

UNITED STATES PATENT OFFICE

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PROCESS OF PRODUCING SULPHONIC ACIDS AND SULPHONATES

No Drawing.

Application filed February 17, 1928. Serial No. 255,178.

This invention relates to a treatment of petroleum oils with a sulphonating agent, particularly, sulphuric acid for the manufacture of highly refined oils and the production of valuable by-products. More particularly, the invention relates to the manufacture of sulphonic acids, particularly sulphonic acids of the water soluble type and the manufacture of water soluble sulphonates therefrom.

One of the objects of the invention is to produce sulphonic acids of a new form which, when neutralized with a metallic oxide or hydrate, provide a superior product for various uses, particularly for use as an emulsifier, spreader, or detergent, as in the manufacture of cutting oils, plant sprays and cleansing compounds or in other products and processes where an agent of this kind is required.

Another object is to disclose a process whereby large yields of desirable sulphonic acids are obtained without producing undesirable sulphonic acids and other compounds in appreciable quantities.

Another object is to disclose a process in which conditions in temperatures, concentration and proportion are specified so that new sulphonic acid and highly refined oils may be readily manufactured from hydrocarbon oils.

Another object is to disclose a process of obtaining large yields of water soluble acids from petroleum oils, without producing appreciable quantities of oil soluble sulphonic acids. Another object is to disclose a process whereby water soluble sulphonates may be produced from petroleum oil stocks.

Although water soluble sulphonic acids have been made heretofore, it has been the practice to treat an oil stock with successive batches of sulphonating agent, particularly, sulphuric acid thereby producing sludges containing both water soluble and oil soluble sulphonic acids, the latter being removed by extraction with a suitable solvent or by selectively discarding the particular sludge batches characterized by the presence of the oil soluble sulphonic acids. These methods result in relatively small yields of the water

soluble sulphonic acid and involve a large number of steps or treatments, thereby necessitating the expenditure of much time, effort and money.

In the present method, the formation of objectionable oil soluble sulphonic acids is largely avoided and such minor quantities of these acids as may be produced are easily removed by mechanical separation during the latter steps of the process. Large yields of the water soluble sulphonic acids are obtained by this process. It is not known exactly how the evolution of the oil soluble sulphonic acids is prevented, but it is thought that the method of applying the sulphonating agent causes a more or less complete and immediate conversion of the sulphonatable ingredients of the oil stock to water soluble sulphonic acids. Conditions of temperature, concentration and quantity of the ingredients apparently have a marked effect upon the results and such conditions as are best suited for the operation of our invention will be hereafter described in detail.

In carrying out the process it is desirable to first determine the proportion of sulphonating agent such as sulphuric acid to be used in order to completely convert that portion of the oil stock capable of entering into the reaction. The proportions of sulphuric acid to be used varies according to the sulphonatables in the oil stock which may be in any amount depending upon the character of the stock used although stocks containing 30% and upwards of such sulphonatables are preferred. Since sulphuric acid in an amount approximately equal to the volume of reactive material is necessary for complete sulphonation, the amount of acid used may vary from about four to about fifteen pounds per gallon of oil stock. In carrying out the small scale test above referred to a sample of the oil to be treated is mixed with an equal volume of sulphuric acid and all of the steps of the process embodying our invention are carried out until a supernatant layer of unreacted oil on a layer of reaction products is obtained. This volume of unreacted oil is subtracted from the volume of original sample, the result being the volume of oil amenable

to sulphonation and upon this volume is based the amount of sulphuric acid or other sulphonating agent to be used in the actual process, thereby obviating the use of excessive amounts of sulphuric acid on a large scale.

Any petroleum oil may be used as the stock for the process embodying the invention, although lubricating oil stocks have been found to be very adaptable thereto. Oil stocks to be used in our process are preferably those which have not been acid treated in the customary manner, as the customary acid treatment results in an incomplete conversion of sulphonatables into oil sludge and some water-soluble sulphonic acids, thereby tending to reduce the yield of desirable water soluble sulphonic acid made in accordance with this invention. In general, therefore, it is preferable to use oil stocks which have not been acid treated and which contain relatively large quantities of sulphonatables amenable to this process. As an example of the process embracing our invention a lubricating oil distillate, preferably one relatively high in constituents amenable to sulphonation, is treated with strong sulphuric acid in the proper amount and strength to insure complete reaction without generation of excessive heat, such proportion being preferably determined by a prior test as herein above stated. The full amount of acid may be placed in a suitable vessel such as a lead-lined agitator or other mixing device and the oil slowly added thereto with violent agitation during the admixture using compressed air, mechanically actuated paddles or other suitable means to secure a thorough and intimate mixture in the form of an emulsion. The rate at which the oil may be introduced is such that emulsification of the oil and acid is immediate and continuous, and at no time during the mixing operation should there be any appreciable amount of unemulsified oil present in the mass. The evolution of heat during this step is a further controlling factor and the oil should not be introduced at a rate which causes excessive heating, the temperature of the mixture being preferably kept at about 125° to 150° F., or below such temperature, as temperatures materially above this tend to cause formation of oil soluble reaction products.

