

UNITED STATES PATENT OFFICE

2,394,320

ORGANIC DETERGENT COMPOSITIONS

Russell Park McGhie, Brooklyn, N. Y., assignor
to Colgate-Palmolive-Peet Company, Jersey
City, N. J., a corporation of Delaware

No Drawing. Application May 19, 1942,
Serial No. 443,638

9 Claims. (Cl. 252—138)

The present invention relates to a process of making detergent compositions and, more particularly, to a process of preparing sulphated and sulphonated organic materials having good wetting, emulsifying and deterging properties, and to the novel product of said process.

Synthetic detergents, particularly those comprising sulphated and/or sulphonated organic compounds, have been made and used for many years, but one of the great difficulties in their manufacture has been the tendency of the materials in the course of manufacture, particularly in aqueous solution, to attack metal parts, such as tanks, drying rolls, spray nozzles and the like, especially those made of iron and steel. This tendency, which is particularly objectionable in compositions having a pH below 7.0, not only results in pitting and corroding away of metal parts, but also causes discoloration of the product and a decrease in its ability to produce foam. The product, as heretofore produced, cannot be stored in metal vessels, except in stainless steel tanks or other expensive corrosion-proof alloys, without corroding the containers. Even though the containers are lined, enamelled, painted or nickel plated, they are still unsuitable for storing this material, as the wetting power of the solution is often so great as to penetrate the minute pores of the coating, loosening the coating from the metal and corroding the metal walls, and as the lining or coating often cracks or breaks for one reason or another to expose the metal wall beneath. Moreover, the action of the sulphonated material upon the metal introduces impurities which result in deterioration of the product, both in color and in clarity of aqueous solutions prepared therefrom.

It is an object of the present invention to provide a process for manufacturing detergent compositions of high clarity and good color stability in aqueous solution.

It is another object of the invention to provide a process of manufacturing sulphated and sulphonated organic materials of light color without corroding ordinary metal apparatus.

It is also an object of this invention to provide detergent compositions and solutions thereof of high clarity and good color stability which can be stored and shipped in ordinary drums and tanks without danger of corroding the same.

Other objects and advantages of the present invention will be apparent from the following description.

According to this invention, it has been found

that the addition of a small proportion of an inorganic phosphate to non-soap detergents, emulsifiers and wetting agents of the type of sulphated or sulphonated organic materials provides a composition which in aqueous solution is clear, color-stable and highly soluble and which is substantially non-corrosive. The use of inorganic phosphates with detergent materials of this type has been taught by the prior art but for a different purpose, requiring different and necessarily larger proportions. Earlier experimenters and investigators employed phosphates in sufficient amount to be effective as adjuvant washing, cleansing, emulsifying and wetting agents and/or for increasing the alkalinity of the composition. It is an unexpected feature of the present invention that the addition of an amount of phosphate equivalent to about 0.001% to about 0.5% of the weight of sulphonated ("true" sulphonated and/or sulphated) material, an amount which is so low as not to modify the detergent properties of the sulphonate nor substantially to alter the pH of the composition, can still provide unusual results in giving very clear, color-stable compositions which are substantially non-corrosive.

The sulphated or sulphonated organic compounds comprised by the novel compositions of the invention may be prepared from organic materials which are applicable for sulphonation ("true" sulphonation and/or sulphation), especially those having about eight to about twenty-six (and preferably about twelve to about twenty) carbon atoms to the molecule, including fatty oils, unsaturated fatty acids, mineral oils, mineral oil extracts, mono- and di-glycerides, partial esters or ethers of polyglycols, esters or ethers of glycols, polyglycols and polyalcohols, aromatic and alkylated aromatic compounds, alcohols and olefines, coal tar distillates, and numerous other organic compounds and mixtures of compounds. Such compounds can be sulphonated by any of several methods and may form any of several products, depending upon the method of sulphonation employed. The sulphated or sulphonated organic compounds include sulphonated mineral oil; conventional mineral oil refinery sludges; sulphonated mineral oil extracts, including the products described in U. S. Patents Nos. 2,149,661, 2,149,662 and 2,179,174; sulphonated fatty acids and oils, including sulphonated castor oil, sulpho-ricinoleic acid, sulphonated olive oil, and sulpho-oleic acid; aliphatic sulphonates and sulphates, including cetyl sulphuric acid, dodecyl acid sul-

