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METHOD OF SYNTHESIZING SULPHUR-BEARING, HIGH MOLECULAR WEIGHT HYDROCARBONS

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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.

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 great 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, a so-called "trichloro paraffin wax" containing 24 percent 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 percent. 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 percent 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 filtration and contained 12.1 and 11.4 percent 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 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 hydro-

carbons 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 percent 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 mixture 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 contents of 10.2 percent, 10.5 percent, 10.3 percent, and 10.8 percent. These are very close to the theoretical chlorine content of 10.0 percent. This monochlor 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 percent added chlorine will produce substantially the equivalent of the monochloro product. The amount of chlorination may vary between 8 percent and 12 percent without being disadvantageous. The percentage of chlorine introduced into the hydrocarbon just described will be approximately 17 percent 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 chlorina-

tion 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 percent chlorine was precipitated. Monochlor wax from this paraffin wax contains theoretically 10.0 percent 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.

We may use as starting materials for our invention either our relatively pure halogenated hydrocarbons as described above or their corresponding relatively pure olefins. From the monochlor paraffin, we may prepare a mono-olefin; from the dichlor paraffin (free from mono- and polychlor paraffin and unhalogenated hydrocarbon) a diolefin; and so on.

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 $\frac{1}{10}$ 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., undersirable 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 percent 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 percents. 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 the higher aliphatic hydrocarbons, we treat chemically the relatively pure halogenated hydrocarbons or their corresponding olefins. The derivatives and methods of preparing may be classified as follows:

I. Sulphur-bearing derivatives of higher paraffin hydrocarbons from relatively pure halogenated hydrocarbons

A. From mono-halogenated hydrocarbons

1. *Mercaptans.*—By treatment with alkali metal hydrosulphides. From these we prepare:
   Disulphides.—By oxidation of mercaptans or mercaptides.
2. *Sulphides.*—By treatment with alkali metal sulphides.
   From these we prepare:
   a. *Sulphoxides.*—By oxidation of sulphides.
   b. *Sulphones.*—By oxidation of sulphides.
3. *Polysulphides.*—By treatment with alkali metal persulphides.

4. *Alkylated sulphur compounds.*—By Friedel-Crafts condensation with suitable sulphur compounds.
5. *Sulphur-bearing derivatives formed from oxygen-bearing derivatives:*
   a. *Sulphites.*—By action of thionyl chloride on alcohols.
   b. *Sulphates.*—By action of SO_2Cl_2 on alcohols or by oxidation of sulphites.
   c. *Xanthates.*—By action of CS_2 and caustic alkalies on alcohols.
   d. *Thiosulphates.*—From sulphites and sulphur.
   e. *Thiophosphates.*—From alcohols and thiophosphoryl chloride ($PSCl_3$).

B. From dihalogenated hydrocarbons.
1. *Thioketones and Thioglycols.*—By treatment with alkali metal hydrosulphides.
2. *Dimercaptans*

II. Sulphur-bearing derivatives from high molecular weight olefins

Resins.—By the catalyzed action of sulphur dioxide on olefins.

Our relatively pure monohalogenated hydrocarbons may be treated with alkali metal hydrosulphides such as NaSH, readily prepared by saturating aqueous or alcoholic caustic with hydrogen sulphide, to form the high molecular weight mercaptans. For this purpose the bromine compounds are more suitable because of greater reactivity and ease of replacement than the chlorine compounds.

Example 1

A solution of 44 parts of caustic soda in 836 parts of water is saturated with hydrogen sulphide gas and then 431 parts of monobrom wax prepared substantially as described above and containing 18 percent bromine is added. The whole is agitated thoroughly while being heated in an autoclave at 275° F. for eight hours; and then the product is separated, washed, and dried. The wax mercaptan contains eight percent sulphur.

These high mercaptans are interesting and useful in themselves and also serve to form the disulphides. These are formed by either of two methods: Oxidation of the mercaptan directly as by nitric acid, or by conversion of the mercaptan to the mercaptide, for example, the lead mercaptide, and treatment of this with sulphur.

Example 2

To 76.8 parts of the wax mercaptan from Example 1 dissolved in 500 parts of light naphtha, we add doctor solution containing 25 parts of lead oxide. The mixture is thoroughly agitated for several hours and then 3.25 parts of sulphur are added in the usual way. On separating the naphtha solution and evaporating we obtain our wax disulphide.

