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MANUFACTURE OF SULPHONATED OILS

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20 Claims. (Cl. 87—12)

This invention relates to the manufacture of water-soluble oils from vegetable and animal oils and fats which are capable of being sulphonated. These water-soluble oils are adapted for a great variety of uses but primarily for use in various treatments of fibrous or textile materials, such as dyeing and finishing of piece goods, and lubricating the fibres for throwing and weaving.

These vegetable and animal oils and fats contain free fatty acids of high molecular weight and esters of these acids, especially the glycerides. These oils in their natural state are unsuitable for use in the various textile treatments under consideration for the reason that they are not capable of impregnating the material undergoing the treatment, being largely immiscible with water. It is therefore customary to subject these oils to a treatment which will convert them into a water-miscible form.

Hitherto, these vegetable and animal oils were converted into water-miscible form by the treatment known as sulphonation. This treatment usually consists of three stages. In the first stage, the oil is acidulated with a predetermined quantity of a concentrated sulphuric acid, usually slightly in excess of the quantity required for sulphonation, at a temperature of about 85° F., for a length of time sufficient to effect complete sulphonation. In the second stage, the sulphonated oil is washed with a water solution of sodium sulphate, (Glauber's salt) or a substance whose water solution has an alkaline reaction to remove the excess of mineral acid and to stop further conversion of the fats into hydroxy fatty acid. This washing is effected by thoroughly mixing the water solution of the salt with the acidulated oil. The mixture of salt solution and oil is then allowed to stand until it separates into two layers, the upper layer being the acidulated or sulphonated oil. The lower layer is drawn off in a third stage of the process and the remaining oil is treated with a suitable alkali, such as caustic soda, caustic potash or ammonium hydroxide. This treatment neutralizes any remaining free mineral acid, also clears the oil, and reduces the content of free fatty acid to the desired percentage for each particular case.

This sulphonation treatment of the natural oil removes therefrom either entirely or substantially entirely the glycerides which were originally present in the natural oil. If the glycerides could be retained in the processed or water-miscible oils or kept as nearly intact as nature provides them in the natural oil, the resulting product would impart to textile materials treated therewith in

dyeing, finishing, throwing or weaving processes, a greater amount of fullness, brilliancy and softness. Moreover, these improved results would be achieved by a smaller quantity of such product than is now used in the achievement of inferior results.

It is an object of my invention to restore to the processed oil or fat all of the original, combined glycerine and to even increase the quantity of combined glycerine, if desired.

Hitherto it has been deemed impossible to esterify the free fatty acids of high molecular weight, such as are contained in animal and vegetable oils, with glycerine in a practical manner. The mere addition of glycerine to the textile treating bath containing the sulphonated oil would not bring about the desired result for the reason that the glycerine would not be uniformly distributed throughout the bath and would lead to the production of a non-uniform product. Consequently, the glycerine must be chemically combined with the sulphonated oil in order to impart to the material under treatment the beneficial properties listed above.

I have found that glycerine can be readily combined with the sulphonated oil in the presence of a small amount of free mineral acid. The sulphuric acid used in the sulphonation is highly effective in this capacity. The action of the sulphuric acid is not completely understood, but it is presumed that it acts as a carrier or a catalyst. As stated above, the sulphonated oil after the second stage of the sulphonation usually contains a small quantity of free sulphuric acid. In practice, this free acid is neutralized by the treatment with alkali in the third or final stage of that process. If glycerine be added to the sulphonated oil after the second stage of the sulphonation process, while there is a quantity of free sulphuric acid present, the glycerine will readily combine with the sulphonated oil to form glycerides. In the event that the free mineral acid is completely washed out in the second stage, it is necessary to add a small quantity of free mineral acid together with the glycerine in order to effect the reaction. Likewise, if the glycerine is not added at such a stage of the sulphonation process in which some free mineral acid is present, it is necessary to add a small quantity of free mineral acid with the glycerine. The best results are obtained by using sulphuric acid having a specific gravity of 66° Baumé. It is important to immediately neutralize the free acid after the combination of the glycerine with the sulphonated oil is completed,

since otherwise, the acid, if allowed to stand in contact with the product for a time, would effect further conversion of the fats into hydroxy fatty acid.

