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TREATMENT OF TEXTILES

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1 Claim. (Cl. 8—127)

This invention relates to the treatment of textile materials with sulphonated mineral oil extracts and particularly to the treatment of fibers and textiles with sulphonic acids and their salts which are prepared by subjecting a solvent extract of mineral oil while dissolved in liquid sulphur dioxide to a comparatively rapid treatment with a sulphonating agent under controlled relatively low temperatures. The product thus generally prepared, and preferably with certain additional processing steps, finds application in an unusually large number of the textile operations requiring deterging, wetting, foaming, solubilizing, penetrating, frothing or emulsifying agents, or, in general, agents which modify the capillary action and surface tension.

These novel sulphonated mineral oil extracts are characterized by their unusually high stability and their suitability for use in neutral, acid or alkaline baths. Moreover, the materials are not affected by hard water.

Among the many operations for which these products are adapted in the textile industry, alone or in admixture with other agents, are: degreasing (decreusage), scouring, degumming, retting, desizing, backwashing, soaking, cleansing, washing, boiling, rinsing, deterging, foaming, frothing, lathering, sudsing, laundering, throwing, steeping, moistening, wetting out, soupling, stripping, souring, bleaching, bucking (bowking), kier boiling, chemicking, animalizing, mercerizing, parchmentizing, carbonizing, spinning natural fiber, spinning artificial fiber, precipitating, desulphurizing viscose, dyeing, improving dye fastness, improving dye affinity, improving dye penetration, equalizing, leveling, penetrating, mordanting, fixing, padding, stencilling, pasting, printing, stripping, exhausting, brightening, reserving, reviving, resisting, milling, fulling, felting, carroting (fur), shrinking, crabbing, decatizing, dispersing, delustering, lustering, emulsifying, potting, peptizing, finishing, dressing, impregnating, absorption improving, moisture controlling, greasing, lubricating, oiling, waxing, sizing, softening, starching, stiffening, weighting, loading, preserving, crimping, goffering, crease proofing, twist setting, anti-slipping, germ proofing, anti-mildewing, insect proofing, moth proofing, dry cleaning, disinfecting, fire proofing, water proofing, insulating (heat and electricity), antistatic, fibre coating, fabric coating (e. g. oil cloth and artificial leather), etc.

The novel sulphonation products contemplated for use in these various operations have been completely disclosed in this applicant's United States Patents Nos. 2,149,661, 2,149,662 and 2,179,174, and copending application Ser. No. 239,553, filed November 8, 1938; of which four this application is a continuation-in-part. The copending application discloses the preferred method of making the products used as contemplated herein.

As a starting material, in the process of the aforementioned disclosures, it is to be understood that any mineral oil or raw distillate therefrom may be used, but it is preferred to employ a lower viscosity naphthene base crude distillate of the Texas Gulf or California type.

The first step in the processes of the applicant's prior disclosures is an extraction of the mineral oil or distillate to be used with liquid sulphur dioxide or other selective solvents.

The hydrocarbon oil extract, together with liquid sulphur dioxide already present or added thereto, obtained by the above processes, may be used directly for sulphonation. It has further been found, however, that considerable improvement in the final products can be effected by additional processing of the material to be sulphonated, which processing may comprise one or more of the following steps: further narrowing of the boiling range of the portion of the oil to be sulphonated, additional fractionation of the material after solvent extraction, or additional or more specific fractionation prior to extraction. It may also include treatment of the material to be used for sulphonation with caustic soda to remove certain undesirable acidic constituents, treatment with sulphuric acid to remove asphalt-like and highly reactive bodies and water, and treatment with contact clay to assist in the sludge removal. The solvent extraction itself is preferably performed at a relatively low temperature, ranging from around —15° to 15° C., when using liquid sulphur dioxide. Although the hydrocarbon extract to be sulphonated may have a boiling range between 200° and 350° at 5 mm. pressure, it usually has a boiling range between 210° and 250° C. at 5 mm. pressure and preferably between 220° and 240° C. at the said pressure.

