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ALKYL - HYDROXY - DIPHENYL SULPHONATES AND METHOD OF PRODUCING THEM

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This invention relates to improvements in alkyl aromatic sulphonates useful as detergent, wetting, penetrating, emulsifying and like agents, and the manufacture thereof. It relates particularly to improvements in alkyl hydroxy-diphenyl compounds and their manufacture and use in washing, laundering, scouring, cleaning and like processes of removing dirt, grease, etc. from materials of various kinds, as well as for use as toilet preparations.

According to the present invention, the disadvantages resulting from the use of ordinary soaps as detergents and cleansing agents are overcome and additional beneficial results are secured by employing for detergent and general cleansing purposes compositions obtainable by processes comprising halogenation of aliphatic hydrocarbon mixtures of the type of petroleum distillates, condensation of the resulting halogenated products or selected fractions thereof with hydroxy-diphenyl compounds, followed by a rearrangement treatment, if necessary, then sulphonation of the resulting products or selected fractions thereof, and conversion of the sulphonated products to their corresponding salts.

Thus, I have found, by chlorinating a petroleum distillate such as kerosene, liquid petrolatum, and the like, condensing the chlorination product with a hydroxy-diphenyl compound, and sulphonating the resulting condensation product, compositions are obtained which, in the form of the free sulphonic acids or their salts (especially the latter), are useful for detergent, cleansing, wetting and other purposes. For example, the said sulphonation products may be used in powder or in paste form, or in solution, as wetting, dispersing, or emulsifying agents instead of the usual soaps, and/or for scouring, cleaning, washing, toilet and other purposes for which ordinary soaps have heretofore been employed, with or without the presence of, or admixture with, abrasive material, e. g. whiting, pumice, etc. They also may be employed in conjunction, or in admixture, with an ordinary soap (a higher fatty acid salt); since it has been found, according to the present invention, that the hydroxy-diphenyl sulphonation products of the present invention, when present jointly with an ordinary soap, serve to increase the detergency of the soap (whereby either a lesser amount of soap may be employed or, with the same amount of soap, a better and quicker cleansing effect may be secured), and they prevent or hinder formation of objectionable precipitates which are otherwise produced by the soap when used in hard water or in acid or salt baths. The sulphonation products of the present invention have the further advantage of being, in general, better wetting agents, of being more readily soluble in water and various organic solvents than the usual soaps, and of leaving goods washed therewith with a soft feel. Inasmuch as water solutions of said sulphonation products in the form of their alkali metal salts are neutral in reaction, they may be safely used for the washing of delicate silks and other fine fabrics, as well as for personal toilet purposes.

As is well known in the art, petroleum distillates are mainly mixtures of aliphatic hydrocarbons, including both saturated acyclic aliphatic hydrocarbons containing straight or branched carbon chains and cyclic aliphatic hydrocarbons as well as various amounts of unsaturated aliphatic hydrocarbons, depending upon the source of the petroleum and the method of distillation and/or purification. When the petroleum distillates are halogenated in the preparation of the products of the present invention, mixtures of various halogenated derivatives of the said aliphatic hydrocarbons are produced (which are generically referred to herein as "alkyl halides"), and the said mixtures of alkyl halides, when condensed with the hydroxy-diphenyl compounds, produce mixtures of alkyl hydroxy-diphenyl compounds in which the alkyl groups correspond with aliphatic hydrocarbons of the petroleum distillate from which they were produced. Accordingly, when the mixtures of alkyl hydroxy-diphenyl compounds are sulphonated, compositions are produced which contain mixtures of sulphonated alkyl hydroxy-diphenyl compounds. The present invention thus makes possible the direct obtainment of the benefits of mixed components in a relatively simple manner.

The present invention has the additional advantage that it provides a relatively simple and direct method of producing products having valuable detergent and other properites from raw material which is readily available in large quantities; thereby making feasible the economical production of such products on a commercial scale.

