

UNITED STATES PATENT OFFICE

2,278,719

METHOD OF SYNTHESIZING SULPHUR-BEARING, HIGH MOLECULAR WEIGHT HYDROCARBONS

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No Drawing. Application September 27, 1940,
Serial No. 358,698

2 Claims. (Cl. 260—139)

Our invention relates to a method of synthesizing sulphur-bearing derivatives of high molecular weight hydrocarbons and more particularly to a method of synthesizing relatively pure high molecular weight sulphur compounds from paraffin hydrocarbons.

This is a continuation-in-part of our copending application, Serial 205,530, filed May 2, 1938.

One object of our invention is to provide a method for synthesizing relatively pure high molecular weight sulphur compounds from petroleum hydrocarbons.

Another object of our invention is to provide a method for converting petroleum fractions and similar hydrocarbons of low value into high molecular weight sulphur compounds of greater commercial value.

A further object of our invention is to provide a method of synthesizing high molecular weight sulphur compounds from paraffin hydrocarbons.

Other and further objects of our invention will appear from the following description.

In accordance with our invention, it is now possible to prepare relatively pure sulphur derivatives of the higher paraffin hydrocarbons without being mixed with other sulphur-containing bodies. We first prepare a relatively pure mono-, di-, or trihalogenated paraffin hydrocarbon, free from unhalogenated hydrocarbon and from each other, and convert these relatively pure halogenated hydrocarbons by chemical means into sulphur-containing derivatives.

In the prior art, references are made to monochloro paraffin, dichloro paraffin, trichloro paraffin, and the like usually considering the product of direct chlorination to be the compound represented by the total chlorine content and therefore the desired compounds. We have found that these materials are very crude mixtures of the chlorinated hydrocarbons and contain unchlorinated hydrocarbons and the mono-, di-, and polychloro derivatives and cannot be considered the desired compounds. For example, the so-called "trichloro paraffin wax" containing 24 per cent chlorine, which corresponds very closely to the percentage of chlorine in the trichloro compound, was separated by means of crystallization from acetone. The first (least soluble) portion consisted of a mixture of monochloro wax and unchlorinated wax. The percentage of unchlorinated wax in the original mixture was found to be 7.2 per cent. Thus, even a "tri-chloro paraffin" as so-called in the prior art because of the total chlorine content, was in fact a crude mixture containing as much as 7.2 per

cent of unchlorinated wax and quantities of mono- and dichloro waxes, as well as trichloro wax and more highly chlorinated waxes. Its use would not give the same results as a trichloro paraffin free of higher and lower chlorinated paraffin.

Even though the appropriate amount of chlorine is introduced in the wax to form a monochloro wax, we have found that the crude chlorination mixture contains, in addition to small amounts of chlorine and hydrogen chloride and the desired monochlor wax, also unchlorinated wax and more highly chlorinated and less highly chlorinated waxes.

In contrast to the use of such a mixture, we have found it possible, as fully described below, to obtain a relatively pure monochlor compound free from unchlorinated hydrocarbon and free from more highly chlorinated compounds. We may thus prepare (1) monohalogenated hydrocarbons substantially free from unhalogenated hydrocarbons and more highly halogenated hydrocarbons, and (2) dihalogenated hydrocarbons substantially free from unhalogenated hydrocarbons and monohalogenated hydrocarbons, as well as from halogenated hydrocarbons containing more than two atoms of halogen per molecule; (3) trihalogenated hydrocarbons free from halogenated hydrocarbons containing fewer or more than three halogen atoms per molecule and free from unhalogenated hydrocarbons. We refer in this specification to these materials as relatively pure monohalogen compounds, relatively pure dihalogen compounds, etc.

We proved the homogeneity of our relatively pure monochlor wax, for example, by chilling until approximately half of the material had solidified. Solid and liquid portions were separated by a filtration and contained 12.1 and 11.4 per cent chlorine respectively. Our monochloro wax is therefore free from both unchlorinated wax and more highly chlorinated wax. Similarly, we may prepare according to our invention di- and polychloro waxes free from unchlorinated wax and monochlor wax, as well as from more highly chlorinated waxes.

