

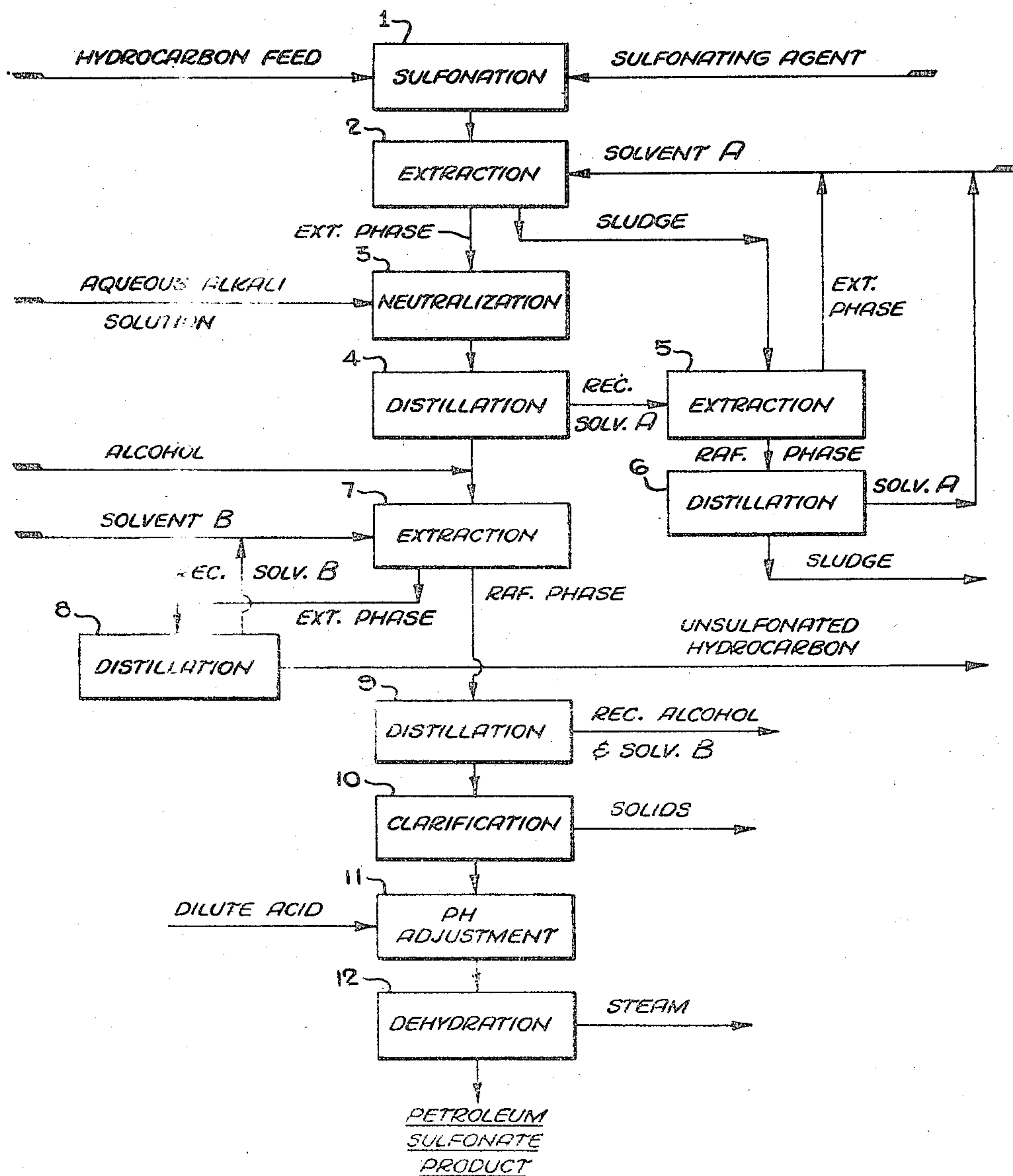
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WATER-SOLUBLE PETROLEUM SULFONATES

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WATER-SOLUBLE PETROLEUM  
SULFONATES

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This invention relates to the production of sulfonic derivatives from hydrocarbons and is particularly directed to the preparation of water-soluble petroleum hydrocarbon sulfonates which are highly active detergents. This invention further relates to a method of producing a particular fraction of petroleum sulfonic acids by an improved method of sulfonation of a selected hydrocarbon feed stock to obtain sulfonic acids and to a method of fractionating these sulfonic acids so as to separate those which are highly detergent as alkali metal salts and are both oil- and water-soluble.

The preparation of organic sulfonic acids and of organic sulfonates for use as detergents having many of the desirable properties of soap is well known in the art. The sulfonic acids as such find wide usage in the textile, leather, paper, glue, petroleum and other industries. The sulfonation product obtained from sulfonating a phenol-aldehyde condensation is used as an aid in leather treating. The alkali metal salts of sulfonated mineral oils are employed alone or in mixtures with fatty acid soaps as efficient surface-active agents. The sulfonation of tetrahydrobenzene, propylene, trichloroethylene, butyl naphthalene, or stearic, oleic, palmitic acids, produces sulfonation products which are efficient wetting or emulsifying agents. Certain sulfonation products obtained by sulfonating the higher molecular weight aromatic hydrocarbons and other compounds are employed in dyeing. The derivatives of isethionic acid with oleic acid and its derivatives are used as detergents. Certain sulfuric acid esters such as esters of cetyl, stearyl, and palmityl alcohols, which are related to sulfonic acids, are used as detergents.

