sulphur content of 2 to 4 per cent forms satisfactory cutting oils of sufficiently high flash and fire points and of low viscosity. The lubricating action of the diluted base in cutting work compares favorably with that of standard lard oil. It has shown itself to be superior to lard oil by actual tests. The diluted sulphurized oil may be mixed with lard oil to improve the action of the lard oil. It has the advantage of being cheaper than lard oil and a better lubricant for cutting metals. The high sulphur oil base may be added to kerosene and other petroleum distillates to make cutting oils for special purposes. It may also be compounded with various other cutting oils to improve their action as cutting lubricants.

In a specific embodiment of the present invention I have treated a heavy cracked distillate fraction made from a Venezuela crude oil. The distillate fraction had the following properties:

A. P. I. gravity at 60° F.	42°
Iodine number—Hanus (0.25 g. sample)	89.5
Per cent sulphur	0.45
Distillation	
Overpoint	180° F.
10% at	287° F.
50% at	350° F.
90% at	408° F.
End point	440° F.
Recovery	98%

One hundred parts of this heavy cracked distillate fraction containing unsaturated hydrocarbons in relatively large proportions were mixed with 18 parts by weight of powdered sulphur and the mixture was digested for five hours in a still heated by steam coils and provided with a reflux condenser. The initial boiling point of the cracked distillate was about 200° F. The temperature of the liquid mixture rose during the first hour to around 250° F. and during the succeeding four hours the temperature rose slowly to 298° F. The reaction taking place did not appear to be sensibly exothermic. The temperature during the 5 hours heating was kept below 300° F. in order to prevent excessive polymerization. The gentle boiling of the liquid distillate was sufficient to keep the powdered sulphur in suspension until the melting point of sulphur, around 235° F., was reached during the first hour of heating and the sulphur then formed a layer of immiscible liquid at the bottom of the still. This layer of liquid sulphur disappeared after heating for about an hour longer and at the end of 5 hours digestion the liquid mass was homogeneous and dark in color. From 100 parts by volume of the original distillate, 109 parts by volume of sulphurized distillate were obtained. If this sulphurized oil is permitted to cool an asphaltic material containing about 5 per cent of the sulphur used separates out from the solution and the decanted liquid contains about 16.7 per cent sulphur. The asphaltic material so separating represents a small excess of sulphur over that forming a stable liquid union with unsaturated hydrocarbons in the distillate.

After decanting, I have found it advantageous to leave the asphaltic residue in the still and proceed with the digestion of a second batch therein. So doing, the reaction appears to be accelerated by the presence of the asphaltic residue. A small amount of residue is all that is required to accelerate sulphurization, and accordingly I remove some of the residue from time to time between successive runs.

The sulphurized distillate was then reduced by vacuum dry distillation at a pressure of 30 mm. of mercury and with the liquid temperature not exceeding 305° F. and a vapor temperature not over 240° F. Detectable amounts of hydrogen sulphid occurred in the distillation vapors and a sulphur balance on the process indicated that not more than about 0.2 per cent of the total sulphur was lost as hydrogen sulphid. Distillation was continued under the stated temperature and pressure conditions until the sulphurized distillate was reduced 65 per cent in volume. The 65 per cent distillate contained 0.91 per cent sulphur. It responded well to the usual heavy acid treatment that is given to the heavy fraction of Venezuela cracked distillate. It is recovered and used for blending with gasoline.

The reduced residue was homogeneous. Upon standing at room temperature for several days a small proportion, about 1 per cent, of asphaltic material separated out but no sulphur separated as such and no additional asphalt material was thrown out after further storage. The reduced liquid showed a sulphur content of 39.8 per cent by weight. It represented 37 per cent by volume of the original cracked distillate and had the following properties:

Gravity: °A. P. I.	6.5
Specific gravity at 60° F.	1.132
Flash point, O. C.: °F.	250.
Fire point: °F.	270.
Viscosity, S. U. V.: 100° F.	440.
Viscosity, S. U. V.: 210° F.	54.

The following table shows the characteristics

of cutting oils formed by dilution of the sulphurized base with various neutral refined oils to various percentages of sulphur content:

	I	II	III
Diluent oil viscosity	155 S. U. V., 100° F.	203 S. U. V., 100° F.	255 S. U. V., 100° F.
Dilution ratio	20:1	13.3:1	10:1
Sulphur, per cent	2	3	4
Flash point (open cup)	375° F.	380° F.	405° F.
Fire point	440° F.	450° F.	465° F.
Viscosity			
S. U. V. at 100° F.	157.5	207.8	250.3
S. U. V. at 210° F.	42.7	45.1	47.4
Specific gravity at 60° F.	0.8990	0.9141	0.9065
A. P. I. gravity at 60° F.	25.9	23.3	24.6
Pour point	18° F.	2° F.	25° F.

The most conspicuous quality of the high sulphur cutting oil base is the moderate viscosity and ready miscibility in all proportions with petroleum lubricants and with fatty oils. In this respect the sulphurized cutting oil base containing from 15 to 40 per cent sulphur is a distinctly superior product. The high sulphur content of this cutting oil base, which permits of a dilution of as much as 20 fold in order to make a cutting oil, makes it possible to add it to any oil having the desired physical properties without materially altering these properties. Cutting oils so made are low in cost and superior to lard oil.

What I claim is:—

1. A method of making a stable cutting oil base of high sulphur content from petroleum oil which comprises heating a cracked distillate with sulphur at temperatures under 350° F. until the sulphur disappears as such and reducing the sulphurized distillate by distillation of unsulphurized hydrocarbons.

2. In the method of claim 1, heating under reflux condensation at atmospheric pressure prior to reduction.

3. In the method of claim 1, reducing the sulphurized distillate at a temperature not exceeding 305° F.

4. A method of making a stable cutting oil base of high sulphur content which comprises subjecting a cracked naphtha distillate and sulphur to a temperature above the melting point of the sulphur but not exceeding 350° F. until a product containing at least 15 per cent of stable compounds of sulphur and hydrocarbon constituents present is obtained, and then subjecting the product to controlled partial distillation at temperatures somewhat below the end boiling point of the original distillate, whereby unsulphurized constituents are removed leaving a residue containing a substantially increased proportion of stable sulphur compounds and suitable for use as a cutting oil base.

5. A cutting oil base comprising a residue from the distillation of a sulphurized cracked petroleum naphtha, containing stable compounds of sulphur and hydrocarbon constituents of said naphtha, the sulphur content being from 15 to 40 per cent by weight of the cutting oil base.

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