The same methods as are described here in detail for the manufacture of a relatively pure chlorinated wax are applicable to the manufacture of chlorine derivatives of the paraffin hydrocarbons of higher and lower molecular weight than that represented by the commonly known paraffin wax, including all those paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves.

The chlorination of most petroleum hydrocarbons lowers their melting points and, up to a certain point, the greater the extent of chlorination; that is, the more chlorine atoms per molecule, the lower the melting point. The decrease in melting point is stepwise, and this permits us to separate the unchlorinated hydrocarbons from the monochloro hydrocarbons and the monochloro hydrocarbons from the dichloro and higher chlorinated hydrocarbons. We can, for example, separate the unchlorinated wax from the air-blown mixture by filter pressing at such temperatures that all of the chlorinated waxes are largely liquids, while the unchlorinated waxes are largely solid. The temperature for the pressing operation will depend, of course, on the character of the wax used initially and will vary considerably depending on this factor. For example, at a temperature of from 80° F. to 90° F. the monochloro product formed by the chlorination of wax having a melting point of 120° F. will be liquid, while the unchlorinated wax will be solid, enabling a ready separation to be effected.

Other methods of separation, as for example, sweating, selective solvent extraction at varying temperatures and the like, may be employed for separating solid unchlorinated wax from chlorinated portions, and for separating the monochloro wax from the more highly chlorinated portions.

The unchlorinated wax separated from the crude chlorination mixture may be recycled to obtain further quantities of chlorinated waxes. It does not represent refractory material, and the same proportions of chlorination products are obtained from it as from fresh wax.

The liquid chlorinated waxes consist largely of monochloro and dichloro waxes when approximately 10 or 20 per cent chlorine respectively is introduced into a starting wax of, say, from 115° to 130° F. melting point, but some polychloro wax may be present. These mono- and dichloro waxes may be separated from each other by crystallization from acetone, using about 12½ gallons of acetone per 100 pounds of crude chlorinated waxes. In preparing the solution, an elevated temperature is employed to insure that the chloro waxes are completely dissolved in the solvent. The solution is then chilled to a temperature of between minus 15° F. to minus 20° F. when a paraffin wax of 115° to 130° F. melting point is used for the initial chlorination. The monochloro waxes are precipitated out nearly quantitatively, while the dichloro and polychloro waxes will remain in solution. The precipitated monochloro waxes may be readily separated by settling, filtering or centrifuging.

We have also used other crystallization solvents such as methyl-ethyl ketone, acetone, benzene, acetone-methylene chloride, and various halogenated solvents. The use of a particular one or combination of these solvents requires the experimental determination of the proper proportions and temperatures necessary to obtain the desired separation of the crude chlorination mixture into the various stages of chlorine contents. Halogenated solvents serve to aid in the precipitation of unchlorinated wax, while benzene increases the solubility of the more highly chlorinated materials.

On further chilling of the solution, or by evaporating off part of the solvent and again chilling, the dichloro and polychloro waxes may be similarly separated.

In this manner, the crude chlorination mix-

ture may be separated into unchlorinated wax, monochloro wax, dichloro, and polychloro wax. It is to be understood, of course, that the separation conditions will vary depending upon the melting point of the starting material.

In preparing monochloro wax, for example, the separated monochloro wax will be found to contain approximately the theoretical chlorine content. In the case of the wax which had the 120° F. melting point, batches showed chlorine content of 10.2 per cent, 10.5 per cent, 10.3 per cent, and 10.8 per cent. These are very close to the theoretical chlorine content of 10.0 per cent. This monochloro wax is substantially free from unchlorinated waxes and polychloro waxes.

Our paraffin hydrocarbons are preferably obtained from petroleum. Any source of materials, rich in hydrocarbons of the methane or C_nH_{2n+2} series, or mixtures relatively rich in these components, may be used as starting materials in practicing our invention. The method of our invention is particularly applicable to the higher paraffin hydrocarbons but is eminently satisfactory on all those hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves. While the product of the preferred embodiment of our invention is a mixture, the monochloro derivatives prepared according to our invention are free from unchlorinated and more highly chlorinated material. The dichloro derivatives are free from unchlorinated hydrocarbons, monochlorinated hydrocarbons, and more highly chlorinated hydrocarbons. The purity of the final product with respect to homologues is determined by the purity of the starting hydrocarbon. It is understood, of course, that when a pure hydrocarbon is employed, a correspondingly pure halide is obtained.