Preparation of these sulfonic acids may be accomplished by contacting the proper raw material with a sulfonating agent under proper conditions for the formation of the desired product. The variety of sulfonating agents is quite large and includes sulfonating agents of widely differing activity from the stronger sulfonating agents such as oleum to the milder sulfonation agents such as sulfur dioxide. These sulfonating agents include concentrated sulfuric acid, oleum, sulfur trioxide, acid sulfates and polysulfates, chlorosulfonic acids, sulfur dioxide, sulfides and acid sulfites, hydrosulfides, N-pyridinium sulfonic acid, aminosulfonic acids, and the like. Generally, concentrated sulfuric acid, oleum, or chlorosulfonic acid are usually employed because of their high reactivity, low cost and ready availability. These sulfonating agents are also nearly always

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employed in the sulfonation of difficultly sulfonatable materials such as naphtha or paraffin hydrocarbons of mineral oil fractions, etc.

The sulfonation of the wide variety of the materials listed above in the preparation of wetting agents, detergents, emulsifying agents, surface-active agents, etc. by using any one or a combination of the sulfonating agents also illustrated above is nearly always a complex and expensive operation. The expense of preparing such detergents in general arises from the requirement that the material being sulfonated must be a relatively pure material and the sulfonating agent employed is often costly. I have found that equally effective detergents, wetting agents, etc. may be prepared by the process of the present invention as hereinafter more fully described by using a particular mineral oil fraction, an inexpensive sulfonating agent, and fractionating the sulfonic acids formed so as to recover the most desirable types. The sulfonation of a mineral oil fraction containing paraffin, naphthene, aromatic or condensed ring hydrocarbons found in such mineral oils for the production of desirable petroleum sulfonic acids requires the stronger sulfonating agents. Concentrated sulfuric acid as the strong sulfonating agent is perhaps one of the least expensive of the reagents suitable to perform the sulfonation according to this invention. The sulfonation product thus obtained and particularly the salts formed from the sulfonation product have been found to be excellent emulsifying and wetting agents and perform at least as well as those prepared from the more expensive relatively pure raw material. It is to the improvement in the method of production of petroleum sulfonates and to the production of improved soluble petroleum sulfonates that this invention is directed.

It is a primary object of this invention to provide an improved process for the production of petroleum sulfonic acids and of petroleum sulfonates.

A further object of this invention is to provide a process for the sulfonation of selected mineral oil fractions and thereby produce a particularly desirable fraction of petroleum sulfonic acids.

It is an additional object to provide a sulfonation process whereby a selected fraction of oil- and water-soluble sulfonic acids may be produced from a selected hydrocarbon fraction with substantially no simultaneous formation of oil- or water-insoluble sulfonic acids.

A correlative object of this invention is to provide an economical process for the production of



surface-active agents from selected hydrocarbon fractions.

Another object of this invention is to provide an oil- and water-soluble sulfonate prepared from selected petroleum hydrocarbon fractions, the petroleum sulfonate being a highly active detergent.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly, this invention comprises the sulfonation of a selected hydrocarbon fraction with a concentrated sulfonating agent so as to produce a particular fraction of hydrocarbon sulfonic acids which are both oil- and water-soluble and which form metal salts which are highly detergent. The crude sulfonation product is subsequently quenched and extracted with a first organic solvent in order to cool the crude product, thereby stopping the sulfonation reaction and to extract from the sulfonation product the particularly desirable fraction of sulfonic acids of this invention. This first extract phase thus formed and which contains the oil- and water-soluble sulfonic acids is thoroughly mixed with a solution of a basically reacting compound thereby forming the corresponding salts of the sulfonic acids and forming simultaneously a stable emulsion containing water, the first organic solvent, the unsulfonated hydrocarbon and the sulfonate salts. This emulsion is subsequently distilled to effect recovery of the first organic solvent which is reemployed in the process and the distillation residue is treated with a water-soluble alcohol to break the aforementioned emulsion. The distillation residue and alcohol is further extracted with a second organic solvent in order to effect separation of the sulfonate salts from the unsulfonated hydrocarbon. The second organic solvent dissolves the unsulfonated hydrocarbon and removes this material as a second extract phase which is subsequently distilled to recover the second organic solvent. The raffinate phase which consists of an aqueous solution of the sulfonate salts is subsequently dehydrated and the sulfonates recovered in substantially pure form as a very light colored free flowing powder.

The present invention may be more clearly understood and the sequence of steps in the process according to my invention may be more lucidly described by reference to the accompanying drawing. This drawing is a schematic flow diagram of the improved hydrocarbon sulfonation process and depicts and integrates the twelve essential steps thereof.

Referring now more particularly to the drawing, the hydrocarbon feed introduced into step 1 is thoroughly contacted under carefully controlled temperature conditions with a sulfonating agent also introduced into step 1. The mixing of these two materials may be carried out in any form of a reactor in which thorough contact of the sulfonating agent and the hydrocarbon feed may be effected and in which simultaneously the heat of reaction liberated may be removed quickly so as to maintain the desired temperature. I have found that these requirements may be fulfilled by contacting the hydrocarbon feed with the sulfonating agent in a horizontal cylindrical reactor which is provided on the outside with a jacket and on the inside with a horizontal rotatable shaft on the same horizontal axis as the cylindrical reactor. The horizontal shaft is provided with longitudinal blades affixed thereto which

continuously scrape the inside surface of the cylindrical reactor. The continuous scraping of the inside surface of the reactor by the blades attached to the rotating shaft assures intimate mixing of the hydrocarbon feed with the sulfonating agent and simultaneously assures good transfer of heat from the sulfonation reaction through the wall of the cylindrical reactor into a heat transfer medium circulated through the outer jacket. Proper selection of the heat transfer medium permits virtually any sulfonation temperature to be maintained within quite narrow limits. Such a reactor as just described and which is well suited to the sulfonation process according to the present invention is commercially available and known to the trade as a Votator manufactured by the Girdler Corporation of Louisville, Kentucky, and is generally described in United States Patents Nos. 2,063,065 and 2,063,066, issued December 8, 1936.