In general, mixtures of sulphonated products of the type herein disclosed which are obtained from aliphatic hydrocarbon mixtures boiling at temperatures falling within the range 80° C. at atmospheric pressure to 380° C. at 50 mm. pressure (and which in general contain not less than

7, and not more than 35, carbon atoms in the alkyl groups), possess such wetting and/or emulsifying action as to render them useful as soap substitutes. While all of the said mixed alkyl hydroxy-diphenyl sulphonic acids of the present invention have detersive properties, those in which the alkyl groups contain predominantly 10 to 19 carbon atoms are especially valuable as cleansing agents. The sulphonated products which are obtained from petroleum distillates having boiling points within the range of about 170° C. at atmospheric pressure to about 215° C. at 50 mm. pressure (and which it is believed contain for the most part 10 to about 19 carbon atoms per molecule) are of particular interest in connection with the present invention in view of their advantageous detersive properties.

For the purpose of this invention ortho-hydroxy-diphenyl or para-hydroxy-diphenyl may be used. Mixtures of hydroxy-diphenyl compounds also may be employed and are preferred. The hydroxy-diphenyl nucleus may be free from further substituents or it may contain one or more additional atoms or groups attached to the carbon atoms of the nucleus; as for example, a halogen atom (e. g., Cl, Br, etc.) or an alkyl group (e. g., a methyl group, etc.). If substituted hydroxy-diphenyl compounds are employed, at least two nuclear positions should be unsubstituted to permit the introduction of a sulpho group and an alkyl group.

The sulphonates may be in the form of the free sulphonic acid or in the form of a salt; for example, a salt resulting either from the replacement of the hydrogen of the sulphonic acid group with its equivalent of a metal (preferably an alkali metal) or from the addition of ammonia or an organic base.

In preparing the sulphonated products in accordance with one preferred method of procedure, an aliphatic hydrocarbon distillate of the character described above is chlorinated or otherwise halogenated in accordance with known processes for the production of chlorinated or other halogenated derivatives of aliphatic hydrocarbons, whereby mixtures comprising chlorinated or other halogenated hydrocarbon derivatives are produced; a hydroxy-diphenyl compound is then converted to a mixture of alkyl hydroxy-diphenyl compounds by a process including reaction of the hydroxy-diphenyl compound with the chlorinated or other halogenated hydrocarbon derivatives, or with a selected portion thereof; and the resulting mixture of alkyl hydroxy-diphenyl compounds, or a selected portion thereof, is then sulphonated. The resulting mixture of sulphonic acids is preferably converted into a mixture of their corresponding salts. If inorganic salts are simultaneously formed, they may be left in the mixture of said sulphonic acid salts, or they may be separated therefrom, as the use of the product may determine.

The invention will be illustrated by the following specific examples. It will be realized by those skilled in the art that the invention is not limited thereto, except as indicated in the appended patent claims. The parts are by weight, the temperatures are in degrees centigrade, and the pressure is atmospheric pressure unless otherwise indicated.

Example 1

Part 1.—Chlorine is passed into 400 parts of a kerosene boiling from about 195° to about 300° (and boiling for the most part from about 225° to 275°), having a specific gravity of 0.799 at 24°, containing about 5.6 per cent of unsaturated hydrocarbons, and having a probable carbon content ranging from 11 to 18 carbon atoms and a probable average content of about 13.4 carbon atoms, at 50° in diffused light until the reaction mixture reaches a specific gravity of 0.91. There is an increase of weight of 81 parts, 2 parts of which is due to dissolved hydrogen chloride. The resulting product comprises unchlorinated hydrocarbon in admixture with mono- and polychlorinated hydrocarbons, the average chlorine content of the mixture being equivalent to about one and one-tenth atoms of chlorine per molecule of hydrocarbon having the stated carbon content.