phate, and tetradecanehydroxy sulphonic acid-1,2; aliphatic ether and ester sulphonates including the dodecyl ether of hydroxy ethyl sulphonic acid, the cetyl ether of glyceryl sulphonic acid, tallow monoglyceride monosulphate, and coconut oil fatty acid monoesters of beta methyl glycerine sulphonic acid; sulphonates prepared by treatment of organic materials with sulphur dioxide and chlorine in the presence of light and hydrolysis of the product; sulphonates prepared by treatment of organic bodies with sulphuryl chloride and an activating agent in the presence of light and hydrolysis of the product; fatty acid amides of amino alkyl sulphonic acids, including lauric amide of taurine and tall oil acid amide of amino glyceryl sulphonic acid; sulphonic acids of naphthenes and naphthenic acids, lignin sulphonic acids; aromatic and alkylated aromatic sulphonic acids, including naphthalene sulphonic acid, octadecyl benzene sulphonic acid, and dodecyl naphthalene sulphonic acid; the product of a mineral oil extract sulphonated while dissolved in liquid sulphur dioxide; and innumerable other organic sulphonic and sulphuric acid derivatives or mixtures thereof. These organic sulphate and true sulphonate compounds include those in which the organic radicals of the molecule are unsubstituted or those which contain substituents such as halogens, halogenoids, hydroxyls, nitrogen-containing groups, acyl groups, acyloxy groups, alkoxy groups, etc. Of these sulphated and sulphonated materials, the most suitable for inclusion in the novel compositions of the present invention are normally non-alkaline, and especially those having carboxylic ester linkages, including the sodium salts of the sulphuric acid esters of coconut oil fatty acid monoglycerides, tallow diglyceride monosulphate, and stearyl monoesters of beta methyl glycerine sulphonic acid.

The inorganic phosphates, which may be added to sulphated and/or sulphonated compounds to achieve the desirable results described, are water-soluble phosphates, including primary, secondary and tertiary sodium orthophosphate and the sodium salts of tetraphosphoric, tripolyphosphoric and pyrophosphoric acids, wholly or partially neutralized, as well as the other alkali metal and ammonium salts of orthophosphoric, tetraphosphoric, tripolyphosphoric and pyrophosphoric acids, wholly or partially neutralized. It is preferred to use salts of phosphoric acids capable of forming water-soluble calcium salts. Any one or more of the phosphates mentioned above may be incorporated in the compositions of this invention, and/or other compounds breaking down or reacting with the sulphonated materials to provide said phosphate salts may be employed. Where the sulphonated compounds are to be neutralized subsequent to addition of phosphatic material, as will be described hereinafter, the phosphate salts may be replaced by the corresponding acids. As has been stated supra, it is preferred to incorporate in these compositions only about 0.001% to about 0.5% by weight of inorganic phosphate based upon the weight of active ingredient, as this amount has the advantage of providing the composition with unusually high clarity in aqueous solution, substantial freedom from corrosive effect, good color stability, high solubility and improved foaming, without substantial modification of the detergent and other desirable properties of the active ingredient. Where it is permissible to modify the detergent

properties, higher percentages of phosphate, say, up to about 3%, or up to about 5% or even higher, may be added, without losing the other advantages described herein. When using a small amount of phosphate in the preferred range, the composition has a further advantage of not salting out from solvent solutions, such as concentrated alcohol solutions and the like, nor forming separate liquid phases. Moreover, where the sulphonated materials are intended for use in dye baths and the like, a large proportion of phosphate salts introduces undesirable ions in objectionable amounts. The inorganic phosphates may be added during any step of manufacture of the sulphonated materials or may be added after completion of the preparation. The addition of the small amounts of phosphates described stabilizes the material in storage in metal tanks and in drums for shipment. This advantage is particularly apparent in concentrated solutions of the sulphonates, say, in aqueous solutions containing about 5% to about 50% of active ingredient, where the art may now dispense with the former practice of employing only stainless steel or non-metallic containers.

