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SOFTENING AND FINISHING OF TEXTILE MATERIALS AND COMPOSITIONS THEREFOR

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This invention relates to a process for treating textile materials and to compositions therefor. More particularly, it relates to a process for softening and finishing textile materials and to treating solutions therefor.

The present application is a continuation-in-part of my co-pending application, Serial No. 216,332, filed June 28, 1938, and is directed to certain textile treating inventions which have been divided out of that application.

An object of this invention is to improve treating textile processes. A further object is to provide a novel process for softening and finishing textile materials. A still further object is to treat synthetic and natural fibers so that they will be soft and supple and smooth to the touch. A still further object is to produce soft, smooth, supple, pliable cellulosic fibers which are free from objectionable odor. A further object is to soften and finish cellulosic fibers especially cellulose derivatives, in such a manner that their strength will not be impaired. Another object is to soften and finish synthetic and cellulosic fibers in such a manner that solubility characteristics are not increased. Other objects include a simple and economical process of softening and finishing textile materials and a general advance in the art. Still other objects will be apparent from the following description.

The above objects are accomplished by the following invention which comprises the preparation and use for treating a textile material of the water-soluble compositions and compounds obtained by reacting organic compounds, particularly higher saturated hydrocarbons with a mixture of sulfur dioxide and chlorine and hydrolyzing and/or neutralizing the resulting products.

In a more limited sense they are accomplished by the use, for treating textiles, of the compositions and solutions containing the water-soluble alkali metal, alkaline earth metal and ammonium salts of the hydrolysis products obtained by reacting non-gaseous saturated hydrocarbons, especially aliphatic hydrocarbons of 12 or more carbon atoms with sulfur dioxide and chlorine and hydrolyzing and neutralizing the resulting products.

The preparation of the water-soluble products has been described in my reissue application, Serial No. 206,274, filed May 5, 1938 now U. S. Reissue Patent No. 20,968, and will be again described herein.

In carrying out my invention, the compound to be substituted, if solid or liquid, needs no

further preparation other than the application of heat to start the reaction when necessary, or the use of a diluent, or chilling when the reaction at the start is too fast. In the case of solids, these may be liquefied either by heat, if possible, without disturbing their chemical structure, or by the use of a solvent, or both.

I have discovered that when compounds of either the aliphatic or aromatic series are treated with a mixture of sulfur dioxide and one of the halogens in the gaseous form, as for example chlorine, by bubbling these two gases through one of the aforementioned compounds a substitution is effected upon the hydrocarbon by replacement of one or more hydrogen atoms of the hydrocarbon and the formation of hydrogen chloride. Continued bubbling of these two gases through the compound appears to effect further substitution by means of the replacement of additional hydrogen atoms as aforesaid. The substituent group or groups may be chlorine and/or a group containing oxygen, sulfur and chlorine.

The substituent group containing oxygen, sulfur and chlorine is relatively unstable and is preferably formed in the absence of water. This group is readily hydrolyzed or saponified, and when formed on compounds of the shorter chain hydrocarbons, it is quite unstable to water, particularly at somewhat elevated temperatures. On the longer chain hydrocarbons there is a lessening of action as the number of carbon atoms increases. Thus, for example, hydrocarbon products containing as many as twenty-four carbon atoms react slowly in water, but more readily with a weak alkaline solution. During the hydrolysis reaction, the substituent group containing oxygen, sulfur and chlorine is modified in such a manner that the reaction product becomes partially if not wholly, soluble. Apparently sulfonyl chloride groups are formed in the first stage of the process and these are hydrolyzed and/or neutralized to sulfonic acid and/or sulfonic acid salt groups.

During the reaction of the hydrocarbon with sulfur dioxide and chlorine, I find that it is important to control the temperature of the reaction so that undesirable reactions accompanied by discoloration do not occur. This is particularly true with compounds of the aliphatic series, and as a specific example, the treatment of paraffin will be used.

EXAMPLE I

Paraffin was heated to 90–95° C. to liquefy the same and chlorine and sulfur dioxide gases were

bubbled through the liquid. After a gain in weight of 20-25%, the temperature was reduced to between 40 and 50° C. for the remainder of the treatment. By controlling the temperature of reaction, polymerization of the paraffin wax is avoided. Experiments have shown that if the temperature is not controlled, this treatment of the paraffin is accompanied by rise in temperature, due to the exothermic reaction, which causes the product to assume a dark color, possibly indicating polymerization, and the resulting product although a substituted paraffin, is not the same product from the standpoint of chemical structure as the product produced by temperature control.