The hydrocarbon feeds from which the soluble petroleum sulfonates according to the present invention are prepared are selected non-lubricating straight run non-cracked fractions of petroleum hydrocarbons, the major portion of which boils at temperatures greater than 500° F., such as between about 500° F. and 800° F. Petroleum distillates prepared during the course of crude petroleum refining and which have a viscosity of less than about 110 SUS (Saybolt Universal Seconds) at 100° F. are suitable. Distillates in particular which have viscosities ranging between about 40 and 110 SUS at 100° F. are applicable. Preferably, distillates having viscosities of between 60 and 100 SUS at 100° F. are used as the hydrocarbon feed employed in step 1 of the present sulfonation process.

Such distillates often include such materials as nitrogen bases, naphthenic acids, phenols, and the like, constituents which lend no improvement to the desired sulfonate product. The hydrocarbon feed may be pretreated to remove these extraneous materials by acid treating eliminating such constituents as nitrogen bases and olefinic materials, if present, which increase the sulfonation acid consumption. Naphthenic acids, phenols, and the like, may be removed by caustic washing, if desired.

Very often in petroleum refining, petroleum extracts are available such as those produced in the sulfur dioxide or sulfur dioxide-benzene treatment of petroleum distillates or other fractions according to the well known Edeleanu process. These extracts contain a higher concentration of aromatic type hydrocarbons and therefore contain a higher percentage of sulfonatable materials. These particular petroleum fractions have been found to produce a desirable water-soluble sulfonate product when treated according to the improved process of the present invention. Extracts suitable to the sulfonation process according to this invention are desirably those having viscosities between about 50 and 180 SUS at 100° F.

In addition to distillates and extracts which are both suitable as hydrocarbon feeds in the present process, selected intermediate fractions of hydrocarbons produced in refining operations may also be employed. These intermediate fractions are exemplified by those materials which are produced during the repeated solvent extraction of a hydrocarbon stock or produced by the addition of a nonsolvent to an extract phase which serves to reject a portion of the extract. Other methods are obviously available to produce



such intermediate fractions but in general the desirable intermediate fractions include those constituents which lie between the extremes of the insoluble and soluble constituents present.

The sulfonating agent employed in step 1 to form the selected sulfonic acids from the preferred hydrocarbon distillates include the stronger and more active sulfonating agents. For certain hydrocarbon feeds the less active agents may be employed. In order to obtain an efficient yield of the desired sulfonic acids the best suited sulfonating agents include strong sulphuric acid, oleum, sulfur trioxide, either in liquid or vapor phase, and chlorosulfonic acid. Of these, strong sulfuric acids having a concentration greater than 80% and preferably a concentration of between about 85% and 99% have been found to be the preferred sulfonating agent for reasons of economy, sulfonation activity, and ready availability.

The quantity of sulfonating agent employed in step 1 in relation to the quantity of hydrocarbon feed to be sulfonated is an important factor in obtaining good yields of satisfactory sulfonic acids. I have found that the volumetric ratio of strong sulfuric acid to hydrocarbon feed should, in general, be less than 0.5 which corresponds to a ratio of one volume of sulphuric acid for every two volumes of hydrocarbon feed. In the preparation of sulfonic acids from selected petroleum distillates as hereinbefore defined, the volumetric acid to feed ratio preferably ranges between about 0.1 and 0.3. Such a volumetric ratio has been found to result in the formation of very satisfactory sulfonic acids and soluble sulfonates. In the preparation of sulfonic acids from the extracts or intermediate fractions previously described which contain a somewhat higher concentration of sulfonatable constituents the desirable ratio of volumes of acid to volumes of feed is between about 0.2 and 0.5, and may under certain circumstances run as high as 0.8.

Another important consideration in obtaining satisfactory oil- and water-soluble sulfonates from the selected hydrocarbon distillates is the temperature and duration of the sulfonation reaction. The preferred conditions of time and temperature in the preparation of sulfonated products from the preferred hydrocarbon distillates in the sulfonation reactor previously described is a residence time of about three minutes and an outlet crude sulfonation product temperature of about 200° F. Although these are the preferred conditions a somewhat modified product may be obtained by employing residence times as high as about fifteen minutes when the crude sulfonating product is removed from the reactor at a temperature of as low as about 50° F. Residence times of less than three minutes, for example, as low as about one-half minute are feasible when outlet temperatures as high as about 300° F. are employed. With distillates which are readily sulfonatable, residence times of less than one minute may be employed at temperatures above about 250° F. The optimum conditions of three minutes residence time and 200° F. outlet temperature was arrived at for consideration of the rate of decomposition of sulfonic acids at temperatures above 200° F. and the low rate of sulfonic acid production at low temperatures with high residence times. It is therefore desirable to maintain the lowest possible residence time by operating at the highest possible sulfonation temperature

without excessive degradation of the desired sulfonic acids.

The crude sulfonation product comprising unsulfonated hydrocarbon feed, sulfonic acids formed in step 1, and sulfuric acid sludge is removed from step 1 and introduced into step 2, as indicated on the accompanying drawing. In step 2 the crude sulfonation product is extracted with an aromatic organic solvent indicated on the drawing as Solvent A. The extraction step 2 may be conveniently carried out in a vertical column packed Berl saddles, Raschig rings, or other packing in which an efficient extraction of the crude sulfonation product by means of Solvent A is accomplished. This extraction may also be carried out in a series of mixing vessels by introducing the crude sulfonate product into the first vessel and continuing on through the series to be mixed and extracted with Solvent A introduced into the last vessel.

