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REACTION OF PETROLEUM OILS WITH
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half to Charles L. Horn, Minneapolis, Minn.No Drawing. Application June 30, 1938,
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12 Claims. (Cl. 260—504)

This invention relates to new and improved surface-active agents prepared from petroleum hydrocarbons and to methods of preparing the same.

This invention has as an object the preparation of surface-active agents from cheap sources of raw materials. A further object is the preparation of detergent and wetting agents from petroleum hydrocarbons. A still further object is the production of organic compounds from commercial white oils containing hydrocarbons of high molecular weight. A still further object is to obtain detergent and wetting agents by a method involving a few simple steps. A still further object is to obtain such compounds by an economical process involving simple apparatus. Still other objects will appear hereinafter.

The above and other objects are accomplished by treating petroleum hydrocarbons possessing certain characteristics which are set forth hereinafter with a gaseous mixture of sulphur dioxide and chlorine. The product so obtained is then hydrolyzed and neutralized with a concentrated solution of a strong alkali metal base. The crude product is purified by diluting the same with water whereupon the unreacted oil separates to the top and the aqueous layer containing an alkali metal salt of the sulphonated oil is drawn off. The solution may be further purified if desired, for example, by extraction with an oil-dissolving solvent and diluted to a standardized strength or dried. Any of the usual methods for drying detergents may be resorted to. Spray or drum drying procedures give good results. There results from this operation a surface active product of excellent wetting and detergent properties.

The refined petroleum hydrocarbons used in accordance with this invention are of fairly high molecular weight and may be normally liquids or solids. This is, they contain paraffins having an average molecular weight of at least 18 and preferably of at least 20 carbon atoms, and may contain hydrocarbons of 100 carbon atoms. The liquid hydrocarbons are preferred although the refined normally solid hydrocarbon fractions have utility, since they may be liquefied under the reaction conditions hereof.

The refined fractions have a specific gravity of at least 0.780 at 25° C. and preferably not more than 0.950. They also have an initial boiling point of at least 300° C. and an end point of at least 360° C., Saybolt Universal viscosity of 42–400 secs. at 100° F., and refractive indices of at least 1.4365 at 20° C. and preferably not

more than 1.500, and are preferably of such purity that they are not strongly discolored by treatment with 80–90% sulphuric acid at room temperature.

The invention will be further illustrated but is not intended to be limited by the following examples in which the parts stated are parts by weight:

Example I

A fraction of a crude oil from a paraffinic base boiling between 325° C. and 400° C. was treated with a gaseous mixture of sulphur dioxide and chlorine in the ratio of three parts of sulphur dioxide to one part of chlorine at a temperature of 45°–50° C. in the presence of light for four hours and then hydrolyzed with a hot solution of concentrated caustic soda. Not more than ten percent of a water-soluble product was recovered.

Example II

An oil of similar source as that described in Example I and having a similar boiling range, but which has been subjected to treatment with sulphuric acid and washed with alkali and then dried, was treated with a mixture of sulphur dioxide and chlorine and hydrolyzed according to the manner set forth in Example I, gave a yield of at least 50% water-soluble product.

In a similar manner a crude oil from a Pennsylvania oil and fractions of furnace oils from Michigan crude oil, in both of which paraffin hydrocarbons predominate, were subjected to the above treatment and yielded only small amounts of water-soluble products. In contrast, refined kerosene and white oils gave good yields of water-soluble surface-active products. These products are useful as mercerizing assistants, wetting agents, dispersing agents, rewetting agents, detergents, penetrating agents, softening agents, and other uses where surface-active compounds are desired.

Example III

Into 400 parts of a fraction of a white oil having an initial boiling point of 350° C. and an end point of 415° C., a specific gravity of 0.8390 to 0.8400 at 25° C., a Saybolt Universal viscosity of 68 sec. at 100° F., and a refractive index at 20° C. of 1.460 were passed a gaseous mixture of about 687 parts of sulphur dioxide and 354 parts of chlorine at a uniform rate over a period of three and one-half hours. The temperature of the reacting mass was 90°–102° C. The reaction was catalyzed by the light from a 60-watt electric

light bulb suspended to one side of the flask. The weight of the reaction mass increased 230 parts during this time. The reaction mass was then poured into 500 parts of 30% sodium hydroxide which had previously been heated to 75° C. The heat of the reaction raised the temperature to 90°-95° C. where it was held by cooling. The crude hydrolyzed mass was alkaline to phenolphthalein. The product was diluted with an equal amount of water and allowed to stand overnight, during which time an oily layer separated on top. The lower layer was drawn off and extracted with petroleum ether to remove a further portion of unreacted oil. The product had valuable surface active properties.