The substituted paraffin produced by temperature control is a moderately viscous oil, light yellow in color, and liquid at room temperature. This product from all indications, where $C_{24}H_{50}$ is representative of paraffin wax, appears to contain molecules which have substituted therein one or more sulfur containing groups and/or one or more chlorine atoms. The number of sulfur containing groups and/or chlorine atoms which are substituted therein is, of course, dependent upon the length of time the paraffin is treated and it will be understood that more or less substitutions could be made.

In place of paraffin wax other paraffin hydrocarbons of high molecular weight, such as scale wax, match wax, wax distillates, Asiatic wax, petrolatum wax, petrolatum refined mineral oils, etc. may be substituted. The solubilized products are good softening and finishing agents and may be substituted in the following examples with similar results.

I prefer, however, to stop this treatment short of complete substitution as I find that the products produced in this manner are readily hydrolyzed or saponified. As pointed out above, the presence of the group containing oxygen, sulfur and chlorine on the shorter chain hydrocarbons renders the product quite unstable in the presence of water particularly at somewhat elevated temperatures, while on the longer chain hydrocarbons there is a lessening of action as the number of carbon atoms increases. With hydrocarbons containing as many as twenty-four carbon atoms, the reactive tendency has slowed down until the chlorinated product is only slowly hydrolyzed in boiling water but more readily hydrolyzed with a weak alkaline solution.

When the substituted paraffin has been hydrolyzed it becomes water soluble. This is also true of any of the aliphatic compounds which have been substituted by my improved method. These hydrolyzed products are soluble in water, ether, alcohol, acids, benzene, carbon tetrachloride, carbon bisulfide, petroleum products and various fats and oils. Due to their wide range of solubility, they are very useful in forming emulsions of normally incompatible substances, for example, paraffin, asphalt, gasoline, or any of the petroleum hydrocarbons and water, any of the vegetable oils or glycerides and water, or ether, carbon tetrachloride, carbon bisulfide, etc. and water. For the above reasons also they are very useful as detergents, and possessing great wetting power they are useful in the textile, leather, paper manufacturing and other industries.

By careful control of the process, the reaction may be kept to a state such that the end product is substituted with a single group containing oxygen, sulfur and chlorine. Through small

amounts of moisture admitted, or hydrolysis by means of a weak alkaline solution, the aforesaid sulfur containing substituent may be modified. For example, by boiling in neutral or slightly alkaline solution, the aforesaid sulfur containing substituent may be modified to form the true sulfonic group:



There is some contamination of the end products, for example there may be some of the original chlorine substituted products with the end products produced by hydrolysis. A slight contamination of the various products is of no material consequence, however, as far as their technical uses are concerned. If desired, they can be separated from one another.

From the above, it is apparent that with the aliphatic hydrocarbons, it is possible by my method to form directly halogen substitutions, sulfur containing compounds, and a mixture of halogen substitutions and sulfur containing compounds.

From the halogen substitutions, sulfur containing compounds, and the mixture of halogen substitutions and sulfur containing compounds, the following compounds may be readily formed: other sulfur containing compounds such as aliphatic sulfonic acids, hydroxy compounds or a combination thereof in a single hydrocarbon compound.

There is apparently no limit in the size of the molecules which will react in accordance with my method provided they are kept in a fluid condition at the temperature of the reaction. With the higher melting substances an inert solvent may be used to obtain this condition.

Those products produced in accordance with this invention which contain a sulfonic acid group and/or a hydroxyl group, as pointed out above, are water soluble and are useful as solvents or detergents. They also have antiseptic properties and may also be used as insecticides. Being water soluble they may be applied in almost any desired strength.

In treating fatty acids by my method, it is not necessary to separate them from the glycerine as the glyceride may be subjected to the two gases, the various subsequent steps of processing carried out, and the glycerine removed, if at all, whenever it is most convenient.

I find that my method of producing substitution products is also applicable to animal or vegetable fats or oils and to mineral hydrocarbons and to those of the aromatic series.

In addition to the specific examples of treating paraffin, cited above, I have also successfully treated lard, olive oil, kerosene, lubricating oil and others.

I find that the reaction during the time that the compound is being substituted is accelerated by heat, light and pressure and by controlling any or all of these conditions, the reaction may also be controlled accordingly.

The product prepared by reacting paraffin or any of the starting materials according to the disclosure may be hydrolyzed with aqueous solutions or hydrolyzed with an alkaline solution. The hydrolysis and/or neutralization is effective with dilute alkali metal base solutions, preferably caustic alkali solutions, and form water-soluble complex mixtures and compounds. A 30% caustic soda solution is very effective. For

convenience this product will be referred to as "solubilized paraffin" in the following examples, which will show the wide utility of the surface active agents. By surface activity, the commonly accepted meaning of the term in this art is intended. Thus, the solubilized products of this invention reduce the surface tension of the solutions in which they are incorporated at least 30%. In water, they have a surface tension lowering effect at least as great as common soap which in general reduces the tension about 50%.