The extraction of the crude sulfonation product by means of Solvent A in step 2 results in a quick reduction in the temperature of the crude sulfonate product thereby quickly stopping the sulfonation reaction. The quenching of the sulfonate product by means of a cooling stream of Solvent A halts the sulfonation reaction at a desired point and minimizes the amount of sulfonic acid degradation. Solvent A also serves to fractionate the desirable water-soluble and oil-soluble sulfonic acids from the crude sulfonation product and effects a rejection of the darker colored undesirable acids to the sludge and retains the lighter colored oil- and water-soluble sulfonic acids in the extract phase. The operations of step 2 may also be performed by mixing Solvent A with the sulfonation product followed by a centrifuging operation to separate the sludge. The extract or Solvent A phase produced in step 2 comprises a solvent solution of unsulfonated hydrocarbon feed together with the desirable sulfonic acids and a small amount of sulfuric acid. The raffinate or sludge phase comprises the sulfuric acid sludge which is subsequently treated as hereinafter more fully described prior to disposal.

The quantity of Solvent A introduced into step 2 to accomplish the previously described operations varies with the type of hydrocarbon feed being sulfonated. In sulfonation of the preferred type of hydrocarbon feed, that is, selected hydrocarbon distillates, the ratio of the volume of Solvent A introduced into step 2 to the volume of hydrocarbon feed introduced into step 1 is about 1.0. However, depending upon the type of distillate employed the Solvent A to hydrocarbon feed ratio may vary between about 0.5 and 3.0. When the hydrocarbon feed being sulfonated comprises extracts which contain an increased concentration of sulfonatable constituents the quantity of Solvent A employed is somewhat greater. The ratio of the volumes of Solvent A to the volume of the hydrocarbon feed in the latter case is generally about 2.0, but may vary from about 1.0 to 4.0 or more, depending upon the characteristics of the particular extract. It is preferred that the temperature of Solvent A be low, for example, at the ambient temperature, because of the fact that the introduction of cool solvent exerts a quenching action on the sulfonation reaction. In particular cases where distillates are employed and a somewhat lower ratio of solvent to feed is employed it is sometimes of advantage to cool the solvent to a temperature as low as about 60° F. in order to more quickly stop the sulfonation reac-



tion. In other cases where the ratio of solvent to feed is higher the solvent need not be cooled but may be introduced at temperatures of about 100° F. or higher. However, a solvent at the ambient temperature or about 80° F. is preferred.

Particular solvents which fulfill the requirements of Solvent A hereinabove disclosed include such aromatic solvents as benzene and its homologs such as toluene, ethyl benzene, xylene, and aromatic hydrocarbons containing less than about ten carbon atoms per molecule, chlorinated benzenes and chlorinated homologs of benzenes such as chlorobenzene and chlorotoluene, etc., together with the normally liquid chlorinated aliphatic hydrocarbons such as carbon tetrachloride, dichloroethylene, etc. Of these particular solvents the preferred solvent in general comprises benzene. As Solvent A, therefore, pure benzene as prepared from petroleum or from coal tar distillates, or aromatic concentrates, extracts prepared from aromatic gasoline and therefore containing benzene homologs besides benzene, and the like, are likewise applicable.

The extract phase produced in step 2 and, with the preferred Solvent A, comprising a benzene solution of sulfonic acids and unsulfonated hydrocarbon feed is introduced into step 3. Within step 3 the benzene solution is thoroughly mixed with an aqueous solution or slurry of a basically reacting agent forming an emulsion of sulfonate salt, solvent, water and unsulfonated hydrocarbon. It is preferred that this aqueous solution be introduced at a temperature of about 120° F., although temperatures as low as room temperature to temperatures higher than 120° F. are applicable. Elevated temperatures, however, are to be avoided in order to minimize sulfonic acid decomposition. Although sulfonates may be prepared by using amines and other nitrogen bases as the basically reacting agent, the preferred neutralizing agent is a basically reacting compound of an alkali metal such as the bicarbonate, the carbonate or the hydroxide of sodium, potassium, or lithium. Because of its availability sodium hydroxide is the preferred alkali metal compound employed to neutralize the sulfonic acids in step 3, although obviously other basically reacting alkali metal compounds may be employed depending upon the particular alkali metal desired in the finished water- and oil-soluble sulfonate. The concentration of this neutralizing solution is preferably between about 5% and 15% by weight in water, the proper concentration being determined by the quantity of water introduced into the system. For subsequent steps a certain amount of water is desirable and it is well to introduce the required amount of water in step 3. The petroleum sulfonic acids, being quite strong acids, are somewhat corrosive and are apt to be contaminated by dissolved iron resulting from corrosion of the materials of construction employed in the equipment used in the first two steps. The iron contamination results in the formation of a dark colored sulfonate salt product which is undesirable.

The quantity of sodium hydroxide introduced into step 3 to form the soluble sulfonates according to this invention is, therefore, preferably somewhat in excess of the theoretical quantity required to convert the sulfonic acids and sulfuric acid present to their sodium salts, forming a slightly alkaline emulsion and thus precipitate the iron as insoluble hydroxides. A slight excess of sodium hydroxide such as from about 1% to as high as about 15% may be employed in step 3 to

neutralize the sulfonic acids and also causes the precipitation of iron hydroxide which may subsequently be separated. The resulting liquids have a pH somewhat greater than 7.0 thereby substantially eliminating acidic corrosion of equipment. Excesses of sodium hydroxide to give a pH of about 7.0 to 10.0 have been found desirable.

