Patented Jan. 3, 1939 2,142,934

UNITED STATES PATENT OFFICE

2,142,934

PETROLEUM SULPHONYL CHLORIDES

Herman A. Bruson and John W. Eastes, Philadelphia, Pa., assignors to Röhm & Haas Company, Philadelphia, Pa.

No Drawing. Application October 30, 1937, Serial No. 171,908

8 Claims. (Cl. 260—543)

This invention relates to mixed sulphonyl chlorides of petroleum hydrocarbons which contain not less than twelve carbon atoms in the molecule. These sulphonyl chlorides possess the general properties of being water-insoluble, heavy, viscous oils or waxy solids which readily are convertible to the corresponding sulphonates, sulphonic acids, sulphonamides or sulphonic acid esters by treatment respectively with hydroxides or carbonates of metals, water, ammonia or primary or secondary amines, and alcohols. They are useful intermediates for preparing capillary-active compounds, as their water-soluble derivatives possess foaming, wetting, emulsifying, and cleansing properties.

These aliphatically-bound mixed sulphonyl chlorides of higher petroleum hydrocarbons are readily obtained in good yields by a modification of the process developed by Treat B. Johnson and described in his application Serial No. 72,983, filed April 6, 1936.

According to the present invention a petroleum hydrocarbon mixture containing not less than twelve carbon atoms is chlorinated until at least one atomic weight of chlorine is introduced for each mol. of hydrocarbon. Two or more chlorine atoms may be introduced if desired. This chlorinated petroleum mixture is then heated with thiourea preferably in a high boiling organic solvent, such as butanol, until a sample of the product is completely soluble in water. This usually requires from 8 to 22 hours boiling. The solvent is then distilled off, leaving behind a viscous, resinous mass of the pseudo-thiourea hydrochlorides of the petroleum hydrocarbon mixture used. This material is dissolved or suspended in water and the solution is chlorinated at about 10–20° C., which causes the mixed sulphonyl chloride of the petroleum oil to separate from the water in the form of a pale yellow or white heavy oil or wax. It may be washed with cold water and can be stored for a considerable period of time without change. Or it can be dissolved in an inert organic solvent such as ether, and the water therein separated mechanically or by anhydrous sodium sulphate or other suitable dehydrating agent. The product necessarily contains the aliphatically-bound sulphonyl chlorides of all of the hydrocarbon components of the oil used, and is, of course, a complex mixture of sulphonyl chlorides.

For the purpose of this invention, we use as raw materials the mono-chlorinated or poly-chlorinated petroleum oils and waxes containing not less than 12 carbon atoms, such as are obtained by treating kerosene, naphtha, paraffin oil, petrolatum, paraffin wax, and lubricating oils of an essentially paraffinic or naphthenic character with chlorine. These chlorinate materials are usually obtained by heating the oils or waxes to about 100° C. and passing in dry chlorine, preferably in the presence of catalysts such as iodine, until the desired degree of chlorination is reached.

From these materials, mixed sulphonyl chlorides are obtained containing from 12 to upwards of 80 carbon atoms in the molecule, depending upon the fractions of the petroleum used. The chlorinated kerosenes will yield mixed sulphonyl chlorides having from about 12 to 30 carbon atoms, while the higher boiling paraffin waxes and lubricating oils and petrolatum will yield sulphonyl chlorides of from about 20 to 80 carbon atoms or thereabouts. The chlorinated petroleum fractions used may be saturated or unsaturated in character.

In order to more fully describe this invention, the following examples are given:

Example 1.—A mixture of 244 g. of dichlorinated paraffin wax (containing 14.5% chlorine), 76 g. thiourea and 250 cc. of butanol was boiled under reflux for 21 hours, after which the butanol was removed by vacuum distillation. The paraffin pseudo-thiourea hydrochloride was dissolved in 1500 cc. of water and stirred rapidly while dry chlorine was passed into the solution until no more chlorine was absorbed. The disulphonyl chloride separated as a white wax which was washed and dried.

Upon boiling this material with 25% caustic soda solution, the corresponding sodium sulphonate of the parffin wax was obtained. It can be salted out from its diluted aqueous solution by means of sodium chloride. When dried, it forms a brownish powderable solid containing aproximately two sulphonic acid groups per average mol. of paraffin wax. It is easily soluble in water to give a soapy solution.

Example 2.—A mixture consisting of 228 g. mono-chlorinated paraffin wax (containing 7.97% Cl), 39 g. thiourea and 250 cc. of butanol, was boiled under reflux for 21 hours and worked up as above. The paraffin mono-sulphonyl chloride separated as a white wax. The mono-sodium sulphonate of paraffin wax which is obtained by boiling this sulphonyl chloride with caustic soda forms a white, viscous paste having a fatty feel. It is soluble in hot water and gels on cooling. It is useful as an emulsifying agent and for softening cotton or rayon.

