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DEWAXING PROCESS WITH 2-STAGE SULFUR TREATMENT

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This invention relates to improved procedure for preparing paraffin wax.

Paraffin wax is known to occur in petroleum oils in varying amounts. It is known that this wax occurs in several forms including a microcrystalline form which has unusual value because of its relatively high tensile strength. These waxes can be separated by treating the petroleum oil with various solvents, usually in conjunction with cooling. For instance, it is known to add methyl ethyl ketone or pentane to the petroleum oil or heavy fraction thereof and cool to cause the wax to precipitate.

This invention has for its object to provide procedure for manufacturing paraffin wax from petroleum crudes or heavy fractions thereof. Another object is to provide improved procedure whereby the yield of microcrystalline wax is increased. Another object is to improve the state of the art. Other objects will appear hereinafter.

These and other objects of our invention are accomplished by adding elemental sulfur to a petroleum crude or fraction thereof, heating the mixture to a temperature above about 125° C. and thereafter separating a paraffin wax from the treated crude or heavy fraction thereof, said paraffin wax being formed by reaction between the elemental sulfur and hydrocarbon components of the crude or heavy fraction thereof.

In the following examples and description we have set forth several of the preferred embodiments of our invention, but it is to be understood that they are given by way of illustration and not in limitation thereof.

The crude or heavy fraction thereof which may be employed in our process may be derived from any source and may comprise any of the various types of petroleum. Thus the crude may be a paraffin type of crude obtained in the Pennsylvanian or other eastern areas of the United States. Alternatively, it may be a naphthenic type crude such as obtained on the west coast of the United States or in the Mid-East. Alternatively the crude may be one of the Mid-Continent type similar to that obtained in the Mid-Continent portion of the United States. Such Mid-Continent crudes are primarily a mixture of naphthenic and paraffinic components. When the crude or heavy fraction thereof contains paraffin wax which is naturally present therein, we prefer for the reasons pointed out hereinafter to first remove the paraffin wax before reaction with elemental sulfur. However, such removal is not necessary, and the paraffin wax may be left in and be present during the reaction with the sulfur. However, this mode of operation decreases the overall yield of paraffin wax obtained from the crude. Also while the entire crude may be treated, we prefer to subject the crude to distillation to remove as distillate components of a low boiling nature and preferably to remove all components including heavy gas oil and lighter components. The heavy residue thus obtained is reacted with the sulfur.

The sulfur may be added in amounts between about 0.01 and 10 percent. Amounts of 0.1 to 3 percent by weight are preferred. Amounts larger than approximately 1 percent do not readily dissolve in the oil so that where such larger amounts are employed, the mixture of sulfur and hydrocarbon charge stock should be agitated during the heat treatment in order to obtain

intimate contact between all of the sulfur and the hydrocarbon. Of course the sulfur should be in finely divided form to obtain intimate contact between the reacting components.

The mixture is heated to a temperature between about 125° and 300° C. and preferably a temperature between about 150° and 170° C. We have found that at a temperature of about 150° C. the maximum rate of reaction between the sulfur and the hydrocarbon components to form paraffin wax takes place. Also we have found that a second maximum rate of reaction takes place at a temperature of about 225° to 250° C. This second reaction is evidently between a different type of component since it results in a larger amount of non-microcrystalline paraffin wax than the temperature in the neighborhood of 150° C. Therefore, as will be explained in more detail later, we prefer to operate the reaction in two stages; first heating to 150° C. more or less to form one type of wax which is removed, then heating to about 225° to 250° C. to form a different type of wax which is removed. In this mode of operation an additional amount of sulfur will be added to the oil prior to the second stage heat treatment if substantially all of the sulfur has been reacted with the oil in the first stage. However, if such reaction is incomplete, which will be the case when larger amounts of sulfur are used, such second addition of sulfur is unnecessary.

The time of reaction may be between about fifteen minutes and eight hours. A heating period of between about one-half and three hours is advantageous. The heat treatment may be carried out in a batch manner preferably with agitation or stirring for the reasons pointed out above. Alternatively, the process may be carried out continuously in which case the mixture will be continuously passed through a heated chamber such as a heated tubular furnace or an elongated heated reaction chamber. The products flowing from the chamber are then treated for removal of the paraffin wax. If desired, the unreacted hydrocarbon may be recycled for re-use in the process. Pressure does not have a material effect on the process. Therefore the reaction may be, and is, advantageously carried out at atmosphere pressure. However, reduced or super-atmospheric pressure may be employed. Thus pressures as low as 1 mm. Hg or as high as 10,000 p.s.i.g. may be used.