The next step after the pretreatment of the hydrocarbon extract consists in dissolving it in liquid sulphur dioxide, or, since, the extract material is already in liquid sulphur dioxide solution from the solvent extraction process, the next step may consist in diluting the solution with additional liquid sulphur dioxide. Usually, the extracted material should be dissolved in approximately one-half to two times its volume of liquid sulphur dioxide.

Having the desired solution of extracted material in liquid sulphur dioxide, the solution is cooled to a very low temperature and is intimately mixed with a precooled sulphonating agent, such as fuming sulphuric acid (20%), also preferably dissolved in liquid sulphur dioxide. The temperature is kept below +5° C. during the initial mixing, and preferably below —5° C. Other sulphonating agents soluble in liquid sulphur dioxide may also be used.

Upon completion of the original mixing of acid with the extracted materials and after the initial evolution of heat of reaction has been dissipated, the reacting mixture is raised to a temperature of about +5° C. by control of cooling apparatus. The original mixing is usually accomplished in a few minutes. The reaction is permitted to continue with agitation for a period, which period generally is not greater than fifteen minutes from the initial mixing of the reactants and preferably no longer than five minutes. However, if desired, a longer reaction time can be employed.

Treatment with the sulphonating agent having been completed, the reaction mixture is diluted with cold water to stop further action of the sulphonating agent. After water dilution, the next step is to separate any unreacted hydrocarbon from the mixture. Several alternatives are possible. One is to add enough water to the liquid sulphur dioxide solution of sulphonation products to form two layers, conducting the operation under suitable pressure. One layer consists of the bulk of liquid sulphur dioxide containing most of the unreacted hydrocarbon oil in solution. The other layer consists of the sulphonic-sulphuric acids in aqueous solution. Another method comprises evaporating off the liquid sulphur dioxide immediately upon dilution of the reaction mixture with water and controlling the quantity of water either to give a dilute solution of sulphonic-sulphuric acids (one phase) or, with a lesser proportion of water, to give a two-phase system consisting of an upper layer of sulphonic-sulphuric acids and a lower layer of sulphuric acid. This sulphonic acid layer is withdrawn and washed with an insoluble low boiling hydrocarbon in order to free it from any unreacted extract.

After removal of the residual dissolved sulphur dioxide and unreacted extract, the aqueous layer, with or without an intermediate boiling step, may then be neutralized with a basic compound, such as soda ash, lime, ammonia, or the like. The solution of neutralized sulphuric acid reaction product, which may also contain a considerable proportion of the sulphate of the neutralizing material as a result of its reaction with the excess sulphuric acid present, may be used in this state for many purposes, or it may be further concentrated by extracting with a solvent, such as a butyl alcohol, in which the active ingredient is soluble, to free it from the by-product sulphate formed in the neutralizing process.

The final material, either with or without the byproduct sulphate, may be formed into beads, flakes, chips, powders, solutions, liquid or plastic emulsions or other forms into which soap or other detergent or emulsifying materials are ordinarily made.

Although the novel textile treating compositions possess their unusual properties because of the sulphonated petroleum extracts, they are not restricted to this type of ingredient but may contain any of the auxiliary agents used in such compositions. Suitable addition agents, are other wetting and emulsifying agents including soaps, rosinates, organic ammonium and pyridinium compounds, monoglycerides, organic phosphorous compounds (e. g. lecithin), long alkyl chain esters of ortho- and pyro-phosphoric acids, and other sulphated and sulphonated compounds such as dodecyl sulphate, sulphonated castor oil or sulphonated oleic acid, etc.; coloring matter, such as dyes, lakes, and pigments; abrasives and inert fillers, such as grit, silex, pumice, feldspar, precipitated chalk, infusorial earth, bentonite, talc, starch, and air; liquids, including carbon tetrachloride, trichlorethylene, glycerine, alcohol, phenol, water, hexalin, pine oil, and naphtha; perfumes and deodorants; fats, vegetable or mineral oils, waxes, gums, or resins; caustic soda and potash and any of the common water-soluble salts, such as borax, sodium sulphate, chloride, acetate, silicate, orthophosphate, perborate, carbonate, bicarbonate, sesquicarbonate, hypochlorite, thiosulphate, hydrosulphite, and hyposulphate, or the corresponding stable ammonium and potassium salts of said anions. The water-soluble, water-softening compounds of the group consisting of tetraphosphoric, pyrophosphoric, metaphosphoric, or hexametaphosphoric acids and their alkali metal, ammonia, and amine salts may also be added to these compositions. The type of addition agent to be used, of course, will depend upon the ultimate use of the composition.