The product obtained before the hydrolysis and neutralization reaction was carried out was similar to the products obtained at this stage according to the previous examples and contained hydrocarbon sulphonyl chlorides, chloro hydrocarbon sulphonyl chlorides and chlorhydrocarbons. These products have great utility in the arts not only as intermediates for the preparation of derivatives, but in the chemical and related arts in general. Thus, they may be used in the refining and dewaxing of mineral oils and gasoline. The refining treatment may be carried out with the unhydrolyzed mixtures or the sulphonyl chlorides may be separated and used. Either the mixtures or the separated compound may be used alone or in conjunction with aromatic or saturated or unsaturated aliphatic hydrocarbons and their derivatives, e. g. benzene, chlorobenzene, benzine, carbon tetrachloride, ethanol, cyclohexanol, ethylene dichloride, trichloroethylene, etc.

Example IV

Into 500 parts of an American type white oil fraction having an initial boiling point of 355° C. and an end point of about 370° C., a specific gravity of about 0.850 a Saybolt viscosity of 300 at 100° F. and a refractive index of 1.470 were bubbled a mixture of gaseous sulphur dioxide and chlorine at a temperature of about 50° to 70° C. for about 6 hours while exposed to light from a 150 watt lamp at a distance of 12 inches. It gained about 350 parts in weight by this treatment.

The reaction mass was withdrawn from the vessel and hydrolyzed with a hot 20% caustic soda solution which was added periodically until it became slightly alkaline while maintaining the hydrolysis bath at about 60° C. It was allowed to stand over night and an oily layer formed on the surface which was separated off. The aqueous solution was clear and had excellent foaming and cleansing properties.

The new compounds of this invention dissolve to give a clear solution in water and may be used as such. They may be dried in any desired manner with or without an inorganic diluent or assistant such as sodium sulphate, any of the sodium phosphates, sodium chloride, bentonite, or other materials customarily added to textile assistants to increase their value. For example, the solution obtained according to the second example may be drum-dried in the conventional manner to yield a flaky product of excellent appearance.

The method of solubilizing these preferred hydrocarbons does not necessarily have to conform to the conditions cited in the examples, as these are merely our preferred conditions. For example, I have varied the ratio of gases intro-

duced from 1 mol of sulphur dioxide to 1 mol of chlorine to 5 mols of sulphur dioxide to 1 mol of chlorine. An excess of sulphur dioxide to chlorine is preferable in many cases, and it is often preferable to operate with 2 to 4 mols of sulphur dioxide to 1 mol of chlorine and particularly 2.5 to 3.5 mols of sulphur dioxide to 1 mol of chlorine. With some oils, such as eicosane or tetracosane, a ratio of 1 to 2 mols of sulphur dioxide to 1 mol of chlorine is preferable.

The temperature at which we react the mixed gases with the hydrocarbons may be varied over a wide range. For instance, temperatures from about 30° C. to about 110° C. have been found to be effective. Lighter colored products are obtained when the temperature is held below 70° C. The reaction proceeds faster when the temperature is above 40° C. It is preferable to operate in the range of 40° C. to 55° C. and more particularly at 45°-50° C., although it may be necessary to start the reaction at a higher temperature if the starting hydrocarbon is solid, and then reduce the temperature to 45°-50° C.

