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SOFTENING AGENT

Luther Bishop Arnold, Jr., Fairville Pa., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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This invention relates to treating agents for paper and textiles, and more particularly to agents for softening leather, paper, and textile fibers. Still more particularly the invention relates to a new type of product based on long-chain aliphatic alcohols having twelve to twenty carbon atoms. This invention relates specifically to the sulfation of mixtures of long-chain aliphatic alcohols and aliphatic hydrocarbons, such as the oils and waxes derived from petroleum, under conditions which do not cause condensation of the components.

This invention has as an object the preparation of softening agents for leather, paper and textiles, combining the surface lubricating properties of aliphatic hydrocarbons with the softening properties of long-chain alcohol sulfate ester salts. The alcohol sulfate ester salts have the property of making fibrous materials, such as cotton, hemp, jute, linen, wool, silk, regenerated cellulose, cellulose acetate and wood pulp, when in the form of filaments or sheets, pliable so that they become very soft when handled. However, the alcohol sulfate ester salts lack surface lubricating properties. It is very desirable that a softening agent have surface lubricating properties in addition to the property of making the fibrous materials pliable as the feeling, or tactual response, of leather, paper, yarn or a fabric is most desirable when it feels very smooth to the touch in addition to being pliable. It is important, though, that the quantity of surface lubricant applied to the fibrous material be carefully adjusted to avoid the excessive quantities which would make it feel greasy. It is further necessary to have surface lubricating properties in softening agents to be used in sizing textiles with starches or other weighting agents in order to soften the starch film in addition to softening the textile material and giving it a smooth surface.

It has been heretofore possible to obtain surface lubricating properties in long-chain alcohol sulfate softeners by leaving a portion of the alcohol unsulfated. The possibilities of this procedure have been found very limited as the long-chain alcohols do not permit a wide variety of surface lubricating effects.

It is also essential that a suitable softening agent for treating fibrous materials, particularly for textile fabrics, form dilute aqueous emulsions which will remain stable even after having been boiled for thirty to forty minutes. Separation of the oily constituents of the softening agent would cause objectionable oily spots to be formed

on the material being processed, requiring the material to be reprocessed to remove the spots with consequent loss of time and labor.

The objects of this invention are accomplished by the sulfation above 0° C. of mixtures of long-chain aliphatic alcohols and aliphatic hydrocarbons, such as refined petroleum oils, petrolatums, and/or waxes with sulfating agents such as sulphuric acid, sulphur trioxide, chlorsulfonic acid and sulfuryl dichloride without the formation of condensation products between the components. The acid mixture is neutralized with an aqueous solution of a metallic base, or with an organic base.

The invention consists of thoroughly mixing a definite proportion of the aliphatic hydrocarbon and the long-chain alcohol, adding not to exceed 100% of the theoretical quantity of the sulfating agent required for complete sulfation of the alcohol, and of neutralizing the mass under conditions of controlled temperature above 0° C. and agitation. As the sulfation of the long-chain aliphatic alcohols does not go to completion even with chlorsulfonic acid, sulfation under these conditions will leave a portion of the alcohol unsulfated. This improves the stability and finishing properties of the product.

The following examples illustrate the process of the invention.

Example 1

19.3 parts by weight of stearyl alcohol (technical) and 12.8 parts by weight of refined petrolatum (m. p. range 40–50° C.; iodine No. 10–20) are melted together, and 7.6 parts by weight of chlorsulfonic acid (92% of theory on weight of stearyl alcohol) are added during agitation of the mass over a period of 30–40 minutes with the temperature maintained at 55–65° C.

The mass is then stirred for 4 to 5 minutes to allow the reaction to come to an end. 60.3 parts by weight of 5.4% sodium hydroxide at 30° C. are added to the reaction mass slowly during stirring.

The product is an homogeneous white paste in appearance. It emulsifies readily in warm water with simple agitation. Dilute emulsions even up to 5% will not separate after thirty to forty minutes boiling nor even while cooling from the boiling point.

The sulfation may also be carried out to obtain still less complete sulfation of the aliphatic alcohol in order to change the finishing effect of the product.