The high molecular weight sulphides are similarly formed from the monohalogenated hydrocarbons by the action of alkali metal sulphides. From these we may prepare both sulph-oxides, R_2SO, and sulphones, R_2SO_2.

Example 3

We add 120 parts of 30 percent hydrogen peroxide to a solution of 734 parts of our wax sulphide described in Example 2 in 1,000 parts of glacial acetic acid. The solution warms, after which it is allowed to stand at room temperature for two days. The sulphoxide is precipitated by dilution with twice the volume of water, washed, and dried.

High molecular weight polysulphides containing as much as 20–50 percent of chemically combined sulphur are prepared using the polysulphides of the alkali metals.

A great variety of sulphur-bearing, high molecular weight materials may be synthesized by condensing sulphur-bearing compounds having aromatic character with our high molecular weight halogenated hydrocarbons by means of Friedel-Crafts catalysts. Thus we may condense our monochlor wax, for example, with thiophene, thianthrene, and other heterocyclics which contain sulphur in a ring and which show aromatic character.

Example 4

To 216 parts of thianthrene, in 1,000 parts of carbon bisulphide, we add 133.5 parts of anhydrous aluminum chloride and then 386.5 parts of our monochlor wax, prepared substantialy as described, as rapidly as the refluxing and evolution of hydrogen chloride permits. The mixture is refluxed until no more hydrogen chloride is evolved and then the mixture is decomposed by poring onto ice and hydrochloric acid. After washing thoroughly to remove aluminum and chloride ions, the solution is dried and evaporated to obtain the alkylated thianthrene.

If our monohalogenated hydrocarbons be hydrolyzed to the corresponding alcohols, these are useful for various sulphur and oxygen-bearing derivatives of high molecular weight. Esters of these alcohols with sulphur-containing inorganic and organic acids are particularly interesting. By means of thionyl chloride, the alkyl sulphites of the type, R_2SO_3 may be formed. These when treated with the theoretical quantity of elemental sulphur are converted into the corresponding thiosulphates, $R_2S_2O_3$. The higher alcohols may be used to produce their sulphates through the action of sulphuryl chloride, or chlorosulphonic acid. The sulphates may also be prepared by the oxidation of the corresponding sulphites.

In preparing esters of sulphur containing organic acids, we first prepare the alcohol corresponding to our relatively pure monochlor (or monobrom) wax:

Example 5

A mixture of 386 parts of the monochlor wax prepared substantially as described above, 44 parts of caustic soda, and 400 parts of water are agitated thoroughly and heated to 400° F. under pressure for eight hours. The alcohol is separated, washed, and dried.

Example 6

We add 368 parts of this alcohol to 60 parts of boiling thionyl chloride and maintain the temperature of the mixture at 200° F. for five hours. The sulphite is then washed with water and dried.

Thiophosphates of the higher alcohols are produced by the action of thiophosphoryl chloride, $PSCl_3$. These products are useful addends to lubricants of all sorts.

Example 7

We reflux a mixture of 1,100 parts of the alcohol of Example 5 with 170 parts of thiophosphoryl chloride in 2,000 parts of xylene for eight

hours, wash with water, and then dry. On distilling off the xylene, we obtain our higher alkyl thiophosphate.

When refluxed with caustic alkalies and carbon bisulphides, the higher alcohols give rise to the alkyl xanthates, for example, octadecyl xanthate, pentacosyl xanthate, and the like.

Example 8

We pass chlorine into a commercial grade of octadecane until the weight of 254 parts has increased to 290 parts. The crude chlorination mixture, after air-blowing, is dissolved in acetone, using four times as much acetone by weight as of the chlorination mixture. On cooling to 40° F. most of the unchlorinated hydrocarbon separates and is removed by filtration. The filtrate is cooled to —20° F. and the monochlorinated hydrocarbon removed similarly. It is a liquid at room temperature.

Example 9

We heat at 400° F. in an autoclave, 145 parts of the monochlor octadecane, 22 parts of caustic soda, and 200 parts of water at 350° F. for five hours. The octadecanol is separated, washed, and dried.