The rate of flow has been varied so that from 2 to 7 hours have been required to complete the reaction when comparable amounts of oil were involved. It is preferable to arrange the flow so that 2 to 4 hours are required to complete the reaction. The reaction may be run in the presence or absence of light, in which latter case a much longer time is necessary to complete the reaction. It is preferable to illuminate the reaction mass with a suitable light such as an incandescent electric light, an arc light such as a carbon arc, metal or metal salt cored carbon arcs, or a vapor lamp such as a mercury or rare gas lamp. The amount of mixed gases passed through the oil has an effect upon the product. It is preferable to let the reaction continue until the oil has gained a weight equivalent to the weight of one mol of sulphur dioxide plus one mol of chlorine per mol of the hydrocarbon being treated. The crude neutralized product may or may not be separated from the unreacted oil before extraction. The extraction may be made with petroleum ether, carbon tetrachloride, trichlorethylene, or any other oil-dissolving solvent. Or if desired, after separating the oily layer from the diluted neutralized material the extraction step may be omitted and the remaining oil may be removed by steam distillation or the solution dried without further removing the oil, the process of drying acting in a manner similar to steam distillation.

This invention is not to be limited to the hydrolysis procedure set forth in the examples. For instance, the concentration of caustic soda used for hydrolyzing the reaction product obtained by treating a hydrocarbon with a gaseous mixture of sulphur dioxide and chlorine may be varied from 5% to 50%. The reaction is somewhat slower with the more dilute caustic soda solutions and almost instantaneous with the more concentrated solutions. Other alkali metal hydroxides such as potassium, caesium, etc., may be used. Likewise, the alkaline earth hydroxides and oxides may be employed. An aqueous solution of ammonium hydroxide may be used to yield the ammonium salt. Substituted ammonium salts or amine salts may be obtained by hydrolyzing the product with aqueous solutions of aliphatic, cycloaliphatic, aromatic and heterocyclic amines, such as dimethylamine, ethylamine, diethylamine and triethanolamine, piperidine, diethyl-cyclohexyl-

amine, pyridine, aniline, toluidine, xylydines, β -naphthyl amine, etc. Thus, the amine salts of chlor-alkyl or alkyl sulphonic acids may be obtained. Also, the strong quaternary ammonium bases such as tetra-methyl-ammonium-hydroxide and tetra-ethyl-ammonium-hydroxide may be used for the hydrolysis. The resulting products would be the tetra-methyl-ammonium salt or the tetra-ethyl-ammonium salt of the hydrocarbon sulphonic acid.

Water-miscible organic solvents may be used during the hydrolysis or neutralization step to promote contact between the reaction mass and the hydrolyzing agents. As examples of such solvents or diluents may be mentioned ethyl, propyl, methyl, etc., alcohols, dioxane, glycol, and its ethers and esters, e. g. ethylene glycol, diethyl ether, dimethyl ether, etc.

The products obtained when the starting oil has been so refined as to have characteristics falling within the limits set forth above, have surface-active properties greatly superior to the products obtained from oils which have part but not all of the said desired characteristics. For example, an oil may have the desired distillation range but have a specific gravity higher than the desired maximum. Products obtained from this oil will be less desirable for many uses. Likewise, a poorer yield of water-soluble products may be obtained. Similarly, an oil may have a specific gravity which falls within the desired range but have a boiling range lower than that desired. The product obtained from this oil will have inferior properties.

In order to obtain an oil which has characteristics within the limits which I have disclosed it may be refined by the known refining methods, i. e. treatment with sulphuric acid and oleum, treatment with absorbing earths, distillation, fractionation, chilling, crystallization etc. During this refining the most, if not all, of the aromatic and unsaturated constituents of the oil are removed and to a greater or lesser extent the naphthenic constituents. The oil remaining is then predominantly paraffinic in nature. The distillation range specified will cover only those straight chain or normal hydrocarbons above about 20 carbon atoms and an almost infinite variety of branched chain hydrocarbons. However, it is believed that when petroleum hydrocarbons are refined to our specifications that a mixture of predominately straight chain hydrocarbons is obtained.

Thus, while it is known that water-soluble and surface-active products may be obtained by treating hydrocarbons with sulphur dioxide and chlorine, it will be apparent from the above that superior detergents may be obtained by using oils whose characteristics fall within a rather narrow range.