While the oil may be added to the entire acid body as described satisfactory results may be obtained by emulsifying oil and acid in the proper proportions using a continuously operating mechanical mixing device from which the oil and acid may be simultaneously introduced into the agitator in the form of an emulsion or any other suitable mixing and emulsifying process or apparatus may be used provided the oil, sulphonating agent, temperatures, and volumes of reagents are controlled substantially as described.

To the emulsion of oil, acid and products of reaction, fresh water may then be added in

a volume approximately equal to the volume of the original acid used and the mixture may again be blown or otherwise agitated to secure a thorough dispersal of water therethrough. Considerable heat may be generated at this stage by the mixing of uncombined sulphuric acid and water and no attempt is necessary in an effort to dissipate such heat. On the contrary, the mixing vessel may be insulated against heat losses in order to take advantage of the effect of heat in improving the efficiency of the later separation of the components of the mixture. An increase of temperature above about 150° F., at this stage of the process apparently does not reduce the yield.

After the water is thoroughly incorporated into the mixture, the mass is then allowed to stand and stratification takes place readily, the emulsion breaking down and separating into three distinct layers, the lower comprising sulphuric acid in relatively dilute solution (containing about 50% to 60% of anhydrous acid whenever the original acid used was of over 93% strength), the middle layer being a sludge consisting almost entirely of water soluble sulphonic acids, and the upper layer being a highly acid treated lubricating oil ready for any desired further processing. While the sulphonic acid sludge is freely soluble in hot water it is not soluble in dilute sulphuric acid of proper concentration, so that practically the entire water content of the mixture goes into the lower layer, leaving the sludge layer substantially undiluted.

It is desirable to regulate the quantity of water added to the mixture in the step just described so as to control the concentration of acid in the dilute solution found. Preferably the resulting dilute acid solution should contain about 50% to 60% of anhydrous acid as this concentration insures proper "salting out" of the water soluble sulphonic acids. Insufficient dilution, that is, the presence of acid in higher concentrations interferes with stratification and results in an incomplete breakdown of the emulsion, while appreciably weaker solutions of acid tend to dissolve the sulphonic acids and thereby reduce the yield.

After removing as completely as possible the lower layer of dilute sulphuric acid, the middle layer comprising water soluble sulphonic acids, together with the top layer of acid treated oil, may be drawn off into storage or treated at once for the production of metal sulphonates which is one of the objects of this invention. Or the middle layer containing the water soluble sulphonic acids may be separated from both the lower layer of dilute sulphuric acid and the upper layer of oil and treated alone in accordance with further steps of this process. In case both the dilute acid layer and the upper oil layer have been removed, hot water in an amount approxi-

mately equal to the original sulphuric acid used may then be added to the middle layer containing sulphonic acids and the resulting solution neutralized with metallic oxide or hydrate or similar substances capable of forming water soluble compounds with such sulphonic acids. It has been found that the solubility of the sulphonic acids increases greatly with temperature and for this reason hot water is used, temperatures in excess of about 160° F., having proven very satisfactory. Hot water is added, as stated, when water soluble sulphonates are the object of the process and its purpose is to assist in the neutralization, the neutralized product being in solution and thus capable of extraction.

While the neutralization step has been described as following the removal of the upper or oil layer the operation may be satisfactorily performed after the removal of only the dilute uncombined sulphuric acid (the lower layer) and the oil layer may later be removed from the neutralized sulphonates, either after the addition of hot water alone or after the addition of both hot water and metallic oxides or hydrates, in which case the use of hot water in the first part of the neutralizing step has the further function of assisting in the separation of the oil present. It has been found desirable to apply a slight excess of neutralizing agent to prevent the entrainment of oil soluble products with the neutralized water soluble sulphonates and for this purpose sufficient alkali is preferably used to give a mixture which, after neutralization, has a hydrogen ion concentration of 10^{-7} to 10^{-11} gram atoms of hydrogen ion per liter. The top or oil layer carries with it the salts of such oil soluble sulphonic acids as may be produced in the original acid treatment, and after separating the oil from the water soluble products such oil soluble salts may be removed in any well known manner such as treatment with a mineral acid and afterward the oil neutralized, washed and otherwise treated for the manufacture of a high grade lubricating oil.