Example 10

We dissolve 270 parts of octadecanol in 1,000 parts of xylene and heat with 25 parts of sodium until the latter dissolves. To the solution, we add 150 parts of carbon bisulphide and heat the mixture at 300° F. under pressure for four hours. On cooling, we wash out the sodium octadecyl xanthate with water and evaporate the solution to obtain our product.

The high molecular weight alcohols and other oxygen derivatives of paraffin hydrocarbons, such as ketones, aldehydes, esters, amides, and the like, may be converted into compounds in which more or less of the oxygen is replaced by sulphur. Such transformations may be accomplished by heating the oxygen derivative with phosphorus trisulphide or pentasulphide. Some of these reactions proceed without solvent, but in general it is advantageous to use an inert solvent such as benzene or xylene together with good stirring at a suitable reaction temperature. It will be apparent that the solvent must be selected so as to permit of the use of an adequate reaction temperature.

Example 11

We heat 368 parts of the alcohol described in Example 5 to 250° F. and pass dry air through it, absorbing the water from effluent gas until 18 parts have been absorbed. The product is essentially the high molecular weight ketone of the same molecular weight as the starting material.

Example 12

Into 1,000 parts of xylene, we introduce 366 parts of the ketone of Example 11 and 100 parts of phosphorus trisulphide and boil the mixture for six hours. The solid material is filtered off and the xylene distilled from the residual thioketone.

Alkali metal hydrosulphides act upon the higher dihalogenated paraffin hydrocarbons to form a mixture of thioketones and thioglycols, depending on whether the halogen atoms are on the same or different carbon atoms. If the halogen atoms are on adjacent carbon atoms, Vicinal thioglycols will be formed; if on non-adjacent carbon atoms, disjoined thioglycols are produced:

$$RCCl_2CH_3+2KSH \longrightarrow RC(SH)_2CH_3+2KCl$$
$$R.C{=}S.CH_3+H_2S$$
Thioketone

$$R.CHCl.CHCl.CH_3+2KSH \longrightarrow R.CHSH.CHSH.CH_3+2KCl$$
Vicinal thioglycol

$$R.CHCl.CH_2.CHCl.CH_3+2KSH \longrightarrow R.CHSH.CH_2.CHSH.CH_3+2KCl$$
Disjoined thioglycol

The process is identical with that of Example 1.

Waxy resins may be produced by the action of sulphur dioxide on our high molecular weight olefins. The reaction is advantageously catalyzed by nitric acid and various nitrates including lithium, ammonium, and silver nitrates. Perchlorates and perchloric acid are also effective catalysts. Generally the product represents equimolecular proportions of sulphur dioxide and olefin condensed together into molecular aggregates of as high as 300,000. These resins are thermoplastic and promise great usefulness. Furthermore, it is possible to produce by this means, oil-soluble materials which are useful for blending in lubricants.

Example 13

A mixture of 5 parts of ammonium nitrate and 350 parts of the wax olefin prepared substantially as described above were sealed in a bomb with sulphur dioxide under 50 pounds pressure. The bomb was heated at 210° F. for 50 hours. The bomb contents were allowed to cool and the pressure released. The product is a waxy resin of high molecular weight.

It is to be understood that any or all of the reactions here described may be carried out under atmospheric or super-atmospheric pressure. Furthermore various other factors and details of the chemical conversion may be changed within wide limits within the spirit of our invention. Most of the chemical conversions of our relatively pure halogenated hydrocarbons and olefins are admittedly old and we wish to claim only such novelty as is herein described. Our invention lies primarily in a method of obtaining high molecular weight sulphur compounds in a relatively pure state as defined and described above and we do not wish to claim the old processes. However we do wish to claim all novelty inherent in our processes as broadly as the state of the art permits.

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.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

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 a relatively pure halogenated hydrocarbon from the crude halogenated mixture, and replacing the halogen of said relatively pure halogenated hydrocarbon with a sulphur-bearing group by means of a sulphur-bearing reagent selected from the class consisting of alkali metal hydrosulphides, alkali metal sulphides, alklai metal polysulphides.

2. A method of synthesizing sulphur-bearing hydrocarbon derivatives of high molecular weight, including the steps of halogenating paraffinic hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating a relatively pure halogenated hydrocarbon from the crude halogenated mixture, and replacing the halogen of said relatively pure halogenated hydrocarbon with a sulphur-bearing group by means of an alkali metal sulphide.

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