EXAMPLE 1

One percent sulfur was added to Redwater crude oil containing 3.89 percent wax having the wax composition shown in Table I, line 1. The mixture was introduced into a reaction bomb which was cooled to a low temperature and subjected to vacuum for removal of air. The bomb was sealed and was then introduced into a furnace and heated to a temperature of 150° C. for a period of 3 hours. Thereafter the bomb was rapidly cooled to below 100° C., the contents of the bomb were removed and analyzed for wax content and wax composition. The total wax content was found to be 11.84 percent. The wax was found to be substantially free of sulfur compounds. Its composition is given in Table I, line 2.

Table I

WAX COMPOSITION

Line No.	Alkanes	Non-Condensed Cyclo-alkanes	Condensed Cyclo-alkanes	Alkyl Benzenes	Naphthalenes
1	75.2	18.6	3.9	2.1	0.2
2	54.6	29.6	11.3	4.2	0.3

EXAMPLE 2

In another experiment, one percent sulfur was added to the same Redwater crude described in Example 1 and the mixture was subjected to the identical treatment except that a temperature of 238° C. was employed during the three hour heating period. The resultant wax was separated from the treated crude in an amount of 8.33 percent. The wax was analyzed and the composition of this wax is shown in Table II.

Table II

WAX COMPOSITION

Alkanes	Non-Condensed Cyclo-alkanes	Condensed Cyclo-alkanes	Alkyl Benzenes	Naph-thalenes
78.3	17.2	3.5	0.9	0.1

From the above data and similar experiments we have determined that crudes contain components which will react with sulfur at a low temperature, in the neighborhood of 150° C., to form wax compositions containing larger amounts of non-condensed cycloalkanes whereas at more elevated temperatures, in the neighborhood of 225° to 250° C., the same or a similar reaction takes place with less reactive components to form a wax having a higher content of alkanes. The wax formed at the lower temperature therefore has a higher content of microcrystalline wax, while the higher temperature product has a higher content of the material ordinarily called paraffin wax.

For these reasons we have found it to be advantageous to react the crude with the sulfur at a temperature in the neighborhood of 150° C. such as 150° to 170° C. to obtain a higher content of microcrystalline wax, to separate the wax thus produced, and to then repeat the same operation at a temperature of about 225° C. to 250° C. and thereafter separate a wax containing a higher content of ordinary wax components. Since the wax naturally present in the crude reacts with sulfur to a certain extent, we also prefer to treat the crude for removal of the naturally contained wax prior to reacting with sulfur. In all of these wax removal procedures, any known or conventionally used wax removal procedure such as chilling in the presence of methyl ethyl ketone, pentane, etc. may be employed.

We claim:

1. The process for preparing paraffin wax in high yield which comprises in combination adding between about 0.01 and 10 percent sulfur to a member of the group consisting of crude petroleum and high boiling fractions of crude petroleum, heating the mixture to a temperature between about 150° and 170° C., subjecting the reaction product to treatment for removal of a first portion of paraffin wax high in microcrystalline components, adding between about 0.01 and 10 percent elemental sulfur to the crude from which the paraffin wax formed during the preceding treatment has been removed, heating the mixture to a temperature of between about 225° and 250° C. and removing a second portion of paraffin wax, said second portion containing a lower percentage of microcrystalline components than the first portion of paraffin wax.

2. The process for preparing paraffin wax in high yield which comprises in combination subjecting a member of the group consisting of crude petroleum which contains paraffin wax and high boiling fractions of crude petroleum which contain paraffin wax to a treatment for removal of a first portion of paraffin wax naturally contained therein, adding between about 0.1 and 3 percent elemental sulfur to the portion freed of paraffin wax, heating the mixture to a temperature of between about 150° and 170° C., subjecting the reaction product to treatment for removal of a second portion of paraffin wax which contains a relatively large amount of microcrystalline components, adding between about 0.1 and 3 percent elemental sulfur to the crude from which the paraffin wax formed during the preceding treatment has been removed, heating the mixture to a temperature of between about 225° and 250° C. and removing a third portion of paraffin wax, said third portion containing a lower percentage of microcrystalline components than the second portion of paraffin wax.

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