5 The amount of free mineral acid which must be present during the esterifying of the sulphonated oil with glycerine will vary with the amount of glycerine to be incorporated in the oil. The presence of a large amount of glycerides in the oils
10 will cause fibers treated therewith to swell up. This action is particularly noticeable in artificial fibers. Other polyhydric alcohols, such as the various glycols, including ethylene glycol, propylene glycol, butylene glycol and the like,
15 erythritol, mannitol, sorbitol, dulcitol, etc., exert a similar favorable action on textile materials when combined with sulphonated oil in the manner described above.

20 My invention can be applied to any animal and vegetable oil or fat, such as neat's-foot oil, fish oils, liver oils, blubber oils, olive oil, castor oil, cotton-seed oil, palm oil, beef tallow, mutton tallow, etc. or mixtures thereof. While my invention is primarily directed to those oils and fats
25 which are capable of being sulphonated, I also contemplate mixing with such oils and fats other oils or fats, which are not of themselves susceptible to sulphonation. For example, cocoanut oil can be mixed with a sulphonated castor oil and the
30 mixture can be treated in accordance with my invention.

35 The following examples are given to illustrate practical embodiments of my invention, but are in no way to be taken as indicative of the scope thereof.

Example 1

40 One part of glycerine is added to four parts of sulphonated castor oil containing $\frac{1}{10}$ of one percent of 66° Baumé sulphuric acid. If the acid is not already present, it must be added. After the mixture is stirred for a short time, the glycerine is completely taken up by the sulphonated castor
45 oil. The termination of the reaction is evidenced by the brilliance which is imparted to the sulphonated oil which of itself presents a rather murky appearance. Sufficient alkali is added to neutralize the free acid. The product can be
50 diluted with water to any desired consistency.

Example 2

55 One part of ethylene glycol is added to four parts of sulphonated olive oil containing $\frac{1}{10}$ of one percent of 66° Baumé sulphuric acid. As soon as the glycol is taken up by the sulphonated oil sufficient alkali is added to neutralize the acid.

Example 3

60 One part of glycerine is added to four parts of sulphonated neat's-foot oil containing $\frac{1}{10}$ of one percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires a brilliant appearance
65 reaction is finished. The reaction mixture is then immediately treated with an alkali substance in order to neutralize the sulphuric acid present.

Example 4

70 One part of glycerine is added to four parts of sulphonated whale oil containing $\frac{1}{10}$ of one percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires the desired appearance reaction is finished. The reaction mixture is

then immediately treated with an alkali substance in order to neutralize the sulphuric acid present.

Example 5

80 One part of glycerine is added to nine parts of sulphonated tallow containing $\frac{1}{10}$ of one percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires the desired appearance the reaction is finished. The reaction mixture is then immediately treated with an alkali substance in
85 order to neutralize the sulphuric acid present.

Example 6

90 One part of ethylene glycol is added to nine parts of sulphonated neat's-foot oil containing $\frac{1}{10}$ of one percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires the desired appearance reaction is finished. The reaction mixture is then immediately treated with an alkali substance in order to neutralize the sulphuric acid present.
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Example 7

One part of ethylene glycol is added to nine parts of sulphonated whale oil containing $\frac{1}{10}$ of one percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires the desired appearance reaction is finished. The reaction mixture is then immediately treated with an alkali substance in order to neutralize the sulphuric acid
105 present.

Example 8

One part of mannitol is added to four or more parts of sulphonated castor oil containing $\frac{1}{10}$ of one percent of 66° Baumé sulphuric acid. If the acid is not already present, it must be added. After the mixture is stirred for a short time, the mannitol is completely taken up by the sulphonated castor oil. The termination of the reaction
115 is evidenced by the brilliance or uniform appearance which is imparted to the sulphonated oil which of itself presents a rather murky appearance. Sufficient alkali is added to neutralize the free acid. The product can be diluted with water
120 to any desired consistency.

Example 9

One part of sorbitol is added to nine parts of sulphonated castor oil containing $\frac{1}{10}$ of one percent
125 or more of 66° Baumé sulphuric acid. If the acid is not already present, it must be added. After the mixture is stirred for a short time, the sorbitol is completely taken up by the sulphonated castor oil. The termination of the reaction is evidenced
130 by the desired appearance or brilliance which is imparted to the sulphonated oil which of itself presents a rather murky appearance. Sufficient alkali is added to neutralize the free acid. The product can be diluted with water to any desired
135 consistency.