Solubilized mineral oil means the water-soluble products which are preferably the hydrolyzed and neutralized products prepared according to the above disclosure.

It has now been found that the products prepared by the above described procedures have good finishing and softening properties for fibers and fabrics. When, for example, fibers, skeins, yarns, fabrics, etc. either synthetic, natural or cellulosic, are treated with solutions containing small amounts of the above compounds, they become soft, supple, pliable and smooth to the touch, free from odor and color and their strength is not impaired.

The compounds are usually employed in the form of a treating solution which is generally aqueous. They may be employed over a wide range of concentration however, for purposes of softening and finishing from 0.001% to 5% of the solution represents a practical range. Various other textile treating agents may be used in conjunction with the agents hereof, for example, sulfonated tallow, sulfonated olive oil, sulfonated tea seed oil, sulfonated castor oil, sulfated fatty alcohols, condensation products of fatty acids and amines before and after treatment with acids, higher alkyl sulfates, long chain quaternary ammonium, phosphonium or sulfonium compounds, carbohydrate amine condensation products, soaps, also oils such as vegetable oils, animal oils and fats, paraffin oils, waxes, and petrolatums, fatty acids, emulsified with suitable emulsifying agents such as, for example, the products of this invention.

EXAMPLE II

Five hundred grams of paraffin wax (commercial "parawax") was melted and a gaseous mixture of chlorine and sulfur dioxide in equimolecular proportions was passed in at 85 to 100° with an incandescent light under the flask. After 7 hours the gain in weight was 409 g. and on blowing with air, 4 g. of dissolved gases was blown out. The total chlorine passed through the reaction mass was 911 g. and the total sulfur dioxide was 1483 g. Two hundred grams of the reaction products which had the analysis (Cl 23.03%, S 11.19%) was placed in a 1 l. flask and 150 cc. 10 normal NaOH was added slowly at such a rate that the temperature did not rise over 50°. The crude product was centrifuged and the cloudy water-soluble supernatant liquor was separated.

Cotton broadcloth of 132/60 construction is padded through a bath containing 0.25% by weight of the above-described sodium salt and then dried. It has a very smooth surface, and is more pliable than before the treatment, is free from odor and does not become rancid. Other cotton fabrics such as muslins, sheetings, percales, twills, drills, etc. may be processed in a similar manner with baths containing from 0.1 to 2.0% of the softening agent to give them an enhanced "feel" when handled. Similarly, the

product may be used in baths containing stiffening and weighting agents, such as starches, dextrans, gelatin, talc, china clay, etc. for sizing textile fabrics, wherein the product serves to lubricate and soften the effect of the stiffening and weighting agents giving the fabric a more desirable finish. The product may also be applied to textile fibers in the staple form before spinning to improve their processing characteristics and to yarn of staple and continuous filament fibers to lubricate them and improve their processing characteristics.

Thus, both may be used to soften cellulose acetate, cotton, natural silk, wool, regenerated cellulose, generally called rayon, regenerated oxycellulose, ramie, linen, jute, casein fibers, and other natural and synthetic fibers, either in the staple form, as yarn, or as fabrics. In addition to producing softening and finishing effects on such fibers and fabrics an appreciable anti-static effect is obtained with solutions having concentrations within the ranges mentioned above.

EXAMPLE III

Improvement of absorption

Solubilizing paraffin and solubilized mineral oils are excellent assistants for improving the absorption capability of all types of fibrous materials. These products are especially useful when fibrous materials are subjected to treatments for the purpose of finishing, softening, stiffening, waterproofing, mildewproofing, shrinking and the like. They may be applied to the material in a separate treatment prior to the final treatment, or they may be incorporated in the final treating mixture. The quantities required vary with the type of material and process of treatment, but in general concentrations up to 0.1% in the bath produce the desired effect, although in some cases concentrations up to 1% may be required. An example of the use of solubilized paraffin to give improved absorption is the application of a finish to 42 x 44 count printed sheeting of 2.85 yards/lb. A 250 gal. treating mixture has the following composition:

	Pounds
Corn starch	75
Sago starch	48
Tapioca starch	48
Sulfonated tallow	90
Solubilized paraffin	5

The finishing mixture is padded on the fabric at 160° to 180° F. on a starch mangle, dried on cans, and then shrunk on a "Sanforizing" machine. Another finishing mixture for use on 80 square printed percale consists of the following quantities for 120 gal.:

	Pounds
Thin boiling starch	30
Glucose	10
Glycerine	4
Tallow softener	35
Solubilized mineral oil	3 65

The finishing mixture is applied at 160 to 180° F. in a starch mangle, the fabric is dried on cans, and then passed through a shrinking machine. A finish for 54 x 48 count undized duonub suiting of 4 yds./lb. consists of 50 lbs. of sulfonated olive oil and 5 lbs. of solubilized paraffin in 160 gal. The mixture is padded on the fabric, and the fabric is dried on cans and "Sanforized." Washing and polishing cloth may be rendered extremely absorbent by treating with

0.05% solubilized paraffin solution in a padding machine and drying on cans. Various other types of fabrics may be made absorbent by the use of the surface active agents.