Example 2

24.1 parts by weight of stearyl alcohol (techni-

cal) and 8.0 parts by weight of refined petrolatum (m. p. range 40–50° C.; iodine No. 10–20) are melted together, and 7.3 parts by weight of chlor-sulfonic acid (70% of theory on weight of stearyl alcohol) are added during agitation of the mass over a period of 30–40 minutes with the temperature maintained at 55–65° C.

The mass is then stirred for 4–5 minutes to allow the reaction to come to an end. 60.6 parts by weight of 5.2% sodium hydroxide at 30° C. are added to the reaction mass slowly during stirring.

The product is an homogeneous white paste in appearance and in general similar to the product of Example 1, except for differences in finishing properties.

The following example illustrates the use of refined mineral oil instead of petrolatum.

Example 3

24.3 parts by weight of cetyl alcohol (technical) and 7.0 parts by weight of refined mineral oil (100 Saybolt units viscosity at 100° F.) are melted together, and 9.4 parts by weight of 98% sulphuric acid (100% of theory on the weight of the cetyl alcohol) are added during agitation of the mass over a period of 50–60 minutes with the temperature maintained at 55–65° C.

The mass is then stirred for 20–25 minutes to allow the reaction to come to an end. 59.3 parts by weight of 6.7% sodium hydroxide at 30° C. are added to the reaction mass slowly during stirring.

The product is an homogeneous white paste in appearance and in general similar to the product of Example 1 except for differences in the finishing properties.

The following examples illustrate the use of paraffin wax as the aliphatic hydrocarbon.

Example 4

20.2 parts by weight of cetyl alcohol (technical) and 11.1 parts by weight of paraffin wax (m. p. range 55–60° C.) are melted together, and 7.8 parts by weight of chloresulfonic acid (85% of theory on weight of cetyl alcohol) are added during agitation of the mass over a period of 30–40 minutes with the temperature maintained at 55–65° C.

The mass is then stirred for 4–5 minutes to allow the reaction to come to an end. 60.9 parts by weight of 5.4% sodium hydroxide at 30° C. are added to the reaction mass slowly during stirring.

The product is an homogeneous white paste in appearance and in general similar to the product of Example 1 except for differences in finishing properties. It will produce a more waxy and stiffer finish than the product of Example 1.

Example 5

20.2 parts by weight of cetyl alcohol (technical) and 11.1 parts by weight of paraffin wax (m. p. range 55–60° C.) are melted together, and 7.8 parts by weight of chloresulfonic acid (85% of theory on weight of cetyl alcohol) are added during agitation of the mass over a period of 30–40 minutes with the temperature maintained at 55–65° C.

The mass is then stirred for 4–5 minutes to allow the reaction to come to an end. 12.8 parts by weight of diethyl cyclohexyl amine are added to the reaction mass slowly during stirring.

The product is an homogeneous, thick paste which is yellowish in color. It produces finishes of similar character to the product of Example 4 but may be more readily removed from the

treated textile fibers for processes where it is desirable to remove the finishing agents. It requires no additional detergents or other assistants in the water in which it is to be rinsed from the textile fibers.

Other organic bases besides diethyl cyclohexyl amine with which neutralization may be carried out are dimethyl cyclohexyl amine, mono cyclohexyl amine, and methyl amine.

It has been found essential that the aliphatic hydrocarbons be mixed with the long-chain aliphatic alcohol before sulfation in order to produce a product which will be stable during and after boiling in dilute aqueous emulsions. If paraffin wax, or petrolatum is added to sodium alcohol sulfate paste, after sulfation and neutralization of the alcohol, in proportions to duplicate the composition of Example 1, the paraffin wax or petrolatum will blend with the alcohol sulfate paste to form an homogeneous paste. The paste thus prepared will form dilute aqueous emulsions which show no separation during boiling, but from which liquefied paraffin wax or petrolatum separates on cooling below the boiling point.

It has also been found that the same difficulty of separation of the petrolatum is encountered if the procedure of Example 1 is revised to the addition of the petrolatum after sulfation of the alcohol, but before neutralization of the sulfation mass. Petrolatum separates from dilute aqueous emulsions after cooling from the boiling point.