The neutralized material formed in step 3 and consisting of water, benzene, unsulfonated hydrocarbon feed, sodium sulfonate and a small amount of excess sodium hydroxide is in the form of a first emulsion and is transferred from step 3 to step 4 wherein this emulsion is heated and distilled to effect the recovery of the Solvent A or benzene. Because of the presence of water in the emulsion the benzene is removed overhead together with water and the operation is in essence a steam distillation. In step 4 better than 90% of the benzene is recoverable by distillation and is ultimately returned and used as Solvent A in the extraction of the crude sulfonation product in step 2. Benzene and other solvents which may be employed as Solvent A are quite soluble in the aqueous sodium sulfonate part of the emulsion and therefore a distillation as carried out in step 4 is necessary to effect a substantially complete benzene or Solvent A recovery.

The sludge produced from step 2 contains a small amount of Solvent A together with a certain amount of the desirable soluble petroleum sulfonic acids. For this reason, the sludge is introduced into step 5 and is extracted by means of Solvent A recovered from step 4. An extract phase is produced consisting largely of Solvent A and contains substantially all of the desirable sulfonic acids present in the sludge. A raffinate phase is also produced consisting of the sludge and a small amount of Solvent A. The extraction in step 5 may be carried out in a counter-current continuous manner in a packed extraction column or in a series of mixing vessels as previously indicated in connection with the description of step 2. The extract phase produced in step 5 is returned and introduced into step 2 together with fresh Solvent A.

The raffinate, or sludge phase, produced in step 5 is introduced into step 6 wherein a distillation of the sludge is effected preferably under conditions wherein the sludge acid is not appreciably diluted, thereby avoiding excessive corrosion of dilute acid. Such a distillation is preferably carried out under reduced pressure whereby the quantities of Solvent A remaining with the sludge extracted in step 5 are removed. The Solvent A present usually amounts to between 5% and 10% of the total quantity used and may be combined with the extract phase from step 5 for return to step 2 for reuse. The extracted and distilled sludge is removed from step 6 and discarded or sent to storage.

The distillation bottoms produced in step 4 and consisting of an aqueous solution of sodium sulfonate and the unsulfonated hydrocarbon feed associated together as a second emulsion is mixed with an alcohol to break the emulsion and is introduced into step 7 for further treatment as hereinafter more fully described. The alcohol is preferably a low boiling water-soluble aliphatic alcohol having less than four carbon atoms per molecule. It has been found that isopropanol is well suited for use at this point in the process, although ethanol and methanol are also applicable and may be used if desired.

The quantity of alcohol introduced may vary



between considerable limits, however, it has been found than an ideal composition of the material introduced into step 7 contains about five gallons of isopropanol (anhydrous) for every 100 pounds of sodium sulfonate together with about 25 gallons of water, which mixture usually also contains of the order of 20 pounds of solubilized unsulfonated hydrocarbon feed. The isopropanol must not necessarily be added in its anhydrous form so long as the composition given above is approximated. These compositions usually exist as two phases, an aqueous phase containing predominantly water, alcohol, sodium sulfonate and sodium sulfate, and an oil phase containing predominantly unsulfonated hydrocarbon. Sometimes when somewhat larger amounts of sodium sulfate are formed, three phases result which include a water and sodium sulfate phase, an alcohol-water-sodium sulfonate phase, and an unsulfonated hydrocarbon phase.

The aqueous and oil phases are introduced together into step 7 wherein they are extracted by a Solvent B in an extraction tower or other means indicated as applicable in previous extraction steps. The function of Solvent B in step 7 is to separate unsulfonated hydrocarbon feed from the material introduced from step 4. Certain requisites of Solvent B must be closely adhered to in order to obtain satisfactory petroleum sulfonate product. Solvent B should be free from odoriferous constituents such as some organic compounds of nitrogen and sulfur which have been found to impart undesirable odors to the product. Solvent B is required to have a high solvent power for the type of hydrocarbon which is unsulfonated in step 1. I have found that a paraffinic naphtha boiling in the lower gasoline range, such as from about 100° F. to 300° F. and containing paraffin hydrocarbons having between about 4 and 10 carbon atoms per molecule is suitable for use as Solvent B in the step 7 extraction and that a sufficient separation of the unsulfonated hydrocarbon feed is obtainable. A petroleum naphtha such as that just described is the preferred form of Solvent B although other materials of the same general character may be employed. If available, pure pentanes or hexanes may be employed as Solvent B and even paraffin hydrocarbons having as few as three carbon atoms per molecule may be employed as Solvent B by conducting the extraction in step 7 under a suitable elevated pressure. The use of low molecular weight paraffin hydrocarbons such as propane has been found to be advantageous because of the ease of removal of the solvent from the extract and traces of solvent from the raffinate produced in such an extraction.

It is possible to produce a sulfonate product which contains as low as about 0.5% by weight of unsulfonated hydrocarbon feed by employing a low boiling naphtha rich in hexanes as Solvent B, and using an extraction column which contains the equivalent of about five equilibrium stages. Temperatures between about 140° F. and 200° F. are preferred for this extraction operation, however, temperatures as low as about 60° F. may be employed, particularly when propane is used as a solvent.

The extract phase produced from step 7 and comprising a naphtha solution of the unsulfonated hydrocarbon feed is introduced into step 8 wherein the extract phase is distilled. An overhead product of Solvent B is obtained and returned to step 7 as previously described. The distillation bottoms produced in step 8 com-

prises the unsulfonated hydrocarbon feed substantially free of Solvent B.