5 The preferred manner of carrying out the hydrolysis is by the use of a concentrated aqueous solution of an alkali metal hydroxide solution for hydrolyzing and neutralizing the reaction products obtained by reacting a hydrocarbon or
10 equivalent material with gaseous chlorine and gaseous sulfur dioxide. While solutions containing at least 10% of the alkali metal hydroxide are very practical and allow the reaction to proceed fairly rapidly, more concentrated solutions such as those of at least 20% strength, give
15 still better results, and those having at least 30% strength are preferred. A fifty or sixty per cent solution is an effective hydrolyzing agent and portions of solid sodium hydroxide or other
20 caustic, particularly finely divided caustic may be used as an addition during hydrolysis. It is advantageous to hydrolyze with a strong caustic solution because the products are usually marketed as solid materials and most of the water
25 must be driven off or otherwise removed.

This invention has the advantage that a very desirable softening and finishing effect can be readily obtained in an economical manner. A further advantage resides in the fact that a
30 fabric, etc. which does not become rancid on standing can be economically obtained.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is
35 to be understood that I do not limit myself to the specific embodiments hereof except as defined by the appended claims.

I claim:

1. Process of finishing a textile fabric including
40 treating the fabric with a solution of a paraffin derivative soap produced by treating paraffin in the liquid phase with chlorine and sulfur dioxide and subsequently hydrolyzing the product by a strong inorganic alkaline solution.

2. Process of finishing a textile fabric including
45 treating the fabric with an aqueous solution of a paraffin derivative soap produced by treating paraffin in the liquid phase with chlorine and sulfur dioxide and subsequently hydrolyzing the
50 product by a strong inorganic alkaline solution.

3. A process which comprises finishing and softening a textile material with a solution of a
55 paraffin derivative soap obtained by reacting a non-gaseous paraffin hydrocarbon of at least 12 carbon atoms with sulfur dioxide and chlorine and hydrolyzing and neutralizing the same with

a strong aqueous solution of an alkali metal base having a concentration of 10% to 60% strength.

4. A process which comprises finishing and softening a textile material with an aqueous
5 solution containing 0.001 to 5.0% of a paraffin derivative soap obtained by reacting a non-gaseous paraffin hydrocarbon of at least 12 carbon atoms with sulfur dioxide and chlorine and hydrolyzing and neutralizing the same with a con-
10 centrated alkali metal hydroxide solution.

5. The process of treating a textile material which comprises padding the same with a solution containing an alkali metal salt obtained by reacting a non-gaseous paraffin hydrocarbon
15 with gaseous sulfur dioxide and gaseous chlorine and hydrolyzing the resulting product with a concentrated aqueous solution of an alkali metal base; and removing the excess solution.

6. A process as set forth in claim 5 wherein 20 the non-gaseous paraffin hydrocarbon contains at least 12 carbon atoms.

7. A process as set forth in claim 4 wherein the non-gaseous paraffin hydrocarbon is a
25 paraffin hydrocarbon wax.

8. A textile treating solution for the softening and finishing of textile materials comprising an aqueous solution containing a paraffin derivative soap obtained by reacting a non-gaseous paraffin
30 hydrocarbon with sulfur dioxide and chlorine and hydrolyzing the resulting product with a strong inorganic alkaline liquid.

9. A textile treating solution for the softening and finishing of textile materials comprising an aqueous solution containing a paraffin derivative
35 soap obtained by reacting a non-gaseous paraffin hydrocarbon of at least 12 carbon atoms with sulfur dioxide and chlorine, and hydrolyzing and neutralizing the resulting product with a strong aqueous solution of an alkali metal base having
40 a concentration of 10% to 60% strength.

10. A textile treating solution for the softening and finishing of textile materials comprising a solution containing from 0.001 to 5% a paraffin
45 derivative soap obtained by reacting a non-gaseous paraffin hydrocarbon of at least 12 carbon atoms with sulfur dioxide and chlorine and hydrolyzing and neutralizing the resulting product with a concentrated alkali metal hydroxide solution.
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11. A process as set forth in claim 4 wherein the textile material is cellulose acetate.

12. A process as set forth in claim 4 wherein the textile material is regenerated cellulose.
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