A better understanding of the process of making the improved compositions used in the novel textile treating compositions may be achieved by a consideration of the following specific example:

According to the preferred process, a distillate from a Texas Gulf Coast crude, boiling between 130° and 350° C. at 5 mm. pressure and having a Saybolt viscosity of 80 seconds at 100° F., is countercurrently extracted with approximately an equal volume of liquid sulphur dioxide by the usual Edeleanu process, the sulphur dioxide is separated from the extract, and the extract is then fractionally distilled in vacuum in the presence of about 0.1% of its weight of caustic soda. The fraction boiling between 220° and 240° C. at 5 mm. pressure is pretreated with about 1% of its weight of 92% sulphuric acid by mixing it therewith for about forty-five minutes. Most of the acid-sludge settles out at once, but a remainder, which is known as "pepper" sludge, has a tendency to remain suspended in the oil and is removed by treating the oil with about 0.2% of its weight of contact clay and heating to 130° to 150° C., excluding air. After hot filtration, the oil is found to be bright and clear. Centrifuging may be employed instead of, or in addition to, the contact clay treatment.

The desired fractions of the extract may be individually or collectively sulphonated, either by the batch method or in a continuous manner. The pretreated extract is dissolved in an equal volume of liquid sulphur dioxide and cooled to −20° C. Over a period of one minute, a liquid sulphur dioxide solution of 20% oleum is added. The quantity of oleum used is equal in weight to that of the hydrocarbon material to be sulphonated and is dissolved in half its volume of liquid sulphur dioxide and cooled to −20° C. The reaction mixture is agitated in a jacketed autoclave provided with stirrer, pressure gauge, thermometer and cooling means. Considerable heat is evolved upon the addition of the acid. Temperature control is maintained by circulating a cooling fluid through the jacket. The temperature during mixing is not permitted to rise above +5° C., and is maintained at that point for about ten minutes, the agitation being continued. The entire operation is conducted under suitable pressure. At the end of the reaction period, water is added, and the sulphur dioxide is separated as a vapor by reducing the pressure.

The resulting aqueous solution or dispersion is immediately batch-washed several times with 20% of its volume of gasoline, end point about 250° F. It is neutralized with caustic soda, and finally

dried upon soap-drying rolls at a roll temperature of around 250° to 275° F.

Although the above example is directed to the preparation of a sodium salt, other salts, such as those of calcium, potassium, magnesium, ammonium, and organic bases, may be prepared either directly or by a base exchange reaction. Examples of suitable organic bases are amines, quaternary ammonium hydroxides and other basic organic nitrogenous substances, such as diethylene triamine, triethylene tetramine, ethylene diamine, mono-, di-, and tri-ethanolamine, mono-, di-, and tri-amyl amine, aniline, dimethyl aniline, napthylamine, tetra-ethyl ammonium hydroxide, heterocyclic nitrogen derivatives, and N alkyl derivatives thereof, including pyridine, quinoline, quinaldine, N dodecyl pyridine, etc.

These products, prepared by sulphonating mineral oil extracts in the presence of liquid sulphur dioxide, serve admirably wherever there is need for deterging, wetting, solubilizing, penetrating, foaming, emulsifying, capillary modification or surface tension reducing action in the baths or operations commonly applied to wool, cotton, silk, linen, rayon, casein fibre and other natural or artificial textile materials. A few examples of the many applications of this invention are set forth by way of illustration in the following examples, wherein the term "sulphonated mineral oil extract" denotes the products produced by the processes above described.