The paraffin sulphonamide obtained from the above sulphonyl chloride by treatment with ammonia formed a thick oil.

By heating the paraffin sulphonyl chloride with triethanolamine, the corresponding paraffin sulphonic acid ester of triethanolamine was obtained. It formed a water-soluble oil having soap-like properties.

By using 140 g. of chlorinated paraffin wax (containing 25.5% Cl) and 76 g. thiourea as above, there was obtained paraffintrisulphonyl chloride as a pale yellow, heavy oil.

The tetra sulphonyl chloride can be obtained as a pale yellow, heavy oil by using 85 g. chlorinated paraffin wax (containing 42.2% Cl) and 76 g. thiourea.

Example 3.—Commercial tri-isobutylene obtainable by the polymerization of isobutylene and containing a number of isomers having the composition $C_{12}H_{24}$ was chlorinated at 50° C. until an amount of chlorine was absorbed equal to one atomic equivalent.

200 g. of this chlorinated material was heated with 75 g. thiourea and 200 cc. butanol for 18 hours, under reflux. The butanol was removed by distillation under reduced pressure. The residue was dissolved in 1000 cc. of water and the solution was saturated with chlorine at 10–20° C. while stirring rapidly. The sulphonyl chloride separated as a yellowish heavy oil.

When boiled with water, it gave a solution of the corresponding sulphonic acid useful as a capillary-active compound. In a similar manner, chlorinated tetra isobutylene yields the mixed sulphonyl chlorides of a C_{16} mixture of olefines.

Example 4.—A mixture consisting of 250 g. of chlorinated petrolatum (containing 15% chlorine) 80 g. thiourea and 250 cc. of butanol was boiled under reflux for 20 hours. The product was worked up as in Example 1 to yield a petrolatum sulphonyl chloride, as a yellowish thick oil.

Example 5.—A mixture consisting of 250 g. of chlorinated kerosene containing 15% of chlorine, was heated with 80 g. of thiourea and 250 cc. of butanol under reflux for 20 hours. The product was worked up as set forth in Example 1. The kerosene sulphonyl chloride was obtained as a pale yellow, thick oil.

Lubricating oils or petroleum naphtha may likewise be treated to yield mixed aliphatic or hydroaromatic sulphonyl chlorides of high carbon content. Any petroleum fraction composed primarily of molecules having not less than 12 carbon atoms which is capable of chlorination is suitable for the purpose of this invention. The petroleums used may be crude or refined and may contain aromatics as impurities. Any nuclear chlorinated aromatics formed do not undergo the condensation with thiourea and are easily separated from the water-soluble pseudo-thioureas of the chlorinated aliphatic and hydroaromatic bodies. However, if alkylated or cyclo-alkylated aromatic hydrocarbons are present in the petroleum used, any aliphatically bound chlorine in these compounds will readily form pseudo-thioureas and consequently be converted to sulphonyl chlorides.

We claim:

1. A mixture of the sulphonyl chlorides of the aliphatic and cycloaliphatic hydrocarbons contained in a petroleum fraction composed primarily of molecules having not less than twelve carbon atoms.

2. A mixture of the sulphonyl chlorides of the aliphatic and cycloaliphatic hydrocarbons contained in paraffin wax.

3. A mixture of the sulphonyl chlorides of the aliphatic and cycloaliphatic hydrocarbons contained in kerosene.

4. A mixture of the sulphonyl chlorides of the aliphatic and cycloaliphatic hydrocarbons contained in a petroleum oil composed primarily of molecules having not less than twelve carbon atoms.

5. A mixture of aliphatic and cycloaliphatic sulphonyl chlorides having not less than twelve carbon atoms resulting from the chlorination in an aqueous solvent of the mixed pseudothiourea hydrohalides derived from the reaction of thiourea with the corresponding chlorinated petroleum hydrocarbons containing not less than twelve carbon atoms.

6. The process which comprises reacting a chlorinated petroleum fraction composed primarily of aliphatic and cycloaliphatic molecules having not less than twelve carbon atoms with thiourea, dissolving the resulting pseudothiourea hydrochloride in water and passing the chlorine through the solution.

7. The process which comprises reacting a chlorinated paraffin wax with thiourea, dissolving the resulting pseudothiourea hydrochloride in water and passing the chlorine through the solution.

8. The process which comprises reacting a chlorinated kerosene with thiourea, dissolving the resulting pseudothiourea hydrochloride in water and passing the chlorine through the solution.

HERMAN A. BRUSON.
JOHN W. EASTES.