The products obtained before hydrolysis according to this invention are probably mixtures of hydrocarbon sulphonyl chlorides and chlor hydrocarbon sulphonyl chlorides, both mono, di- and poly, and are useful for preparing a wide variety of derivatives for which purpose the crude reaction mixture or the purified individual compounds may be used. In addition to the hydrolysis and neutralization reactions above described, they may be reacted with alcohols, either alone or in the presence of alkali metals or organic or inorganic bases to yield esters which are useful as plasticizers for cellulose derivatives and resins. Examples of such are the ethyl, butyl and hexadecyl esters.

By reactions of the sulphonyl chlorides with amines alone or in the presence of aqueous alkalies, amides and substituted amides are obtained, which products are useful as plasticizers, petroleum chemicals, and insecticides. Thus, ammonia, dimethylamine, isobutylamine, aniline, cyclohexylamine, n-dodecylamine may be used as reactants.

The products prepared according to the disclosure of this invention thus serve as intermediates for the preparation of numerous derivatives, for example, amides, sulphonyl esters, sulphinic acids, sulphonic acids and water-soluble salts which have surface activity. The hydrolyzed and neutralized compounds disclosed herein, as well as the last mentioned derivatives, may be useful as mercerizing assistants, plasticizers for paints, nitro cellulose lacquers, varnishes, Cellophane, etc., corrosion inhibitors, gum solvents for gasoline, extractants for the refining of gasoline, pour point depressants, insecticides, fly spray ingredients, weed killers, soil fumigants, cotton immunization chemicals, anti-shrinking agents for wool, foaming agents, mold inhibitors, lubricants for steel drawing and metal working, crease-proofing agents, viscose modifiers, pharmaceuticals, detergents, wetting agents, rewetting agents, for improving textile treating processes, including wool scouring, carbonizing, fulling, sizing, desizing, bleaching, mordanting, lime soap dispersing, improvement of absorption, delustering, degumming, kier-boiling, felting, oiling, lubricating, resisting cotton in an acid bath, dyeing, printing, stripping, creping, scouring viscose rayon, etc. They may also be useful in improving dye compositions, printing pastes, the preparation of lakes, the preparation of inorganic pigments and household dye preparations. They may also be useful in improving processes of dyeing leather and textiles including dyeing with developed dyes, dyeing in neutral, acid or alkaline dye baths, dyeing of animal fibers with vat dyes, etc. They may also be useful in treating oil wells and to improve flooding oil bearing sands. They may also be used to improve radiator cleaning compositions, cleansing compositions as household detergent compositions, shampoos, dentifrices, washing of paper mill felts, etc. They may also be used to improve fat liquoring and leather treatment processes as well as for fat spitting agents. They may also be useful in improving the preservation of green fodder. They may also be useful in improving the removal of fibrous layers from surfaces and in metal cleaning. They may also be used to improve flotation processes of ores, pigments, coal, etc. They may also be useful in breaking petroleum emulsions or in different concentrations as emulsifying agents. They may also be useful in improving food preparations. They may be useful in improving the cooking of wood pulp. They may also be useful in providing improved ceramic assistants and processes to improve the setting of cement. They may be useful in storage batteries and dry cells. Other uses for these products or their derivatives are as fungicides, accelerators, delusterants, extreme pressure lubricants, moth proofing agents, antiseptics, fire-proofing agents, mildew preventers, penetrating agents, antiflexing agents, tanning agents, lathering agents, dust collecting agents, antioxidant, color stabilizer in gasoline, etc.

The surface activity of some of the agents may be enhanced by electrolytes or by the addition of other surface-active agents, e. g. alkylated naph-

thalene sulphonic acids and their water-soluble salts, salts of higher alkyl sulphuric acid esters as described in Bertsch Patents Nos. 1,968,794 to 1,968,797, long chain betaine derivatives both of the C- and N- and open type which are illustrated by Daimler et al. Patent No. 2,082,275, Balle et al. 2,087,565, Platz et al. Patent 2,097,864, and Balle et al. 2,101,524, long chain ammonium, sulphonium and phosphonium compounds, as well as numerous other soap substitutes.