Example 10

One part of mannitol is added to nine parts of sulphonated neat's-foot oil containing $\frac{1}{10}$ of one
140 percent or more of 66° Baumé sulphuric acid. As soon as the oil acquires the desired appearance reaction is finished. The reaction mixture is then immediately treated with an alkali substance in order to neutralize the sulphuric acid
145 present.

It will be understood, with reference to all the foregoing examples, that if sufficient combined alkali is present in the product for absorption of the mineral acid, no further alkali need be added.
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What I claim as new and desire to secure by Letters Patent is:—

1. The process of producing an agent for the treatment of textile materials which comprises
5 reacting a substance selected from the group consisting of sulphonated vegetable and animal oils and fats in the presence of free sulphuric acid, with a polyhydric alcohol in an amount at least sufficient to restore to said substance the
10 percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation.

2. The process of producing an agent for the treatment of textile materials which comprises sulphonating a substance selected from the group
15 consisting of vegetable and animal oils and fats capable of sulphonation and reacting the sulphonation product in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said product the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation.

3. The process of producing an agent for the treatment of textile materials which comprises
25 sulphonating a substance selected from the group consisting of vegetable and animal oils and fats capable of sulphonation and reacting the sulphonation product in the presence of free sulphuric acid with glycerine in an amount at least sufficient to restore to said product the percentage of combined glycerine contained in the oils and
30 fats before sulphonation.

4. The process of producing an agent for the treatment of textile materials which comprises
35 reacting a substance selected from the group consisting of sulphonated vegetable and animal oils and fats in the presence of free sulphuric acid with glycerine in an amount at least sufficient to restore to said substance the percentage of combined glycerine contained in the oils and fats before sulphonation.

5. The process of producing an agent for the treatment of textile materials which comprises
45 reacting sulphonated castor oil in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

6. The process of producing an agent for the treatment of textile materials which comprises
50 reacting sulphonated olive oil in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

7. The process of producing an agent for the treatment of textile materials which comprises
60 reacting sulphonated castor oil in the presence of free sulphuric acid with glycerine in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

8. The process of producing an agent for the treatment of textile materials which comprises
65 reacting glycerine with sulphonated olive oil in the presence of free sulphuric acid with glycerine in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

9. The process of producing an agent for the treatment of textile materials which comprises
75 reacting a substance selected from the group con-

sisting of sulphonated vegetable and animal oils and fats in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said substance the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation.

10. The process of producing an agent for the treatment of textile materials which comprises sulphonating a substance selected from the group consisting of vegetable and animal oils and fats capable of sulphonation and reacting the sulphonation product in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said sulphonated product the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation.

11. The process of producing an agent for the treatment of textile materials which comprises reacting sulphonated castor oil in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

12. The process of producing an agent for the treatment of textile materials which comprises reacting sulphonated olive oil in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the oil before sulphonation.

13. The process of producing an agent for the treatment of textile materials which comprises
110 reacting a substance selected from the group consisting of sulphonated vegetable and animal oils and fats in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said substance the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation, stirring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

14. The process of producing an agent for the treatment of textile materials which comprises sulphonating a substance selected from the group consisting of vegetable and animal oils and fats capable of sulphonation and reacting the sulphonation product in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said product the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation, stirring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

15. The process of producing an agent for the treatment of textile materials which comprises
135 reacting sulphonated castor oil in the presence of free sulphuric acid with a polyhydric alcohol in an amount at least sufficient to restore to said sulphonated oil the percentage of combined polyhydric alcohol contained in the castor oil before sulphonation, stirring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

16. The process of producing an agent for the treatment of textile materials which comprises
145 reacting sulphonated castor oil in the presence of free sulphuric acid with glycerine in an amount at least sufficient to restore to said sulphonated oil the percentage of combined glycerine contained in the castor oil before sulphonation, stir-

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ring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

17. The process of producing an agent for the treatment of textile materials which comprises reacting a substance selected from the group consisting of sulphonated vegetable and animal oils and fats in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said substance the percentage of combined polyhydric alcohol contained in the oils and fats before sulphonation, stirring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

18. The process of producing an agent for the treatment of textile materials which comprises reacting sulphonated olive oil in the presence of free sulphuric acid with ethylene glycol in an amount at least sufficient to restore to said oil the percentage of combined polyhydric alcohol contained in the olive oil before sulphonation, stirring the mixture until the sulphonated substance presents a brilliant appearance and then neutralizing the free acid.

19. The product of the process of claim 1.

20. The product of the process of claim 7.

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