EXAMPLE I.—*Washing loose wool*

A liquor satisfactory for washing loose wool is prepared as follows:

2.5 oz. of the sulphonated mineral oil extract (sodium salt), containing the sodium sulphate formed in the process by neutralizing the sulphonated mixture, is dissolved in 5 gallons of water, and the washing is conducted at about 50° C.

EXAMPLE II.—*Scouring raw wool*

Raw wool may be very satisfactorily scoured in a solution containing 3 grams per liter of the sodium salt of sulphonated mineral oil extract and 1 gram of sodium carbonate per liter. The solution should be held at about 110° F. Depending upon conditions the wool may be removed from the above bath, squeezed to remove most of the liquor, and washed in a fresh bath containing 2 grams per liter of the sodium salt of sulphonated mineral oil extract containing the sodium sulphate formed in the process by neutralization.

EXAMPLE III.—*Mercerizing yarn or fabric*

The efficiency of a mercerizing bath comprising a 55° Tw. caustic soda solution, for the treatment of yarn or a fabric, may be greatly increased by adding ¼ oz. of the sodium salt of the sulphonated mineral oil extract for each gallon of the bath employed.

The above example may be modified by previously wetting the material to be mercerized in a bath containing 1 oz. of the sodium salt of the sulphonated mineral oil extract to each 4 gallons of the wetting bath and then squeezing out excess wetting solution before introduction to the mercerizing bath.

EXAMPLE IV.—*Dyeing*

The salts of the sulphonated mineral oil extracts possess such remarkable wetting and emulsifying properties that they may be employed with advantage in various textile dyeing operations. For example, in the preparation of a liquor for dissolving soluble dyes, it has been found that the addition of the sodium or other water soluble salts of the mineral oil extract sulphonates results in more rapid penetration and more even dyeing. In some cases, more concentrated dye solutions may be employed, and, in the case where the dye is insoluble or nearly so, the presence of the mineral oil sulphonate emulsifies it to such an extent that it may be handled as an ordinary solution. To illustrate: 20 lbs. of the pyridine salt of a sulphonated mineral oil extract are combined with 30 lbs. of a mixture of polyalkylated water insoluble pyridine homologues, and the mixture is incorporated in 50 lbs. of water. A clear, water-soluble preparation is obtained which is excellent for dispersing dyes and possesses high wetting power in general. The solution is eminently suited for use in color baths in the textile industry.

This example may be modified by replacing the pyridine homologues with 30 lbs. of a mixture of alkylated pyridines and quinolines. If 20 lbs. of tetrahydroquinoline are substituted for the pyridine homologues in this example, a soluble product of oily consistency is obtained, displaying high wetting and dye dissolving properties.

EXAMPLE V.—*Bleaching and washing crude wool*

It has been found that a satisfactory wool degreasing agent and bleach may be prepared by adding sodium bisulphite to the sodium salt of the sulphonated mineral oil extract containing the sodium sulphate formed by the neutralization process. For this operation, a solution containing 8 grams per liter of the sulphonated mineral oil extract and 5 grams of sodium bisulphite is prepared. The raw wool is placed in this solution, held at about 120° C. for 15 minutes and gently agitated. After removing the wool from this bath, it is rinsed with clear warm water, squeezed and dried. The dried wool will be found clean and white and of good odor.

EXAMPLE VI.—*Spinning viscose*

About 3 grams of the sodium salt of sulphonated mineral oil extract (free of sodium sulphate) is added to each liter of ordinary viscose before spinning. The resulting solution is especially adapted for continuous spinning and produces a filament which is extremely uniform in its behavior and which responds uniformly to dyeing.

EXAMPLE VII.—*Spinning bath*

Threads of great fineness are produced by spinning viscose and/or casein solutions in a spinning bath containing 10% sulphuric acid, 1% mineral oil extract sulphonic acids, and 10% sodium sulphate. The operation may be conducted at 20° C. If desired, zinc and/or magnesium sulphate can be added to the bath.