The product resulting from this process consists of water soluble sulphonates in aqueous solution and may be concentrated to any desired degree for use as an emulsifier, spreader or detergent. This concentration may be effected in a suitable evaporator, or it may be avoided entirely as a separate step by changing the amount of water added in the neutralizing step, thus controlling the proportion of water in or the concentration of the final product.

For neutralization any oxide or hydroxide of a metal capable of forming water soluble compounds with the sulphonic acids may be used. For example, oxides or hydroxides of sodium, potassium, lithium, rubidium and even ammonium are suitable.

While sulphuric acid of sufficient strength for the reaction without causing excess heat

was specified, it is believed that an acid above 90% H_2SO_4 should be used to insure complete sulphonation and maximum yield, and acids ranging from 93% to fuming acid of about 103% equivalent have been uniformly successful.

As a more specific example of this invention 50 gallons of 95% sulphuric acid were charged into a lead-lined agitator equipped with means for air blowing. One hundred gallons of lubricating oil distillate, about 100 seconds viscosity, and having a flash point of 300 F°, and containing about 50% of constituents sulphonatable in the strength of acid used, were slowly added to the acid while the contents of the agitator were violently agitated and such agitation was continued until complete mixture was obtained as indicated by an emulsified mass of acid and oil. Fifty gallons of fresh water were then rapidly added, thoroughly mixed with the mass and the mixture allowed to settle. Dilute sulphuric acid, present as a lower layer was then drawn off and fifty gallons of hot water were added to the remaining sulphonated solution and oil and the resulting solution neutralized with potassium hydroxide. The mixture was then allowed to stand for several hours until the unsulphonated oil accumulated at the surface and the desired water soluble sulphonates were then withdrawn for use, storage or concentration.

While particular products and methods of procedure have been described, it is to be understood that the process is not limited to lubricating oil distillates, nor to strength or quantity of sulphuric acid used, nor to kind or character of neutralizing agent, the invention being of the scope of the following appended claims.

We claim:

1. A process of treating petroleum oils to produce sulphonic acids comprising, forming an emulsion by bringing an oil containing sulphonatable constituents, such sulphonatable constituents not having been removed from such oil to an appreciable extent by prior treatment with a sulphonating agent, into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, adding water to stratify the unreacted sulphuric acid in dilute solution and then collecting the water soluble sulphonic acids.

2. A process of treating petroleum oils to produce sulphonic acids, comprising, forming an emulsion by bringing an oil containing sulphonatable constituents, such sulphonatable constituents not having been removed from such oil to an appreciable extent by prior treatment with a sulphonating agent, into intimate contact in one application with sulphuric acid in quantity and strength

adapted to sulphonate substantially all constituents amenable to sulphonation.

3. In a process of treating petroleum oils to produce sulphonic acids, adding an oil containing sulphonatable constituents, during agitation, in one application, to a body of sulphuric acid of sufficient quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, to form an emulsion.

4. In the manufacture of sulphonic acid from petroleum oils, the step of sulphonating an untreated lubricating oil distillate, by adding the distillate to a body of sulphuric acid of such quantity and strength as to sulphonate substantially all constituents amenable to sulphonation and present in said distillate, and form an emulsion in one application of acid.

5. In the manufacture of sulphonic acids from petroleum oils, the steps of sulphonating an untreated lubricating oil distillate, by adding the distillate to a body of sulphuric acid in such quantity and strength as to sulphonate substantially all constituents amenable to sulphonation and present in said distillate, in one application of acid, agitating the distillate and acid during admixture to form an emulsion, and maintaining the temperature of said emulsion during formation thereof at a temperature below about 150° F.

6. A process of treating petroleum oils to produce sulphonic acids comprising, bringing an oil containing sulphonatable constituents, such sulphonatable constituents not having been removed from such oil to an appreciable extent by prior treatment with a sulphonating agent, into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, agitating the mixture to form an emulsion substantially free of appreciable quantities of unemulsified oil or acid, dispersing water throughout the emulsion to cause stratification and removing water soluble sulphonic acids from the stratified mixture.