Part 2.—A mixture of 300 parts of the chlorinated hydrocarbon prepared in Part 1 of this example, 200 parts of para-hydroxy-diphenyl and 35 parts of anhydrous zinc chloride is heated under a reflux condenser to refluxing temperature, with agitation, for 7 hours. The mixture is cooled, a sufficient amount of ether and alcohol (equal parts) is added to dissolve the solid organic material which is present, and the alcoholic-ether solution is washed with water and distilled in vacuo. The portion boiling from 230° to 300° at 5 mm. pressure is separately collected. It is a yellow liquid comprised of a mixture of C-alkyl-p-hydroxy-diphenyls. It is insoluble in water, aqueous caustic potash and ammonia. It is soluble in alcohol, ether, benzene and alcoholic caustic alkali. Its specific gravity is less than that of water.

Part 3.—To 25 parts of the mixture of alkyl p-hydroxy-diphenyls prepared in Part 2 of this example, there is slowly added 27 parts of sulphuric acid monohydrate. The mixture is agitated at 75° for about 25 minutes, cooled, poured into water, the aqueous solution made neutral to Brom Cresol Green paper by addition of caustic soda thereto, and then evaporated to dryness. The resulting product comprises a mixture of the sodium salts of C-alkyl-p-hydroxy-diphenyl sulphonic acids. It is a white friable solid which dissolves in water, and in aqueous solutions of mineral acid or of water-soluble alkalies. The aqueous solution has great wetting and detergent powers.

It will be realized by those skilled in the art that changes may be made in the products, and in the processes of preparing and using them, hereinbefore described, without departing from the scope of the invention.

Thus, the mixed sulphonated alkyl hydroxy-diphenyl compounds of the present invention may be prepared in various ways from various fractions of petroleum distillates including straight-run products and those resulting from cracking processes. The more important sources of raw material for preparation of the alkyl hydroxy-diphenyl compounds employed as intermediate products for the production of the sulphonated products are the kerosene fractions derived from paraffinic and/or asphaltic petroleums; as for example, those obtained from Pennsylvania, Texas, or Oklahoma petroleums, those obtained from petroleum of the type of Pennsylvania petroleum being especially preferred. While those hydrocarbon fractions of petroleum distillates which contain as low as 7 carbon atoms yield sulphonated products having high wetting power and those having from about 23 to 35 carbon atoms yield sulphonated products having valuable dispersing properties, for general use as detergents, products are preferred which

are derived from petroleum distillates consisting predominantly of aliphatic hydrocarbons having a carbon content of 10 or more carbon atoms, and particularly 10 to 19 carbon atoms, and boiling for the most part between about 170° C. at atmospheric pressure and about 215° C. at 50 mm. The invention includes products prepared from various fractions of petroleum distillates and boiling over a wide or narrow range of temperatures. For general use the products are prepared from kerosene fractions of wide boiling range. For individual purposes, preferred products are obtained by employing as initial material a kerosene fraction of a narrow boiling point range. Thus, for control of desired detergent properties, fractions of petroleum distillate of small boiling range, as for example a range of 5° to 20° C. may be employed and the mixtures of alkyl hydroxy-diphenyl compounds derived from different fractions may be blended before sulphonation or the sulphonated alkyl hydroxy-diphenyl compounds derived from different fractions may be blended. The use of fractions of petroleum distillates of relatively small boiling range has the advantage of facilitating the separation by distillation of the free hydroxy-diphenyl, free hydrocarbon and alkyl hydroxy-diphenyl from each other, or of the halogenated hydrocarbons from residual unhalogenated hydrocarbons. Further, individual alkyl halides of the stated carbon content and derived from other sources may also be employed.

The chlorination of the petroleum hydrocarbon may be carried out by any well known process. The approximate extent of chlorination may be determined by the increase in the weight of the hydrocarbon material chlorinated, or by the increase in the specific gravity of the mixture. Various chlorination temperatures may be employed; for example temperatures within the range 0° to 70° C., and preferably in the neighborhood of 50° C. If desired, or necessary, the chlorination may be carried out with the aid of chlorine carriers, catalysts or adjuvants, as for example, phosphorus trichloride, iodine, sunlight, etc.