The raffinate phase produced from the step 7 extraction and comprising a water solution of sodium sulfonate and a small amount of sodium sulfate together with alcohol and a small amount of Solvent B is introduced into step 9 and distilled at a temperature of around 200° F. to recover a substantial amount of the alcohol and remove substantially all of the Solvent B present. The distillation in step 9 may be carried out by simple heating, or with the aid of steam and/or vacuum to facilitate the removal of the alcohol and Solvent B at as low a temperature as is possible. It is desirable to avoid overheating of the sodium sulfonate product although the sulfonates are not as thermally sensitive as the parent sulfonic acids. The overhead product obtained in the distillation of step 9 may be retreated to separate the alcohol and Solvent B. The distillation bottoms from step 9 comprising a concentrated aqueous solution of the sodium sulfonate product is introduced into step 10 for clarification.

It is highly desirable that soluble petroleum sulfonates be substantially free of suspended solids or color bodies such as iron hydroxides and it is to this end that an excess of sodium hydroxide or other basically reacting neutralizing agent is employed in step 3. In step 10 the aqueous sodium sulfonate solution may be treated in a centrifuge or in settling basins to permit the removal therefrom of any solid materials. Iron hydroxide introduced through corrosion is removed from the alkaline solution in this manner. Step 10 may also comprise an adsorbent treatment whereby color bodies are adsorbed from the solution if present. It is sometimes feasible to employ a filter in step 10 for clarifying the sodium sulfonate solution. Under proper control a substantially clear aqueous solution of sodium sulfonate product is produced from step 10.

It is often desirable to increase the quantity of sodium sulfate present over the amount which normally is present in the product as previously described. The sodium sulfate may be introduced into the aqueous sulfonate solution immediately before dehydration step 12 in which the solid product is obtained. When this is done quite concentrated sodium sulfate solutions may be added. In another method, the sodium sulfate may be added to the aqueous raffinate prior to clarification step 10, in which case any impurities may be removed from the sodium sulfonate.

The aqueous solution of sodium sulfonate produced in step 10 is introduced into step 11 wherein a required amount of dilute acid is added in order to neutralize the remaining excess of sodium hydroxide or other neutralizing agent present. The dilute acid employed is preferably sulfuric acid since a certain amount of sodium sulfate invariably arises in step 3 by neutralization of the small quantity of sulfuric acid present in the extract phase produced from step 2 as previously mentioned.

The aqueous sodium sulfonate product solution discharged from step 11 having a pH of about 7 is introduced into step 12 wherein the solution is dehydrated for the production of the sodium sulfonate product as a granular solid. The apparatus involved in step 12 may comprise an evaporator followed by a spray drier, or may comprise an evaporator followed by



evaporators wherein sodium sulfonate may be separated in substantially pure form from the sodium sulfate which is present. The apparatus may consist of low pressure evaporator feeding a highly concentrated solution of sodium sulfonate into a drum or vacuum tray drier, or the like. A considerable quantity of steam is produced from step 12 together with the alcohol which was not recovered during the distillation of step 9, and it is desirable that the alcohol containing vapor thus produced be returned to the process. This material may be employed in making up the aqueous neutralization solution or fed to an alcohol recovery unit which may conceivably follow step 9. The solid petroleum sulfonate product produced according to the process just described in general contains between 75% to 85% by weight of a water-soluble sodium sulfonate and between about 15% and 25% by weight of sodium sulfate. The latter percentage may be increased by adding sodium sulfate to the solution introduced into step 10. If in step 12 a spray drier is employed the product is a nearly white free-flowing finely divided powder which is highly soluble in water and mineral oils and in solutions of brine. In case the sodium sulfonate solution was dehydrated in conjunction with a drum drier, or the like, the product may be in the form of a granular solid having larger particle sizes.

Absolute quantities and characteristics of the operation as applied to a particular hydrocarbon feed may be more readily understood by reference to the following example:

#### Example I

The hydrocarbon feed employed in a specific sulfonation operation according to this invention comprised a spray oil distillate boiling in the range of from about 500° F. to about 800° F. and having the following properties:

Gravity, 22.0° A. P. I.  
Viscosity at 100° F., 85.6 S. U. S.  
Viscosity at 210° F., 36.5 S. U. S.  
Acid solubility, 36% by volume  
Flash point, 295° F.  
Fire point, 320° F.  
Pour point, -55° F.  
Color, 4¾ N. P. A.

The sulfonation of 65 gallons or about 500 pounds of spray oil distillate having the above-described properties was carried out with 182 pounds of 98% sulfuric acid as the sulfonating agent. The sulfonation reaction was conducted in a Votator, with hot water passing through the jacket of the sulfonation reactor. A residence time of three minutes and a crude sulfonation product outlet temperature of 200° F. was employed in this operation.

The crude sulfonation product obtained from the Votator was mixed with 65 gallons of benzene at 80° F., an amount which corresponded to a spray oil distillate-benzene ratio of 1.0. Over the period of the run 65 gallons of benzene were added. The crude mixture resulting was centrifuged and the benzene-extract phase and the raffinate sludge phase separated.

The benzene-extract phase, containing the desirable sulfonic acids according to this invention, was neutralized at about 120° F. with an aqueous solution comprising 22 pounds of sodium hydroxide in 25 gallons of water which is equivalent to 230 pounds of a 9.6 weight per cent solution of caustic soda. The neutralization was carried out

with thorough agitation and the resulting emulsion distilled to effect recovery of 58.5 gallons of benzene which was reused in the process.