7. A process of treating petroleum oils to produce sulphonic acids comprising, bringing an oil containing sulphonatable products, such oil not having been previously treated with acid for the removal of sulphonatable products into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all products amenable to sulphonation, agitating the mixture to form a complete emulsion, dispersing water throughout the emulsion to cause stratification and separately removing dilute sulphuric acid and water soluble sulphonic acids from the stratified mixture.

8. A process of treating petroleum oils to produce water soluble sulphonates comprising, bringing an oil containing sulphonat-

able products into intimate contact with sulphuric acid in strength and quantity sufficient to sulphonate substantially all products amenable to sulphonation, agitating the mixture to form a complete emulsion, dispersing water through the emulsion to cause stratification thereof, separately removing dilute sulphuric acid and water soluble sulphonic acids from the stratified mixture and then neutralizing said water soluble sulphonic acids with an excess of alkali to form a solution of sulphonates.

9. A process of treating petroleum oils to produce sulphonic acids comprising, bringing an oil containing sulphonatable products into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all products amenable to sulphonation, agitating the oil and acid during said contacting to form a complete emulsion, dispersing water throughout the emulsion to cause stratification thereof, separately removing dilute sulphuric acid and un-sulphonated oil and oil soluble sulphonic acids from the stratified mixture, and collecting the remaining water soluble sulphonic acids.

10. A process of treating petroleum oils to produce sulphonic acids comprising, adding an oil containing sulphonatable constituents, such oil not having been previously acid treated for the removal of sulphonatable constituents, during agitation, to a body of sulphuric acid in strength and quantity sufficient to sulphonate substantially all constituents amenable to sulphonation, forming an emulsion by such agitation and addition, and maintaining the temperature of the emulsion at below 150° F.

11. A process of treating petroleum oils to produce water soluble sulphonic acids comprising, adding an oil containing sulphonatable constituents, during agitation, to a body of sulphuric acid in strength and quantity adapted to sulphonate substantially all constituents amenable to sulphonation, forming an emulsion by such agitation and addition, maintaining the temperature of the emulsion at below 150° F., dispersing water throughout the emulsion in sufficient quantity to cause stratification but not sufficient to form a dilute sulphuric acid solution in which sulphonic acids are soluble, and separately removing dilute sulphuric acid and water soluble sulphonic acids from the stratified mixture.

12. In a process of treating petroleum oils to produce sulphonic acids as described in claim 11, the step of neutralizing an aqueous solution of sulphonic acid with an excess of alkali so as to form an aqueous solution of sulphonates.

13. A process of treating petroleum oils to produce sulphonic acids comprising, forming a complete emulsion by bringing an oil hav-

ing the characteristics of lubricating oil distillate and containing sulphonatable constituents into intimate contact, with accompanying agitation, with sulphuric acid of quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, maintaining the temperature of the emulsion at a temperature below about 150° F., dispersing water throughout the emulsion to cause stratification thereof, removing dilute sulphuric acid from the stratified mixture, and collecting water soluble sulphonic acids from the residue.

14. A process of treating petroleum oils to produce sulphonic acids comprising, bringing an oil containing sulphonatable products, such oil not having been previously treated with acid for the removal of sulphonatable products, into intimate contact in one application with sulphuric acid in quantity and strength adapted to sulphonate substantially all products amenable to sulphonation, agitating the mixture to form an emulsion substantially free of appreciable quantities of unemulsified oil or acid, adding water to the emulsion to cause stratification, removing dilute sulfuric acid from the stratified mixture, agitating the residual mixture with hot water to extract water soluble sulphonic acids therefrom, and separating unsulphonated oil from the aqueous solution.

15. A process of treating petroleum oils to produce water soluble sulphonates comprising, bringing an oil containing sulphonatable products into intimate contact in one application with sulphuric acid in quantity and strength adapted to sulphonate substantially all products amenable to sulphonation, agitating the oil and acid during said contacting to form an emulsion having no appreciable quantities of unemulsified oil or acid, dispersing water throughout the emulsion to cause stratification thereof, removing dilute sulphuric acid from the stratified mixture, bringing the residual mixture in contact with hot water to dissolve water soluble sulphonic acids, and neutralizing said sulphonic acids with a metallic oxide or hydrate capable of forming water soluble sulphonates.