In general, the extent of chlorination of the petroleum hydrocarbon may be regulated by a weight increase corresponding to a product containing a ratio of about 0.25 to 2.5 atoms of chlorine per molecule of hydrocarbon, about 1.1 to 1.5 atoms being preferred, but it will be understood that other ratios may be used. Ordinarily, the greater the amount or extent of chlorination, the greater is the amount of high boiling residues obtained. In general, the mono-chloride boils about 15° to 20° C. higher than the petroleum distillate from which it is derived. If desired, the chlorinated products may be fractionally distilled so as to obtain a further selection and restriction of alkyl compounds having a selected content of chlorine atoms. Instead of chlorine, other halogens may also be employed, e. g., bromine, etc., in effecting halogenation.

The condensation of the halogenated hydrocarbon with the hydroxy-diphenyl compound may be carried out with the aid of other condensing agents than zinc chloride (anhydrous); as for example, metals (such as, zinc or iron), other metal halides (such as, anhydrous aluminum chloride, anhydrous ferric chloride). In general, anhydrous zinc chloride is the preferable condensing agent since, on the whole, it gives a more uniform product and better yields.

The proportion of mixed alkyl halides with respect to the hydroxy-diphenyl compound employed in the preparation of the alkylated hydroxy-diphenyl compounds may be varied. Preferably, the proportion of mixed halogenated hydrocarbons employed with respect to the hydroxy-diphenyl compound is such that not more than two long chain alkyl radicals are contained in the resulting alkyl hydroxy-diphenyl compounds, and preferably only one. Thus, at least one and three-fourths mols of hydroxy-diphenyl compound per mol of mixed halogenated hydrocarbons is preferably employed in the condensation. A ratio as low as 1 to 1 may be employed, but the yield of the resulting alkyl hydroxy-diphenyl compounds containing one long alkyl group will be less. Further, the amount of condensing agent employed may vary over a wide range. For example, in using anhydrous zinc chloride as the condensing agent, in some cases as little as 1 per cent, and in others about 5 to 10 per cent or more by weight of anhydrous zinc chloride, based upon the amount of halogenated aliphatic hydrocarbon, may be employed. The condensation reaction may be carried out at any suitable temperature. However, when zinc chloride or an equivalent condensing agent is employed, temperatures between 60° C. and refluxing are ordinarily preferred.

The duration of the condensation treatment may also be varied, the particular period of condensation being dependent to some extent upon the condensation temperature employed as well as the particular condensing agent used and nature of the desired product. The condensation is ordinarily complete in about 1 hour at refluxing temperature, or in about 3 to 6 hours at about 135° C., when employing a metal halide condensing agent. With anhydrous zinc chloride as the condensing agent, the period of heating may be extended to 16 hours or more without seriously harming the quality or decreasing the yield of alkyl hydroxy-diphenyl compounds.

The alkyl hydroxy-diphenyl compounds may be purified by fractional or steam distillation, or by other suitable processes. Purification is not essential, but it is to be noted, by the employment of mixtures of alkyl hydroxy-diphenyl compounds which have been purified by fractional vacuum distillation, products having superior detergent properties are obtained as compared to those produced when a relatively less pure mixture of alkyl hydroxy-diphenyl compounds is sulphonated.

The sulphonation of the mixture of alkylated hydroxy-diphenyl compounds may be carried out with any suitable agent, as for example, sulphuric acids of various strengths (66° Bé., 100%, 26% oleum, 65% oleum, etc.), chlorsulphonic acid, etc. The sulphonation may be carried out in the presence of inert solvents or diluents, as for example, the halogenated aliphatic or aromatic hydrocarbons (carbon tetrachloride, tetrachlorethane, ethylene dichloride, dichlorbenzene, etc.), or sulphonation may be carried out in their absence. When an inert solvent or diluent is used, it may be separated mechanically or by evaporation from the alkaline aqueous solution of the sulphonic acid salts of the alkyl hydroxy-diphenyl compounds which results upon diluting the sulphonation mass with water and adding an alkali. If desired, the sulphonation assistants may be employed; as for example, the lower fatty acids and their anhydrides (e. g., acetic acid, acetic anhydride, etc.), or the alkali metal sulphates (e. g., sodium or potassium sulphate, etc.). The