The manufacturing process is greatly improved by introducing the inorganic phosphate, in any proportion, at a point in the manufacture prior to the hydrolyzing and/or neutralizing step. While the proportion of phosphate to active ingredient is advantageously low in the final product to avoid modification of detergent properties, it is desirable to employ larger proportions, say, of the order of about 10% to about 50% and even as high as 100% or higher, during manufacture to avoid corrosion of metal equipment.

The neutralizing step may be carried out in batch operation or continuously and/or in the presence of previously neutralized material, and water or aqueous solutions of salts and/or acids or alkalies may be used therefor. Alkaline agents are most commonly employed, a sulphonate salt resulting from the neutralization, and agents suitable therefor include sodium and potassium hydroxides, carbonates, silicates, etc., pyridine, methyl morpholine, piperidine, alkyl amines, alkanolamines and other organic and inorganic bases and alkaline materials, and mixtures of these. The alkaline agent may be introduced in aqueous solution, in alcoholic solution, or in solutions of other solvents, or may be substantially anhydrous and/or substantially undiluted. The amount of solvent introduced with the alkaline or saponifying agent has a bearing upon the water or organic solvent content of the finished product.

The neutralization may be carried out by intimately mixing sulphonated material with an alkaline agent in the presence of inorganic phosphate in a reaction vessel under atmospheric, superatmospheric or reduced pressure. The inorganic phosphate may be admixed with the sulphonate salts thus formed by introducing it into the reaction mixture in the sulphonating vessel, either separately or mixed with the sulphonating agent, and/or it may be admixed by mixing the phosphate with the sulphonated material and/or the neutralizing agent before contacting, and/or by simultaneously passing into the neutralizing vessel a solution containing phosphate salts.

When adding the phosphatic material prior to neutralization, the phosphoric acids corresponding to the phosphate salts hereinbefore described as suitable for use in the new compositions of the

invention may replace all or part of the phosphate salts. However, when employing a phosphoric acid, especially during the sulphonating step, the proportion of phosphoric acid to sulphonating agent must be sufficiently low to avoid phosphorylation of a substantial amount, if any, of the organic compound under the operating conditions. Thus, an amount of phosphoric acid equivalent to from about 10% to about 35% of the weight of sulphonating agent has provided satisfactory results.

Heating and/or cooling means associated with the neutralizing vessel may be provided, as desired. Where the product is to be dried, heat may advantageously be supplied to the reaction mixture in the neutralizing vessel. The heat of neutralization may alone be sufficient to raise the mixture to the desired temperature, depending upon the materials employed and the subsequent operating conditions, or heat from external sources may be supplied. Either or both of the reactants may be preheated by steam or other means before being run into the vessel and/or the mixture may be heated during and/or after admixture. The neutralization step may also be operated in conjunction with a spraying step for obtaining substantially granular and/or hollow particles, the material from the reaction vessel being forced in fluid form into a spinner bowl or spray nozzle, and, upon atomization, coming in contact in a spray tower with a current of inert gas, preferably air. The air current may be heated, and it is preferably passed through the tower countercurrent to the sprayed material, although concurrent passage of the air is also contemplated.

Another method of neutralization is to mix the reactants in a mixing vessel with inorganic phosphates, and then to pass the neutralized product containing phosphate salts to a vapor separation chamber at a lower pressure. The sulphonated material and neutralizing agent may also be reacted at an elevated temperature under pressure and in the presence of phosphates and then flashed into a vapor separation chamber at a lower pressure, whether superatmospheric, atmospheric or reduced, thereby vaporizing any solvent present, if used, and any vaporizable reaction product. A suitable condensation system can be provided to recover vaporized materials.

