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PROCESS FOR THE MANUFACTURE OF CYCLIC SULPHUR COMPOUNDS SUCH AS THIOPHENE AND ITS DERIVATIVES

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This process relates to the manufacture of products for pharmaceutical purposes containing thiophene and its derivatives, or other hydrocarbons of a cyclic nature having a sulphur atom directly on the ring structure.

In carrying out my process I preferably employ a crude oil containing hydrocarbon sulphur compounds and over fifty percent (50%) of unsaturated hydrocarbons and having an asphaltic base. The oil is first subjected to an ordinary distillation process. The first fractions of lower boiling points consisting of gasoline and kerosene are, in the case where crude oil is employed, collected separately and not used for manufacture of cyclic sulphur compounds for the reason that they are usually saturated. In the case where synthetic oils are used, which are commercially produced by cracking processes, the lighter fractions may be used for this process. Fractions distilling after the kerosene fraction and consisting of gas oil, spindle oil, light and heavy lubricating oils, are the base materials for this process, while the residue remaining in the still and comprising mainly asphalt is discarded. The base materials thus obtained are placed in a vacuum still and heated slowly in the presence of an oxygen containing compound of the iron group. Of these substances an iron oxide has been found very effective and economical. As the reaction products formed in the vacuum still are highly corrosive, the still, vapor lines and condensers are preferably made of cast iron.

Any iron compound, as long as it is a combination of oxygen, or hydroxyl with iron, can be used. I have found that the most suitable form of applying the iron oxide for this particular process is in the form of long and light iron turnings or shavings which have been submitted to the action of gasoline and a diluted acid and afterwards exposed to the air for several weeks. The turnings are then placed in cast iron baskets and hung in the vacuum still. In some instances I have found that the oxidation of the internal walls of the still, which occurs in my process, will provide sufficient iron oxide for the purpose described.

The still containing the oil to be treated is first heated up without the application of a vacuum and maintained at a temperature around 200 degrees C. for two hours. I then add very slowly to the contents of the still a thin paste of flowers of sulphur, powdered iron oxide and oil, at the same time constantly maintaining the temperature between 200 and 250 degrees C. The basket of iron turnings may now be removed from the still. The vacuum may then be slowly applied throughout the system until it reaches twenty-eight to twenty-nine inches of vacuum, which is maintained during the remainder of the distillation process. The fire is increased gradually and distillation is started and continued. At the same time superheated steam at approximately 300 degrees C. is slowly blown into the bottom of the still.

The first part of the distillation is accompanied by the formation of hydrogen-sulphide gas, which is absorbed to a small extent by the lighter distillates, giving them a bad odor. This odor may be eliminated by heating these distillates. The heavier bodies have no or a very slight odor.

The sulphur compounds having cyclic structures with sulphur directly on the ring are not effected by this treatment, and they will be found unchanged after reaction has taken place, but the mercaptans and hydrocarbon sulphides of open or cyclic structure are converted into metal salts and the metal salts being unstable under heat are decomposed forming metal sulphides, and, at the same time, molecular sulphur is taken into the hydrocarbon molecule, forming to a great extent sulphur compounds of cyclic nature, such as thiophene or its derivatives.

Another reaction takes place, as follows:—

The molecular sulphur at a temperature of over 200 degrees C. has a tendency to form sulphides by entering the hydrocarbon molecule on an unsaturated or double bond. These sulphides are not very stable, having a tendency to form polymerization products, and finally being converted into heavy asphaltic masses. However, in the presence of a metal

oxide, metal salts are formed instantly and the polymerization is instantly stopped. These metal salts react in the same manner as above described, forming thiophene or its derivatives.

Having described my invention what I claim is:

1. A process for the manufacture of organic sulphur compounds of cyclic nature bearing sulphur in the ring structure which consists in submitting hydrocarbon sulphur compounds containing sulphur in non-cyclic combinations to the action of an oxygen containing compound of the iron group and molecular sulphur under heat and distilling in the presence of a vacuum and super-heated steam.

2. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in submitting hydrocarbon sulphur compounds of straight chain structure to the action of an oxygen containing compound of the iron group and molecular sulphur under heat and distilling in the presence of a vacuum and superheated steam.

3. A process for the manufacture of organic sulphur compounds of cyclic nature from a hydrocarbon oil containing sulphur compounds which consists in eliminating light hydrocarbons of low boiling point and heavy residues of high boiling point from said hydrocarbon oil, submitting the remaining fractions to the action of an oxygen containing compound of the iron group, and molecular sulphur under heat and distilling the mass in the presence of a vacuum and superheated steam.

4. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in submitting a body of hydrocarbon oil having unsaturated constituents to the action of an oxygen containing compound of the iron group and molecular sulphur under heat and distilling the mass in the presence of a vacuum and superheated steam.

5. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in distilling a hydrocarbon oil having an asphaltic base and containing hydrocarbon sulphur compounds, separating out the lighter oils and asphaltic residue, submitting the remaining fractions to the action of an oxygen containing compound of the iron group, and molecular sulphur under heat and distilling the mass in the presence of a vacuum and superheated steam.

6. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in submitting a hydrocarbon oil containing sulphur compounds and unsaturated constituents to the action of heat in the presence of an oxygen containing compound of the iron group at an elevated temperature, adding molecular sulphur and maintaining the temperature between 200 and 250 degrees C. progressively applying a vacuum to the mass thus formed up to approximately twenty-nine inches, and continuing the distillation of said mass in the presence of said vacuum and superheated steam.

7. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in submitting a hydrocarbon oil containing hydrocarbon sulphur compounds and unsaturated constituents to the action of heat in the presence of an oxygen containing compound of the iron group, adding molecular sulphur, applying a vacuum to the mass thus formed and distilling said mass in the presence of said vacuum and superheated steam.

8. A process for the manufacture of organic sulphur compounds of cyclic nature which consists in submitting a hydrocarbon oil containing hydrocarbon sulphur compounds and unsaturated constituents to the action of heat in the presence of an oxygen containing compound of the iron group adding a mixture of molecular sulphur, oil and powdered metal oxide of the iron group, applying a vacuum to the mass thus formed and distilling said mass in the presence of said vacuum and superheated steam.

9. In a process for the preparation of hydrocarbons of a cyclic nature containing sulphur in the ring, the step which comprises heating unsaturated open chain hydrocarbons with molecular sulphur in the presence of an oxygen containing metal compound, the metal constituent of which belongs to the iron group.

10. The process of preparing hydrocarbons of a cyclic nature containing sulphur in the ring, which comprises heating unsaturated open chain hydrocarbons free from asphaltic residues with molecular sulphur in the presence of an iron oxide and distilling the mass under relatively high vacuum.

11. The process of preparing hydrocarbons of a cyclic nature containing sulphur in the ring, which comprises heating a mineral oil containing a relatively large proportion of unsaturated aliphatic hydrocarbons and free from asphaltic residues and lower boiling fractions with molecular sulphur in the presence of an oxygen containing metal compound, the metal constituent of which belongs to the iron group, maintaining a temperature during the reaction of about 200° C. to 250° C. and distilling the mass under a relatively high vacuum in the presence of an inert gas.

Signed at Chicago, Illinois, this 20th day of July, 1927.

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