temperature at which the sulphonation is carried out may vary within wide limits. For example, temperatures as low as about 0° C. and as high as about 140° C. may be employed. In general, the more vigorous the sulphonation agent the lower is the preferred temperature. Preferred sulphonation temperatures lie between about 15° C. and about 90° C. Ordinarily, the completion of the sulphonation is carried out at a temperature of about 35° to 80° C. In using sulphuric acid monohydrate as the sulphonating agent, a temperature of about 30° to 70° C. is preferred.

The ratio of sulphonating agent employed with respect to the mixture of alkyl hydroxy-diphenyl compounds also may be varied. Thus, for complete sulphonation the sulphonating agent in terms of 100 per cent sulphuric acid may range from about 0.3 to 5 times or more the weight of the alkyl hydroxy-diphenyl compounds to be sulphonated. The extent to which the sulphonation is carried out may vary with the particular material being sulphonated, the duration or time of sulphonation, and the use to be made of the sulphonated product. In some cases, a degree of sulphonation which corresponds with a product having maximum detergent properties is not completely soluble in water to form a clear solution and/or may cause some precipitation of lime salts. On the other hand, a product which causes no precipitation of lime salts may not have maximum obtainable detergent properties because of excessive sulphonation. Furthermore, in some cases the degree of sulphonation may not be the same for products to be used as detergents in soft water, in hard water and in alkaline solutions. (As a standard of comparison, an aqueous solution of calcium chloride equivalent to 0.224 gram calcium oxide per liter of solution is employed as a standard hard water.) For use of the products in accordance with the present invention, a degree of sulphonation corresponding with maximum detergent action (approximately monosulphonation) is preferred.

The sulphonated products may be employed in the form of their free sulphonic acids or in the form of salts. They are preferably employed in accordance with the present invention in the form of salts of the alkali metals. The salts may be obtained in any suitable manner; for example, by reacting the sulphonated product with a metal oxide or hydroxide, ammonia or an organic base, or of a suitable salt of one of these, in an amount adapted to form a neutral product. Among the bases, oxides and salts which may be combined with the sulphonated products to produce salts useful as detergents in accordance with the present invention are, for example, sodium, potassium and ammonium hydroxides; sodium, potassium and ammonium carbonates and bicarbonates; ammonia; magnesium oxide; ethylamine; pyridine; triethanolamine; propanolamines; butanolamines; diamino propanol; ethylene diamine; triethylene tetramine; aniline; o-toluidine; etc.

The reaction mixtures resulting from the sulphonation of the mixed alkyl hydroxyl-diphenyl compounds may also be directly employed for the formation of mixed products, as for example, mixtures of salts of the alkyl hydroxy-diphenyl sulphonic acids and other acids present in said reaction mixtures, which mixtures of salts are also useful as detergents in accordance with the present invention. Thus, the sulphonation reaction mixture resulting from the treatment of the mixed alkyl hydroxy-diphenyl compounds with an amount of sulphonating agent in excess of that theoretically required to effect the desired degree of sulphonation may be treated with a suitable inorganic or organic base or basic salt (as for example, one of those mentioned) and the resulting mixture of the salt of the sulphonated alkyl hydroxy aromatic compounds and the inorganic salt (as for example, sodium sulphate) may be jointly isolated from the reaction mixture and employed as such as a detergent. If it is desired to produce salts of the sulphonated alkyl hydroxy-diphenyl compounds in a form substantially free from inorganic salts (for example, inorganic sulphates) this may be accomplished either by taking advantage of their greater solubility than the inorganic salts in alcohol and other organic solvents, or by using an amount of chlorsulphonic acid such that no excess, or only a relatively small excess, of same is present in the final sulphonation mass or mixture.