The sulphonated material and the neutralizing agent may be forced under relatively high pressures through a reaction conduit, such as a pipe, together with inorganic phosphates and with or without the application of heat. The materials are thoroughly contacted in the conduit, and, operating preferably continuously, the neutralized sulphonate salts and the phosphates can be discharged to a low pressure zone, preferably through a constricted outlet or nozzle. Heat may be supplied to the pipe, if necessary, to raise the temperature of water or other solvent therein to the vaporization point at the pressure within the pipe, and the temperature and pressure at any point in the pipe may be kept substantially constant or may be varied in a cyclic manner for the purpose of creating greater turbulence in the reaction conduit by alternately establishing and destroying a vapor phase therein. Upon flashing into the lower pressure zone, the heat of the reaction product is employed to vaporize the water or other solvent at the low pressure of the separation chamber, and the vaporized material goes off at the top, while the sulphonate salt containing phosphates mixed therewith and having

at least a portion of water and other volatile materials removed, falls to the bottom.

By contacting the neutralization mixture, momentarily and just before discharge into the low pressure flash zone, with an inert gas at a considerably higher temperature, less heat need be supplied to the neutralization and preheating conduit and/or a higher absolute pressure may be employed in the separation chamber. The contact of the reaction mixture with an inert gas, such as superheated steam, kerosene vapor, carbon dioxide, flue gases, stack gases, etc., is preferably made at extremely high velocity and for a minimum time period before introduction into the flash chamber. The contacting can be advantageously accomplished by a nozzle designed to permit intimate but only momentary direct contact and a minimum of indirect contact before admission into the flash chamber. Employing this modification, the length of the hydrolyzing and/or neutralizing conduit can be appreciably shortened, if desired, and less heat need be supplied thereto by external heating of the conduit and/or by preheating of the sulphonated material and/or the neutralizing agent.

In another procedure, it is possible, by means of superheated steam or other inert gas, to supply sufficient heat at an optimum temperature and velocity in order to effect instantaneous hydrolysis and/or neutralization along with flash distillation of the materials to be withdrawn as a vapor. This procedure avoids plugging of pipes and nozzles, because the aqueous mixture is not under flashing conditions for any appreciable time before introduction into the nozzle, where it attains high velocity and adequate heat in momentary time before its discharge into the flash chamber.

Although the present invention is especially directed to concentrated solutions of the novel compositions provided, the proportions of superheated steam introduced into the nozzle in these various modifications can be so regulated in practice that a dry product or a hydrated product of any degree of hydration can be produced. The product may be made in a more or less finely divided condition, which permits its ready transformation into flakes or other physical forms, for example, by passing between a pair of properly spaced rolls, or by pressing into cakes, or by other means, with or without addition or modifying agents.

The presence of inorganic phosphates during neutralization and subsequent operations substantially prevents corrosion of metal parts of apparatus and equipment, including mixers and tanks, pipe lines and conduits, spray nozzles, spinner bowls, drying rolls, etc., even at the higher temperatures disclosed. Furthermore, due to the presence of the phosphates, the product retains its original color.

Adjuvant materials may be admixed with the sulphonate salts containing a small proportion of phosphates thus formed by mixing the adjuvant materials with the sulphonated organic compounds and/or the neutralizing agents before neutralization or flashing, by simultaneously flashing a second solution containing such adjuvant materials, and/or by mixing the final product therewith. Such adjuvant materials may include fatty acid soaps, resin acid soaps, naphthenic and alkylated naphthenic acid soaps, alkaline soap builders, additional water-soluble, water-softening compounds of acids of phosphorus, and other salts including sodium carbonates, sodium silicates, borax, sodium bicarbonate, sodium sul-