EXAMPLE VIII.—*Penetrating in dyeing wool*

100 parts of wool are immersed in a luke-warm dye bath containing:

	Parts
Alizarine sky blue B	1
Mineral oil extract sulphonic acids	0.05
Glauber's salt	10 to 15
Sulphuric acid	2

The bath is then boiled for about 1½ hours, whereupon 2 parts of dilute sulphuric acid are added, and the boiling is continued for another hour. After rinsing and drying, the wool thus treated is uniformly dyed.

EXAMPLE IX.—*Printing paste*

A stock composition is prepared with:

	Parts
Durindone red 3B powder	2
Potassium salt of sulphonated mineral oil extract (inorganic salt-free)	1
Water	7
British gum solution (30%)	6.3

and 80 parts of this stock composition are mixed with:

	Parts
Glycerine	5
Caustic soda solution (76° Tw.)	4
Soda ash	5
Potassium carbonate	5
Formosul	8

The entire mixture is heated for 15 minutes at 55° C. on a water bath and, after cooling, is printed on cloth.

EXAMPLE X.—*Sizing*

The sodium salts of the mineral oil extract sulphonate, by virtue of their strong emulsifying and wetting out powers, may be used to advantage for sizing operations. A yarn soaked in a liquor containing 2 oz. of corn starch and ½ oz. of the sodium salts of the sulphonic acids per gallon of the liquor employed was found to be considerably improved in appearance and in the amount of size absorbed, when compared to yarn sized without the mineral oil sulphonate present in the bath liquor.

EXAMPLE XI.—*Bleaching cotton fabrics*

The powerful emulsifying properties of the mineral oil sulphonic acids or their salts have been found useful in connection with the bleaching of cotton fabrics. Not only may the goods be kier boiled for a shorter period of time than is usual, but, of even more importance, the strength of the caustic solution employed may be reduced. A sample of cotton fabric was boiled 45 minutes in an open vat in a one and one-half per cent caustic liquor containing one ounce per gallon of the sodium salt of the sulphonic acid from the mineral oil extract, consisting of approximately one-half sulphonate and one-half sodium sulphate. After removal and rinsing, the fabric was dipped in bleaching powder solution and air dried for about an hour. A weak acid wash followed by water washing and drying yielded a fabric that dyed in cold water solution with great readiness.

EXAMPLE XII.—*Dry cleaning*

A dry cleaning fluid having good detergent properties and which is neither inflammable nor combustible is prepared by adding 0.01% to 1.0% by weight of the ammonium salt of sulphonated mineral oil extract (by-product salt-free) to:

	Per cent
Carbon tetrachloride	60
Tetrachlorethylene	20
Petroleum naphtha	20

EXAMPLE XIII.—*Wetting*

A 20% aqueous solution of the sodium salt of sulphonated mineral oil extract is mixed in equal proportions with 10% commercial formalin (40%), and the mixture is dissolved in oil-free water in proportions of 1.0 to 1.5%. The product is characterized by its marked wetting properties when applied to textiles.

Throughout these examples, which illustrate but a few of the vast number of applications, the term "sulphonated mineral oil extract" is to be construed as the product disclosed in the applicant's United States Patents Nos. 2,149,661, 2,149,662 and 2,179,174, and copending application Ser. No. 239,553, already referred to. Whereas the product is probably a sulphonic acid or salt thereof, the invention should be construed to include the sulphuric acid reaction product set forth in these disclosures, whether or not it is a true sulphonate or sulphonic acid. As will be evident from the foregoing, use of the sulphonated mineral oil extract is contemplated with other sulphonic acids and their salts, sulphates, wetting agents, bleaching agents, dyes, waxes, etc., and, in fact, all of the compounding agents commonly employed in textile operations generally, as more fully set forth hereinbefore.

I claim:

A method of mercerizing cellulosic material which comprises treating a cellulosic material with a concentrated aqueous caustic soda solution containing a small proportion of a salt of a sulphonated mineral oil extract prepared by sulphonating, while in a liquid sulphur dioxide solution, an unsaturated mineral oil solvent extract having a boiling range between 200° and 350° C. at 5 mm. pressure.

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