The sulphonated products in the form of metallic salts or salts of inorganic bases are usually yellowish to white, friable solids; and in the form of salts of organic bases vary from viscous oils to semi-solids to solids. In general, the salts are readily soluble in water and in neutral, acid or alkaline aqueous solutions to form solutions which are colorless, or faintly colored brown or yellow, which are of a soapy nature, and foam readily. Certain of the salts, such as the impure salts of organic polyamines, are oils which generally are insoluble in water but soluble in organic solvents (as for example, alcohol, benzene, gasoline, etc.), in which they exert detergent action, and in aqueous solutions of alkalies (presumably by conversion to the salts of the alkalies).

The sulphonated products may be dried in any suitable manner; as for example, on atmospheric or vacuum drum driers; in spray driers; etc. The particular type of drier employed will obviously be selected with a view to the physical nature and chemical stability of the particular product. Preferably the sulphonates derived from organic bases are dried under vacuum conditions.

The following additional examples illustrate the use of the mixed sulphonated alkyl hydroxy-diphenyl compounds hereinbefore described. They are directed to the use of the products of Example 1, in the form of the sodium salts, and containing sodium sulphate and other impurities resulting from the process of said example, unless otherwise specified. It will be understood, however, that these examples are merely illustrative and that other sulphonated products herein described may be similarly employed.

Example 2

2 parts of the alkyl hydroxy-diphenyl sulphonate product of Example 1 are dissolved in 500 parts of water. The solution is a cleaner for soiled wool or other textile materials and may be applied in any convenient or chosen manner. The solution may be made in hard water or sea water without detriment to the cleansing properties of the resulting solution.

Example 3

A mixture of 1 part of a good grade of soap (e. g., Marseilles) and 2 parts of the alkyl hydroxy-diphenyl sulphonate product of Example 1 are added to hard water in the proportion of 2 grams of the mixture per liter of water. (The hard water may contain the equivalent of, for ex-

ample, as much as 0.404 gram calcium oxide in the form of a salt in solution—so-called 42° hardness.) The presence of the alkyl hydroxy-diphenyl sulphonate inhibits the precipitation of any insoluble soap (insoluble alkaline earth metal salts of soap) in the form of curds or visible (or tacky) deposits, and improves the detergency of the solution.

In addition to their usefulness as detergents as herein disclosed the alkyl hydroxy-diphenyl sulphonates may be employed either in the form of the free acids or their metal, ammonium or organic ammonium salts as wetting, impregnating, dispersing, assisting, penetrating, insecticidal and fungicidal agents.

It is to be noted that mixtures of two or more of the sulphonated products hereinbefore referred to may be employed. Furthermore, any of the said sulphonated products or their mixtures may be employed in connection with other hydrotropic substances; dispersing, emulsifying and/or penetrating agents; aliphatic or aromatic sulphonic acids; acid alkyl esters of sulphuric acid; sulphonation products of petroleum oil; alkyl aryl sulphonates free from a nuclear hydroxyl group; and/or their derivatives.

This application is a continuation-in-part of my application Serial No. 737,777, filed July 31, 1934.

I claim:

1. An alkyl derivative of a hydroxy-diphenyl sulphonate of which the alkyl group is derived from a hydrocarbon of a petroleum distillate containing 7 to 35 carbon atoms.

2. A mixture of monoalkyl derivatives of a hydroxy diphenyl sulphonate of which the alkyl groups are derived from a petroleum distillate containing 7 to 35 carbon atoms, which is obtainable by the halogenation of the petroleum distillate to form a mixaure of alkyl halides containing 7 to 35 carbon atoms, conversion of a hydroxy-diphenyl compound selected from the group consisting of unsubstituted hydroxy-diphenyls, halogenated hydroxy-diphenyls and alkylated hydroxy diphenyls, to a mixture of monoalkyl hydroxy-diphenyl compounds by a process including reaction thereof with resulting mixed alkyl halides, and sulphonation of a resulting mixture of monoalkyl hydroxy-diphenyl compounds.