The hydrolysis products or water-soluble salts of the above-described sulphonyl chlorides which have surface active properties may be used in admixture with one another and/or in admixture with soap and/or soap substitutes of the prior art, for various purposes wherein soap and/or soap substitutes have previously been used or are capable of use. A few representative uses are set forth in Reed application, Serial No. 216,332, filed June 28, 1938, and it is to be understood that the products produced according to this invention may be substituted in like amount for the products of each of the examples of that case.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments hereof except as defined in the appended claims.

I claim:

1. The process which comprises reacting a petroleum hydrocarbon fraction predominating in paraffin hydrocarbons, essentially free from aromatic and unsaturated constituents said fraction having an initial boiling point of at least 300° C. and an end point of at least 360° C. with a gaseous mixture of sulphur dioxide and chlorine.

2. The process which comprises reacting a petroleum hydrocarbon fraction predominating in paraffin hydrocarbons, essentially free from aromatic and unsaturated constituents and said fraction having an initial boiling point of at least 300° C., an end point of at least 360° C., a specific gravity of at least 0.7800 at 25° C., a Saybolt Universal viscosity of at least 40 secs. at 100° F., and a refractive index of at least 1.4360 at 20° C., with a gaseous mixture of sulphur dioxide and chlorine.

3. The process which comprises reacting a petroleum hydrocarbon fraction predominating in paraffin hydrocarbons, essentially free from aromatic and unsaturated constituents and said fraction having an initial boiling point of at least 300° C., an end point of at least 360° C., a specific gravity of at least 0.7800 at 25° C., a Saybolt Universal viscosity of at least 42 at 100° F., and a refractive index of at least 1.4360 at 20° C., with a gaseous mixture of sulphur dioxide and chlorine, and hydrolyzing the resulting product.

4. The process which comprises reacting a petroleum white oil predominating in paraffin hydrocarbons, which will not appreciably discolor upon treatment with 80-90% sulphuric acid, has a specific gravity of at least 0.7800 at 25° C., an initial boiling point of at least 300° C., an end point of at least 360° C., a Saybolt Universal viscosity of at least 42 secs. at 100° F., and a refractive index of at least 1.4360 at 20° C., with a gaseous mixture of sulphur dioxide and chlorine in the presence of actinic light, and hydrolyzing the product.

5. The process which comprises reacting a petroleum white oil predominating in paraffin hydrocarbons, which will not appreciably discolor upon treatment with 80-90% sulphuric acid, has a specific gravity of at least 0.7800 at 25° C., an initial boiling point of at least 300° C., an end point of at least 360° C., a Saybolt Universal viscosity of at least 42 secs. at 100° F., and a refractive index of at least 1.4360 at 20° C., with a gaseous mixture of sulphur dioxide and chlorine in the presence of actinic light at a temperature between 30° and 110° C., and hydrolyzing the product.

6. The process which comprises reacting a petroleum white oil predominating in paraffin hydrocarbons, which will not appreciably discolor upon treatment with 80-90% sulphuric acid, has a specific gravity of at least 0.7800 at 25° C., an initial boiling point of at least 300° C., an end point of at least 360° C., a Saybolt Universal viscosity of at least 42 secs. at 100° F., and a refractive index of at least 1.4360 at 20° C., with a gaseous mixture of sulphur dioxide and chlorine in the presence of actinic light at a temperature between 30° and 110° C., and hydrolyzing the product with a solution of an alkali metal base.

7. The hydrocarbon sulphonyl chloride mixtures resulting from the process of claim 1.

8. The hydrocarbon sulphonic acid compound mixtures resulting from the process of claim 3.

9. The hydrocarbon sulphonic acid compound mixtures resulting from the process of claim 5.

10. The hydrocarbon sulphonic acid compound mixtures resulting from the process of claim 6.

11. The process which comprises reacting a petroleum hydrocarbon fraction predominating in paraffin hydrocarbons, essentially free from aromatic and unsaturated constituents said fraction having an initial boiling point of at least 300° C. and an end point of at least 360° C. with a mixture of sulphur dioxide and chlorine.

12. A process for the production of organic compounds containing sulphur, chlorine and oxygen which comprises bringing paraffinic hydrocarbons in the liquid state into contact with sulphur-dioxide and chlorine while irradiating with short-waved light.

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