It has been found desirable that the ratio of the aliphatic hydrocarbon to the long-chain alcohol should not exceed certain limits in order to minimize the risk of separation of the hydrocarbon from hot dilute aqueous emulsions of the sulfation product. The limits are dependent on the specific hydrocarbon or hydrocarbon mixture, on the specific alcohol or alcohol mixture, and also on the neutralizing base used. A preferred preparation which is made from equal parts of petrolatum (m. p. range 40–50° C.; iodine No. 17) and technical stearyl alcohol sulfated with approximately 100% of the theoretical quantity of chloresulfonic acid on the weight of the alcohol shows no separation of petrolatum from hot dilute aqueous emulsions. In similar preparations made from a technical mixture of cetyl and stearyl alcohols, the ratio of petrolatum to alcohol usually does not exceed 4:5. However, it is not intended to limit the ratio of petroleum hydrocarbon to alcohol to these particular proportions.

As previously stated, the product prepared by the process of Example 1 has the advantage over paper and textile softening agents prepared by the sulfation of long-chain aliphatic alcohols that it provides an oily lubricating film of the aliphatic hydrocarbon mixture in petrolatum on the surface of paper and of textile fibers in addition to making them pliable through the action of the alcohol sulfate. This type of product provides a more suitable lubricating film than the unsulfated long-chain alcohols, and it is more economically prepared as the aliphatic hydrocarbons from petroleum are in general much cheaper than long-chain aliphatic alcohols.

The variety of combinations of aliphatic hydrocarbons from petroleum and long-chain aliphatic alcohols which it is possible to obtain permit the preparation of a wide variety of products which make available to the art new types of softening effects not hitherto obtainable. Light mineral oils of 50–100 Saybolt units vis-

cosity at 100° F., heavy mineral oils of 100–300 Saybolt units viscosity at 100° F., petrolatums, and/or paraffin waxes of the many different types available may be mixed with the different long-chain aliphatic alcohols having twelve to twenty carbon atoms and sulfated. It is, of course, preferable that the aliphatic hydrocarbons be mixed with the alcohols before sulfation and that the ratio of hydrocarbon to alcohol not exceed that which will produce a product forming dilute aqueous emulsions stable to prolonged heating.

The leather, paper, and textile softening agents formed in the preferred processes, as illustrated in Examples 1–4 incl. have the distinct advantage over those softening agents well known to the art, such as sulfonated fats and oils from animal and vegetable sources, that they will not turn rancid during storage or hot calendering or hot ironing to develop objectionable odors and to discolor the paper or textiles to which they have been applied. This is an important property as leather, paper, and textiles are frequently spoiled with consequent loss in value by deterioration of the sulfonated fats or oils with which they have been treated.

Leather is softened and "fattened" by treating it in a bath containing a 1–5% solution of the product of Example 1 or similar products prepared according to the process of the invention.

Paper is softened by passing it through a box preferably in the calender stack containing a ½–5% solution of the product of Example 1 or similar products prepared according to the process of the invention. It will have a smooth, pliable finish adding to its desirability for many purposes such as towelling, absorbent padding, and similar purposes for which soft paper is required. The treatment will also improve the absorbency of the paper.

Textiles in the form of the loose fibers, yarns or woven fabrics are softened by treating them in aqueous solutions of the product of Example 1 or similar products prepared according to the invention. Cotton raw stock can be softened and its carding or combing and spinning properties improved after dyeing in a circulating type machine by adding 3 pounds of the product of Example 1 per 1000 pounds of cotton to the rinse waters after the dyeing is completed.

Cotton and viscose yarns can be softened and the winding properties improved by the use of 5 ounces of the product of Example 1 per 100 gallons of water.

Woven fabrics of cotton are given a very soft, smooth finish by treating them in a pad mangle with the various products of the invention as indicated in the following examples.

Example 6

Light weight printed dress fabric.—7 pounds of the product of Example 1 are mixed with 100 gallons of water and preferably applied at 60–80° C.

Example 7

Medium weight printed shirting fabric.—2 pounds of the product of Example 1, ¾ pound of glycerine, and 12 pounds corn starch are mixed with 100 gallons of water. The mixture is boiled for 3 minutes and preferably applied at 60–80° C.