3. A mixture of alkyl derivatives of a hydroxy-diphenyl sulphonate of which the alkyl groups are derived from the hydrocarbons of an aliphatic hydrocarbon mixture which boils between 80° C. at atmospheric pressure and 380° C. at 50 mm. pressure, and obtainable by a process comprising halogenation of the aliphatic hydrocarbon mixture to form mixed alkyl halides, and condensation of resulting mixed alkyl halides with a hydroxy-diphenyl compound selected from the group consisting of unsubstituted hydroxy-diphenyls, halogenated hydroxy-diphenyls and alkylated hydroxy-diphenyls, followed by sulphonation.

4. A mixture of alkyl derivatives of a hydroxy-diphenyl sulphonate the alkyl groups of which are derived from a petroleum distillate which boils between 80° C. at atmospheric pressure and 380° C. at 50 mm. pressure.

5. A mixture of alkyl derivatives of a hydroxy-diphenyl sulphonate the alkyl groups of which contain from 10 to 19 carbon atoms and are derived from mixed alkyl chlorides resulting from chlorination of a petroleum distillate which boils mainly between 170° C. at atmospheric pressure and 215° C. at 50 mm. pressure.

6. A mixture of alkyl derivatives of a hydroxy-diphenyl sulphonate the alkyl groups of which are derived from a kerosene fraction of paraffinic petroleum boiling for the most part between 170° C. at atmospheric pressure and 215° C. at 50 mm. pressure.

7. A mixture of monoalkyl derivatives of para-hydroxy-diphenyl sulphonate of which the alkyl groups are derived from a halogenated Pennsylvania petroleum distillate which boils mainly between 170° C. at atmospheric pressure and 215° C. at 50 mm. pressure.

8. A method of making a sulphonated product which comprises condensing a mixture of alkyl halides containing at least 7 carbon atoms with a hydroxy-diphenyl compound selected from the group consisting of unsubstituted hydroxy-diphenyls, halogenated hydroxy-diphenyls and alkylated hydroxy-diphenyls, with the aid of a metal halide condensing agent, and sulphonating resulting mixed alkyl hydroxy-diphenyl compounds.

9. A method of making a sulphonated product which comprises condensing a mixture of alkyl chlorides containing 10 to 19 carbon atoms with a hydroxy-diphenyl compound selected from the group consisting of unsubstituted hydroxy-diphenyls, halogenated hydroxy-diphenyls and alkylated hydroxy-diphenyls, with the aid of a metal halide condensing agent, and sulphonating resulting mixed alkyl hydroxy-diphenyl compounds.

10. A method of making a sulphonated product, which comprises halogenating an aliphatic hydrocarbon mixture which boils between 80° C. at atmospheric pressure and 380° C. at 50 mm. pressure, to form a mixture of alkyl halides, condensing a resulting mixture of alkyl halides with a hydroxy-diphenyl compound selected from the group consisting of unsubstituted hydroxy-diphenyls, halogenated hydroxy-diphenyls and alkylated hydroxy-diphenyls, and sulphonating.

11. A method of making a sulphonated product, which comprises halogenating a petroleum distillate which boils mainly between 170° C. at atmospheric pressure and 215° C. at 50 mm. pressure to form a mixture of alkyl halides containing predominantly between 10 and 19 carbon atoms, condensing resulting mixed alkyl halides with a hydroxy-diphenyl to produce a mixture of alkyl hydroxy-diphenyls, and then sulphonating a mixture of said alkyl hydroxy-diphenyls.

12. A method of making a sulphonated product, which comprises chlorinating a Pennsylvania petroleum distillate which boils mainly between 170° C. at atmospheric pressure and 215° C. at 50 mm. pressure, carrying out the chlorination under conditions resulting mainly in the formation of alkyl monochlorides, condensing the resulting mixture of alkyl monochlorides with para-hydroxy-diphenyl with the aid of a metal halide condensing agent, and sulphonating a resulting mixture of alkyl derivatives of para-hydroxy-diphenyl.

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