phate, sodium chloride, sodium acetate, sodium hypochlorite, sodium thiosulphate, sodium perborate, sodium tartrate, sodium citrate, sodium oxalate and the corresponding ammonium, substituted ammonium and potassium salts of the corresponding acids; insecticidal, germicidal, styptic and medicinal agents, including aluminum chloride, mercuric chloride and various copper and lead salts; coloring agents, abrasives, fillers and water-dispersible gums, including dyes, lakes, pigments, silica, kieselguhr, silica gel, feldspar, precipitated chalk, pumice, infusorial earth, bentonite, talc, starch, Irish moss, sugar, methyl cellulose, agar, gum tragacanth, gum arabic and polyvinyl alcohol; liquids, such as ethyl alcohol, glycerol, cyclohexanol, naphtha, benzene, kerosene, turpentine, pine oil, decalin, and tetralin, and the like. The type of addition agent will depend upon the ultimate use of the new composition.

The following examples, described herein, are merely illustrative of the present invention, and it will be understood that the invention is not limited thereto.

Example I

About 154 pounds of pyrophosphoric acid is dissolved in about 666 pounds of fuming sulphuric acid of about 102.8% strength. The acid mixture is then mixed with about 33 pounds of anhydrous (about 99.5%) glycerine in a mixer of ordinary steel and equipped with cooling means to keep the temperature at about 30° C. The resulting mixture is then passed to a similar mixer and is there mixed with about 216 pounds of coconut oil and about 272 pounds of tallow, heating during the mixing operation to about 50° C. The agitation is continued for about forty minutes, after which the reaction product is passed to a neutralization tank of ordinary steel and is there mixed with about a 30% aqueous solution of caustic soda. The product is brought to a pH of about 6.0 to 7.0 and comprises a mixture of tallow and coconut oil diglyceride monosulphates with sodium sulphate, containing an amount of sodium pyrophosphate equivalent to about 15% of the weight of the tallow and coconut oil diglyceride monosulphates.

Example II

Coconut oil monoglyceride monosulphate is prepared in accordance with the disclosure set forth in U. S. Patent No. 2,130,361 to Muncie. This active organic ingredient, as prepared, is disposed in a mixture in the proportion of about 40 parts of said active organic material to about 60 parts of sodium sulphate, and this mixture is dissolved in water to form an aqueous solution containing about 40% of solids. Disodium orthophosphate in an amount equivalent to about 0.3% by weight of the active ingredient is added to the solution. The resulting solution is clear and of a light color and can be shipped in metal containers without danger of corroding the same.

Example III

About 3 parts of a Pennsylvania white mineral oil of paraffin base and having an average molecular weight of about 235 is treated at below about 0° C. with a gaseous mixture of approximately 1 part by weight of chlorine and about 2 parts by weight of sulphur dioxide in the presence of light. The time of treatment is regulated to effect a weight increase of about 20%, at which point the reaction mass contains approximately

50% of mineral oil sulphonyl chlorides. The crude material thereby formed is simultaneously purified and extracted with about 2 parts of liquid sulphur dioxide, the liquid sulphur dioxide phase being continuously removed. The sulphonyl chlorides contain some of the unsulphonated oil, and separation can be accomplished by re-extracting the sulphur dioxide solution with ligroin. The sulphur dioxide is then removed, and about 2.25 parts of syrupy pyrophosphoric acid having about 82% phosphorus pentoxide is added to the residue. The resulting mixture is hydrolyzed and neutralized by stirring with an aqueous 30% solution of sodium hydroxide at a temperature of about 90° C., and the mixture is diluted so as to contain about 10% of the sulphonated product. The sulphonate solution is treated with sulphuric acid to neutralize excess alkali, thus forming a certain amount of sodium sulphate. Additional sodium sulphate is also added to bring the salt content to a desired proportion. The solution is passed to steam-heated drying rolls of ordinary steel, and a flaky, snow-white product is obtained.