Example 8

Bleached suiting fabric.—11 pounds of the product of Example 3, 20 pounds of corn starch,

and 10 pounds tapioca starch are mixed with 100 gallons of water. The mixture is boiled 3 minutes and preferably applied at 60–80° C. This white bleached fabric will not develop discoloration when it is hot ironed nor develop rancid odors as it might were it softened with a sulfonated vegetable oil or a sulfonated animal fat.

Example 9

Dyed heavy suit lining fabric.—9 pounds of the product of Example 4 and 1 pound glycerine are mixed with 100 gallons of water and preferably applied at 60–80° C.

These latter examples illustrate the use of products of this invention on textiles in actual mill practice. The fabrics treated with the products have a smoother and softer finish than when treated with equal quantities of softening agents made from long-chain alcohols alone. The fabrics treated in this manner are free from the danger of discoloration developing on white or lightly colored portions when hot calendered or hot ironed and are free from the danger of rancid odors developing during storage in warm places as compared with fabrics treated with those softening agents most generally used heretofore which were prepared by sulphonation of oils and fats from animal and vegetable sources.

The products of this invention are also useful, in addition to their applications in leather, paper, and textile processing, in the preparation of lubricants for wire drawing and metal pressing, of compositions for polishing various types of surfaces such as metal, synthetic resin, wood, and other surfaces, and for cosmetics, as well as many other types of emulsions.

The above description and examples are intended to be illustrative only. Any modification or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the appended claims.

I claim:

1. A process of preparing a softening agent which comprises reacting a mixture of a substantially saturated higher aliphatic petroleum hydrocarbon and a long chain aliphatic alcohol having from 12 to 20 carbon atoms with a quantity of a sulfating agent which is not greater than that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of the mixture.

2. A process of preparing a softening agent which comprises reacting a mixture of a higher aliphatic petroleum hydrocarbon selected from the group consisting of mineral oils, petrolatums, and paraffin waxes and a long chain aliphatic alcohol having from 12 to 20 carbon atoms with a quantity of a sulfating agent which is not greater than that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of the mixture, and neutralizing the sulfated mixture with a solution of an alkali metal hydroxide.

3. A process of manufacturing a softening agent which comprises reacting a mixture of technical stearyl alcohol and refined petrolatum with a quantity of chlorosulfonic acid which does not exceed that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of the mixture, and neutralizing the

sulfated mixture with a solution of sodium hydroxide.

4. A process of manufacturing a softening agent which comprises reacting a mixture of cetyl alcohol and paraffin wax with a quantity of
5 chlorosulfonic acid which does not exceed that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of
10 the mixture, and neutralizing the sulfated mixture with a solution of sodium hydroxide.

5. A softening agent prepared according to the process defined in claim 1 which contains some unsulfated alcohol.

15 6. A softening agent prepared according to the process defined in claim 2 which contains some unsulfated alcohol.

7. A softening agent manufactured according to the process set forth in claim 3 which contains
20 some stearyl alcohol.

8. A softening agent manufactured according to the process set forth in claim 4 which contains some cetyl alcohol.

25 9. A process of preparing a softening agent which comprises reacting a mixture of a higher aliphatic petroleum hydrocarbon selected from

the group consisting of mineral oils, petrolatums, and paraffin waxes and a long chain aliphatic alcohol having from 12 to 20 carbon atoms with
5 a quantity of a sulfating agent which is not greater than that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of the mixture, and neutralizing the
10 sulfated mixture with an organic base.

10. A process of manufacturing a softening agent which comprises reacting a mixture of cetyl alcohol and paraffin wax with a quantity of
15 chlorosulfonic acid which does not exceed that required for complete sulfation of the alcohol in the mixture under relatively mild conditions to avoid the condensation of the components of the mixture, and neutralizing the sulfated mixture
20 with an organic base.

11. A softening agent prepared according to the process defined in claim 9 which contains
25 some unsulfated alcohol.

12. A softening agent manufactured according to the process set forth in claim 10 which contains some cetyl alcohol.

LUTHER B. ARNOLD, JR.