The sludge-raffinate phase formed by centrifuging the mixture of benzene and crude sulfonate product was extracted with 58½ gallons of benzene recovered, as just described, so as to recover from the sludge raffinate a small quantity of desirable sulfonic acids which would otherwise be discarded therewith. The extracted sludge was subjected to a vacuum stripping operation at about five pounds per square inch absolute pressure and 3.3 gallons of benzene recovered. Make-up benzene in the amount of 3.2 gallons was added so that a total of fresh benzene, benzene recovered from vacuum stripping of the acid sludge and benzene extract obtained from the sludge-raffinate extraction amounted to 65 gallons. This quantity of material was recirculated and employed in the benzene extraction of the crude sulfonation product produced from the Votator. The acid sludge, substantially free of benzene and the desired type of sulfonic acids, was discarded.

The residue remaining following recovery of benzene from the emulsion formed comprised a very stable emulsion of water, unsulfonated hydrocarbon feed, the sodium soaps of the sulfonic acids, and the small amount of benzene. Five gallons of isopropyl alcohol were added in water to break this emulsion into an aqueous phase and an oil phase. These two phases were subsequently extracted with 50 gallons of a petroleum naphtha boiling between about 170° F. and 220° F. This naphtha extraction was carried out in a packed extraction column at a temperature of about 170° F. About 95 gallons of extract was obtained which consisted predominantly of the naphtha solvent and the unsulfonated hydrocarbon feed. Due to the wide differences in boiling point of these two materials, the extract was distilled in a column having less than five theoretical trays to effect the recovery of 45 gallons of naphtha, which was re-employed in the process, from 49 gallons of unsulfonated hydrocarbon feed.

The raffinate obtained from the naphtha extraction comprised an aqueous solution of sodium sulfonates, isopropyl alcohol, together with small amounts of solubilized naphtha and unsulfonated hydrocarbon feed. This material was distilled at a temperature of about 220° F. and about 2.5 gallons of alcohol and about 2.5 gallons of naphtha were recovered. No additional sodium sulfate was added to the aqueous distillation bottoms which were subsequently passed through a centrifuge and a small quantity of solids consisting namely of ferric hydroxide removed from the solution. The clear liquid obtained following centrifuging of the distillation bottoms had a pH of about 9 due to a small excess of sodium hydroxide purposely employed in the neutralization of the sulfonic acids present in the benzene extract. The pH of this aqueous sodium sulfonate solution was adjusted by the addition of dilute sulfuric acid so that the resulting solution had a pH of 7.0.

The neutral aqueous solution of sodium sulfonates thus obtained contained 100 pounds of sodium sulfonates in about 25 gallons of water. In order to obtain the sodium sulfonate as a dry powder the neutral solution was introduced at room temperature through an atomizer into a spray drier. The drier employed flue gases introduced at a temperature of 600° F. as the source



of heat. The flue gases were generated by burning natural gas at a constant rate and the drier outlet gas temperature was maintained at a value of 230° F. by varying the rate of introduction of the aqueous sulfonate solution into the drier. These gases containing the sodium sulfonate as a suspended powder was removed from the drier and passed through a series of cyclone separators for recovery of the sodium sulfonate product.

The dry sodium sulfonate product was a nearly white colored free-flowing finely granulated material having virtually no odor. It was found to be soluble in water and to form a foam of high stability. The dry sodium sulfonate was also found to be soluble in benzene, methanol, and in mineral oils such as the spray oil distillate from which it was prepared. This material was further found to be substantially insoluble in acetone and 20° Baumé sodium chloride brine solutions. This dry powdered sulfonate product having the above solubility characteristics was shown to contain 19% sodium sulfate and 81% sodium sulfonates, which latter comprised the active ingredient.

The above example is intended merely to illustrate the preferred modification of the process of preparing the sulfonic acid and sulfonates of the present invention. The above example is not intended to describe limitations of the present invention but rather to more clearly define the scope thereof. Although strong sulfuric acid is employed as the sulfonation agent other of the stronger sulfonate agents such as sulfur trioxide, chlorsulfonic acid, sulfonylchloride, and the like, may be substituted without departing from the scope of the present invention. The preferred sulfonation stock has been described as comprising a hydrocarbon distillate having particular properties of viscosity, however, the extracts prepared from such distillates or other fractions of such distillates may be treated according to the methods herein defined. High molecular weight alcohols, vegetable oils such as castor oil, etc. may be sulfonated according to the method of the present invention in order to obtain sulfonates of somewhat different characters than the product obtained from petroleum distillates.

This product, prepared according to the foregoing example, has many distinct advantages over sulfonates prepared by different methods. First, it contains an extremely high concentration of the active sodium sulfonate ingredients thereby permitting the employment of a smaller amount of material for a given application. Second, the sodium sulfonates, according to this invention, are prepared from inexpensive raw materials and not from highly purified and manufactured chemicals allowing a low cost of production. Third, the product is produced by a continuous process using inexpensive and readily available solvents and reagents. Fourth, the product obtained is soluble in both oil and water forming solutions having high detergent powers, and is also soluble in dilute brines and hard waters.

This sulfonate product has been found to be at least equal in effectiveness to more expensive sulfonate type detergents prepared from alkylated aromatic type hydrocarbons or from high molecular weight alcohols. This is believed to be at least partly due to the substantial absence in the sulfonate product of by-products of side reactions of the sulfonation reaction.

The foregoing description and examples are

not to be taken as in any way limiting but merely illustrative of my invention for many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims:

I claim:

1. A process for the production of water-soluble hydrocarbon sulfonates which comprises reacting a hydrocarbon oil fraction boiling substantially between 500° F. and 800° F. with a strong sulfonating agent at an elevated temperature to produce a crude sulfonation product, extracting said crude sulfonation product with a first solvent consisting essentially of at least one organic solvent selected from the class consisting of liquid aromatic hydrocarbons having 6 to 9 carbon atoms per molecule, monochlorinated liquid aromatic hydrocarbons having 6 to 9 carbon atoms per molecule and polychlorinated aliphatic hydrocarbons having 1 to 2 carbon atoms per molecule to form a first extract phase and a sludge phase, separating said first extract phase from said sludge phase, neutralizing the sulfonic acids in said first extract phase with an aqueous solution of a basically reacting alkali metal compound to form a first mixture, separating said first solvent from said first mixture leaving a second mixture, extracting said second mixture with a second solvent consisting essentially of at least one liquid aliphatic hydrocarbon having between about 3 and 10 carbon atoms to form a second extract phase and an aqueous phase, separating the second extract phase from the aqueous phase, and recovering said sulfonate salts from the aqueous phase.