16. A process of treating petroleum oils to produce water soluble sulphonates comprising, bringing an oil containing sulphonatable constituents into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, diluting the mixture with water to cause stratification of emulsion thus formed, separately removing unreacted sulphuric acid and water soluble sulphonic acids from the mixture, and neutralizing the sulphonic acids in the aqueous solution with an excess of a metallic oxide or hydrate capable of forming water soluble sulphonates.

17. A process of treating petroleum oils to produce water soluble sulphonates, comprising, bringing an oil containing sulphonatable products into intimate contact in one application with sulphuric acid in quantity and strength adapted to sulphonate substantially all products amenable to sulphonation, agitating the mixture to form an emulsion, dispersing water throughout the emulsion to cause stratification thereof, removing dilute sulphuric acid from the stratified mixture, bringing the residual mixture into contact with hot water to dissolve water soluble sulphonic acids, neutralizing said sulphonic acids with a metallic oxide or hydrate capable of forming water soluble sulphonates and then separating unsulphonated oil, together with oil soluble sulphonates from the neutralized solution.

18. A process of treating petroleum to produce water soluble sulphonic compounds comprising, bringing an oil containing sulphonatable constituents into intimate contact with sulphuric acid in quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, agitating the mixture to form an emulsion, maintaining the temperature during mixing at below about 150° F., mixing the emulsion with water in an amount approximately equal to that of the original acid, removing dilute sulphuric acid from the stratified mixture, adding hot water to the residual mixture in an amount depending upon the desired concentration of product, neutralizing sulphonic compounds present in the diluted mixture with an alkali using such an excess of alkali as will make the hydrogen ion concentration of the aqueous component of the mixture from 10^{-11} to 10^{-7} gram atoms of hydrogen ion per liter, and separating unsulphonated oil with oil soluble sulphonates from the neutralized solution.

19. A process of treating petroleum oils to produce sulphonic acids comprising, adding an oil containing sulphonatable constituents to sulphuric acid in quantity and strength adapted to sulphonate substantially all constituents amenable to sulphonation, agitating the oil and acid during admixture to form an emulsion, adding to the emulsion with agitation, a volume of water approximately equal to that of the original acid to cause stratification of the emulsion, removing dilute sulphuric acid from the stratified mixture, bringing the residual mixture into intimate contact with a volume of hot water approximately equal to that of the original acid, and separating unsulphonated oil and oil soluble sulphonic acids from the diluted mixture.

20. A mixture of water soluble sulphonates obtained from an emulsion of petroleum oil containing sulphonatable products and sulphuric acid in strength and quantity sufficient

to sulphonate substantially the entire content of sulphonatable products, said mixture of water soluble sulphonates being in aqueous solution of alkaline reaction.

5 21. A mixture of water soluble sulphonates obtained from an emulsion of petroleum oil containing sulphonatable products and sulphuric acid in strength and quantity sufficient to sulphonate substantially the entire content of sulphonatable products, said mixture
10 of water soluble sulphonates being in an aqueous solution having a hydrogen ion concentration of from 10^{-11} to 10^{-7} gram atoms of hydrogen ion per liter.

15 22. A mixture of water soluble sulphonates substantially free from oil soluble products obtained by neutralizing a water solution of sulphonic acids with sufficient alkali to form an aqueous solution of water soluble
20 sulphonates having a hydrogen ion concentration of from 10^{-11} to 10^{-7} gram atoms of hydrogen ion per liter.

23. A mixture of water soluble sulphonic acids obtained by forming an emulsion by
25 bringing a petroleum oil having the characteristics of an untreated lubricating oil distillate into intimate contact, in one application, with sulphuric acid in quantity and strength adapted to sulphonate substantially
30 all constituents amenable to sulphonation that are present in such oil, and separating water soluble sulphonic acids from the emulsion.

24. A mixture of water soluble sulphonates
35 obtained by forming an emulsion by bringing a petroleum oil having the characteristics of an untreated lubricating oil distillate into intimate contact, in one application, with sulphuric acid in quantity and strength adapted
40 to sulphonate substantially all constituents that are amenable to sulphonation that are present in such oil, separating water soluble sulphonic acids from the emulsion, and then converting said sulphonic acids to sulphonates.
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25. A mixture of water soluble sulphonates obtained by forming an emulsion of, and sulphonating substantially all constituents amenable to sulphonation that are present
50 in, a petroleum oil by one application of sulphuric acid to a petroleum oil.

Signed at Richmond, California, this 1st day of February 1928.

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