Having selected the hydrocarbon in accordance with the desired final product, we chlorinate the hydrocarbon until approximately that amount of chlorine is absorbed which will produce the monochloro compound when that is the desired product, or approximately that amount of chlorine which will produce the dichloro compound when that is the desired product, etc.

In the case of paraffin hydrocarbons having from 18 to 24 carbon atoms per molecule; that is, a material having a melting point of approximately 120° F., about 10 per cent added chlorine will produce substantially the equivalent of the monochloro product. The amount of chlorination may vary between 8 per cent and 12 per cent without being disadvantageous. The percentage of chlorine introduced into the hydrocarbon just described will be approximately 17 per cent when a dichloro product is desired. The amount of chlorine introduced will be less in the case of the high molecular weight, higher melting hydrocarbons, and more in the case of the lower molecular weight, lower melting hydrocarbons, for a given number of chlorine atoms per molecule. The chlorination may be accomplished in any suitable manner. We prefer to heat the hydrocarbon to a temperature at least that of its melting point and pass chlorine gas through the melted hydrocarbon. Agitation increases the efficiency of chlorine absorption but is not essential. The chlorination reaction is exothermic and the heat of reaction is ordinarily ample to maintain the mixture in the liquid state without the addition of other heat. Large quantities of hydrogen chloride gas are evolved which are conducted from the reaction chamber, together with unreacted chlorine. The material being

chlorinated is constantly weighed while the chlorination is in progress, in order to determine the extent of chlorination as indicated above. Samples may be removed from time to time, and the specific gravity of these may be determined in order to follow the chlorination process. If desired, chlorine analyses may be conducted on samples of the material being chlorinated. After sufficient chlorine has been introduced, we blow the mixture with air or an inert gas, such as carbon dioxide, until the hydrogen chloride and free chlorine, if any, are substantially removed.

As an example of the manufacture of a relatively pure chlorinated hydrocarbon, we describe here the manufacture of a relatively pure monochloro wax which contains approximately 26 carbon atoms per molecule. We started with 723.4 parts of a hydrocarbon wax having a melting point of 120° F. The wax was chlorinated until 72.5 parts by weight of chlorine had been absorbed. The chlorinated wax was air-blown to remove hydrochloric acid and uncombined residual chlorine, and then pressed at 85° F. The unchlorinated wax was reserved for further chlorination. The liquid portion was then dissolved in acetone, 350 parts of crude chloro wax being dissolved in 3,226 parts of acetone. The solution was chilled to minus 18° F. and 185 parts by weight of solid monochloro wax containing 10.3 per cent chlorine was precipitated. Monochloro wax from this paraffin wax contains theoretically 10.0 per cent chlorine. The monochloro wax was normally liquid at room temperatures.

Dichloro waxes and polychloro waxes prepared according to our method are suitable for use in any of the applications described in the prior art, where such dichloro waxes and polychloro waxes are required. Since they contain no unchlorinated wax or lower chlorinated waxes, they are particularly efficient in these applications and are a distinct improvement over the prior art which used crude chlorination mixtures of approximately the proper chlorine content but which consisted of unchlorinated wax and more highly chlorinated wax.

While chlorine has been referred to above almost exclusively, it is to be understood that any of the halogens are suitable to make halogen derivatives of the paraffin hydrocarbons according to our method. Thus bromine, iodine, and fluorine may suitably be used to obtain the corresponding bromides, iodides and fluorides. For some purposes to which the halides are to be put, the bromine compounds are much to be desired over the chlorine compounds, since they are considerably more reactive. Where this is the case, we halogenate with bromine, using a halogen carrier, such as halides of antimony, phosphorus, iron, various metals, and the like, and separate the brominated mixture into its components as described above in the case of the chlorine compounds. The iodine compounds of the paraffin hydrocarbons may be prepared by direct iodination or by an indirect method. By the indirect method, the above described separation of mono-, di-, and polyhalogen derivatives may be employed in any step of the process. Thus we may separate a relatively pure mono- or dichloro paraffin and convert it to the corresponding iodine compound, or we may convert the crude halogenated mixture into a crude iodinated mixture and then separate into the various stages of halogenation. Fluorine may

be introduced into paraffin hydrocarbons directly or indirectly by analogous methods. For most purposes, however, we prefer to use the chlorine compounds on account of the cheapness and availability of chlorine above all the other halogens.