2. A process according to claim 1 in which the hydrocarbon oil is a petroleum distillate having a viscosity between about 40 and 110 Saybolt Universal Seconds at 100° F., the sulfonating agent is sulfuric acid having a concentration greater than about 80% by weight, the ratio of sulfonating agent to hydrocarbon oil employed in the sulfonation reaction is between about 0.1 and 0.5, and the sulfonation reaction is carried out at a temperature between about 50 and 300° F. for a time between about 0.5 minutes and 15 minutes.

3. A process according to claim 1 in which the hydrocarbon oil is an aromatic extract from the selective solvent treatment of a petroleum distillate and has a viscosity between about 50 and 180 Saybolt Universal Seconds at 100° F., the sulfonating agent is sulfuric acid having a concentration greater than about 80% by weight, the ratio of sulfonating agent to hydrocarbon oil is between about 0.2 and 0.8, and the sulfonation reaction is carried out at a temperature between about 50 and 300° F. for a time between about 0.5 and 15 minutes.

4. A process for the production of water-soluble hydrocarbon sulfonates which comprises reacting a hydrocarbon oil fraction boiling substantially between about 500° F. and 800° F. with between about 0.1 and 0.8 volumes of sulfuric acid having a concentration greater than about 80% by weight at a temperature between about 50 and 300° F. and a time between about 0.5 and 15 minutes to produce a crude sulfonation product, extracting said crude sulfonation product with a first solvent consisting essentially of at least one organic solvent selected from the class consisting of liquid aromatic hydrocarbons having 6 to 9 carbon atoms per molecule, monochlorinated liquid aromatic hydrocarbons having 6 to 9 carbon atoms per molecule and poly-



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chlorinated aliphatic hydrocarbons having 1 to 2 carbon atoms per molecule to form a first extract phase and a sludge phase, separating said first extract phase from said sludge phase, neutralizing the sulfonic acids in said first extract phase with an aqueous solution of a basically reacting alkali metal compound to form a first mixture, distilling said first solvent and a portion of the water from said first mixture, leaving a second mixture, adding to said second mixture a water-soluble aliphatic alcohol containing less than 4 carbon atoms, extracting the resulting mixture with a second solvent consisting essentially of at least one liquid aliphatic hydrocarbon having between about 3 and 10 carbon atoms to form a second extract phase and an aqueous phase comprising an aqueous solution of said alcohol and said water-soluble hydrocarbon sulfonate salts, separating said phases, and recovering said sulfonate salts from the aqueous phase.

5. A process according to claim 4 in which the first solvent is an aromatic hydrocarbon having less than 10 carbon atoms.

6. A process according to claim 4 in which the basically reacting alkali metal compound is sodium hydroxide.

7. A process according to claim 4 in which after the second extract phase is separated from the aqueous phase, the aqueous phase is distilled to separate therefrom any residual second solvent, the alcohol, and part of the water, and the residual aqueous solution of water-soluble hydrocarbon sulfonates is clarified by separating undissolved solid material therefrom, before recovering the sulfonates.

8. A process according to claim 4 in which an excess of sodium hydroxide is employed as the basically reacting alkali metal compound for neutralization, the second extract is separated from the aqueous phase, the aqueous phase is distilled to recover the alcohol therefrom, and the remaining aqueous solution is clarified by removal of undissolved solids therefrom and neutralized before recovering the sulfonates.

9. A process for the production of water-soluble petroleum sulfonates which comprises reacting a petroleum distillate boiling substantially in the range of about 500° F. to 800° F. and having a viscosity between about 40 and 110 Saybolt Universal Seconds at 100° F. with about 0.1

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to 0.5 volumes of sulfuric acid having a concentration between about 80 and 99% by weight for a time of about 3 minutes at a temperature of about 200° F. to produce a crude sulfonation product, extracting said crude sulfonation product with an approximately equal volume of a first solvent consisting essentially of an aromatic hydrocarbon having less than 10 carbon atoms to form a first extract phase, and a sludge phase, separating said first extract phase from said sludge phase, neutralizing the sulfonic acids in said first extract phase with an excess of an aqueous solution of sodium hydroxide to form a first mixture comprising said first solvent, water, unsulfonated oil, and water-soluble sodium sulfonates, distilling said first mixture to separate therefrom said first solvent and a portion of the water, adding sufficient isopropyl alcohol and water to the residue to form a second mixture comprising water, sodium sulfonates, isopropyl alcohol, and unsulfonated oil in the proportions of about 5 gallons of isopropyl alcohol for every 100 pounds of sodium sulfonates and every 25 gallons of water, extracting said second mixture with a second solvent consisting essentially of a paraffinic naphtha boiling between about 100° F. and 300° F. to form a second extract phase and an aqueous phase containing said aqueous solution of alcohol and sulfonates, separating the second extract phase from the aqueous phase, distilling the aqueous phase to recover said alcohol, separating undissolved solids from the remaining aqueous phase, neutralizing the resulting aqueous phase with sulfuric acid, and dehydrating the product to form a mixture of sodium sulfonates and sodium sulfate.

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