Example IV

The Edeleanu extract of a naphthene base mineral oil is dissolved in about twice its volume of liquid sulphur dioxide and sulphonated with oleum in accordance with the disclosure in U. S. Patent No. 2,149,661 to Brandt. Following the procedure described therein, a dry, fluffy powder is obtained, and this is dissolved in water to form an aqueous solution containing about 15% of the active sulphonated mineral oil extract. An amount of sodium tetraphosphate equivalent to about 0.2% of the weight of the active ingredient is added to this solution. The solution thus produced is clear and almost colorless and can be stored and shipped in ordinary steel tanks.

The use of the term "sulphonated" with reference to organic compounds in the following claims will be understood to include sulphated as well as "true" sulphonated materials.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention. Such variations and modifications are believed to be within the scope of the present specification and within the purview of the appended claims.

I claim:

1. As a new composition of matter, a non-soap detergent comprising a sulphonated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and having a pH in aqueous solution below 7.0, and an amount of a water-soluble inorganic phosphate about 0.001% to about 3% by weight of said sulphonated organic compound, said composition providing a clear aqueous solution which is color-stable and substantially non-corrosive to iron-containing metals.

2. As a new composition of matter, a non-soap detergent comprising a sulphonated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and having a pH in aqueous solution below 7.0, and an amount of a water-soluble inorganic phosphate about 0.001% to about 0.5% by weight of said sulphonated organic compound, said composition providing a clear aqueous solution which

is color-stable and substantially non-corrosive to iron-containing metals.

3. As a new composition of matter, a detergent comprising a water-soluble salt of a sulphated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and having about eight to about twenty-six carbon atoms to the molecule, said salt having a pH in aqueous solution below 7.0, and an amount of a water-soluble inorganic phosphate about 0.001% to about 3% by weight of said salt of a sulphated organic compound, said composition providing a clear aqueous solution which is color-stable and substantially non-corrosive to iron-containing metals.

4. As a new composition of matter, a non-soap detergent comprising alkali metal salts of the sulphuric acid esters of coconut oil fatty acids monoglycerides, and an amount about 0.001% to about 3% by weight of said alkali metal salts of a water-soluble inorganic salt of a phosphoric acid capable of forming a water-soluble calcium salt, said composition providing a clear aqueous solution which is color-stable and substantially non-corrosive to iron-containing metals.

5. As a new composition of matter, a detergent comprising a mineral oil sulphonate produced by treating a mineral oil with sulphur dioxide and chlorine in the presence of actinic light and substantially neutralizing the product of said treatment, and an amount of a water-soluble inorganic phosphate about 0.001% to about 3% by weight of said mineral oil sulphonate, said composition providing a clear aqueous solution which is color-stable and substantially non-corrosive to iron-containing metals.

6. A clear, color-stable non-corrosive aqueous

solution having a pH below 7.0 and comprising water, a sulphonated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and an amount of water-soluble inorganic phosphate about 0.001% to about 3% by weight of said sulphonated organic compound.

7. A clear, color-stable non-corrosive aqueous solution having a pH below 7.0 and comprising water, a sulphonated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and an amount of a water-soluble inorganic phosphate about 0.001% to about 0.5% by weight of said sulphonated organic compound.

8. A clear, color-stable non-corrosive aqueous solution having a pH below 7.0 and comprising, in addition to water, about 5% to about 50% of a sulphonated organic compound having an inorganic sulphur-containing radical bound to an aliphatic carbon and an amount of a water-soluble inorganic phosphate about 0.001% to about 0.5% by weight of said sulphonated organic compound.

9. As a new composition of matter, a detergent comprising an alkali metal salt of a sulphonated aliphatic compound having about twelve to about twenty carbon atoms to the molecule and having an inorganic sulphur-containing radical bound to one of said carbon atoms, and an amount of a water-soluble inorganic phosphate about 0.001% to about 3% by weight of said alkali metal salt, said composition providing a clear aqueous solution which is color-stable and substantially non-corrosive to iron-containing metals.

RUSSELL PARK MCGHIE.