In making relatively pure mono-olefins, the monochloro compound is dehalogenated by a simple method of our discovery; namely, the heating of the monochloro compound with $\frac{1}{16}$ or more of its weight of lime for a period of one-half minute or less to one hour at approximately 200° F. to 550° F. A temperature of from 390° F. to 550° F. is usually satisfactory for the treatment of chlorinated waxes. At lower temperatures, the action is slower and longer times of heating will be required. At temperatures much higher than 550° F., undesirable side reactions such as cracking and polymerization of the resultant olefins will occur, and the product is less satisfactory. Under the conditions described, the olefin is formed by the lime removing chlorine from the monochloro compound as hydrogen chloride, which is in turn neutralized by the excess of lime or driven off as a gas. A hydrocarbon product containing less than one per cent of residual chlorine may be obtained in this manner. Four batches thus treated resulted in olefins having chlorine contents of .95, .59, .20, and .09 per cents. By settling and decanting, by centrifuging, or by filtering, the excess of lime and other solid reaction products may be removed to obtain the olefinic hydrocarbons. The lime may be washed with a solvent to recover additional olefins.

In making olefins for some uses, hydrogen chloride may be removed by heat alone. The color may not be as good, but the chemical characteristics are satisfactory.

The theoretical iodine value for an olefinic hydrocarbon having the formula $C_{25}H_{50}$ is 75.6. Actual iodine values for the olefins obtained from various batches were 74.1, 72.2 and 72.1. The resultant product is an olefin showing reactions typical of the general class of olefins.

In preparing sulphur-bearing derivatives of these higher aliphatic olefins, we treat chemically the relatively pure olefins with certain sulphur-bearing reagents. The derivatives and methods of preparing may be classified as follows:

1. *Sulphides of phosphorus*.—We treat the olefins with phosphorus trisulphide P_2S_3 or phosphorus pentasulphide P_2S_5 or other sulphides of phosphorus to obtain sulphur and phosphorus containing derivatives.

2. *Halides of sulphur*.—We treat the olefins with sulphur monochloride (S_2Cl_2) or sulphur dichloride (S_2Cl_4) or other halides of sulphur to obtain sulphur and halogen containing derivatives.

It is to be understood that any or all of the reactions here described may be carried out under atmospheric or super-atmospheric pressure.

It will be seen that we have accomplished the purpose of our invention; namely, to provide relatively pure sulphur-bearing derivatives of high molecular weight paraffin hydrocarbons, each substantially free from other types of sulphur compounds and from unreacted paraffin hydrocarbons.

Our new sulphur-bearing derivatives of high molecular weight are particularly useful in the manufacture of high-quality lubricants. Automotive engineers are using bearings containing cadmium, silver, copper, lead, and other metals.

These new bearing compositions, while possessing certain mechanical advantages over the old tin-babbitt bearings, are more susceptible to corrosion. Furthermore, modern solvent-treated lubricating oils are readily oxidized in use to form particularly corrosive oxidation products. The addition to lubricants of all kinds and especially to solvent-treated oils of our new sulphur-bearing derivatives of high molecular weight inhibits the formation of these oxidation products and prevents corrosion of engine parts.

Having thus described our invention, we claim:

1. A method for the synthesis of sulphur-bearing derivatives of high molecular weight, including the steps of halogenating paraffinic hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating relatively pure halogenated hydrocarbons

from the crude halogenated mixture, dehalogenating the said relatively pure halogenated hydrocarbons to form olefins and reacting thereon with a reagent selected from the group consisting of sulphides of phosphorus and halides of sulphur.

2. A method for the synthesis of sulphur-bearing derivatives of high molecular weight, including the steps of halogenating paraffinic hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating relatively pure halogenated hydrocarbons from the crude halogenation mixture, dehalogenating the said relatively pure halogenated hydrocarbons to form olefins and reacting thereon with a halide of sulphur.

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