

UNITED STATES PATENT OFFICE

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DETERGENT AND EMULSIFYING AGENT

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This invention relates to derivatives of poly-hydroxy alcohols. It relates more specifically to derivatives of these alcohols in which one or more of the hydroxyls is replaced by an alkyl or acyl group and in which there is present in addition a residue of boric acid. Such compounds, according to this invention are then treated with a solubilizing agent such as a sulfating, sulfonating or phosphating agent, if desired, to produce compounds that have cleansing, preserving, wetting and emulsifying action and are excellent detergents.

Examples of the poly-hydroxy alcohols that may be employed are ethylene glycol, propylene glycol, glycerine, B-methyl glycerine, erythritol, diglycerol, poly-glycerols, sugar alcohols such as mannitol and sorbitol, sugar acids, reaction products of the poly-hydroxy alcohols with ethylene oxide and other poly-hydroxy compounds. In certain methods of preparation, the chlorhydrin or glycide derivatives of the poly-hydroxy alcohols may be employed.

The alkyl group must contain at least eight carbon atoms and be attached to the poly-hydroxy alcohol residue by an ether linkage. Such ethers are derived by known methods by reaction of the poly-hydroxy alcohol with alcohols straight chain or branched, and primary, secondary or tertiary. Such alcohols are those derived from fatty or other naturally occurring acids by reduction of the carboxyl group, from olefins derived from petroleum or other sources, by reduction of ketones and by the oxidation of paraffin. Examples are lauryl alcohol, alcohols obtained by the reduction of mixed fatty acids of coconut oil or tallow or their esters, oleyl alcohol, di-caproyl alcohol, abietanol, montanol.

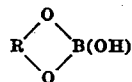
The acyl group, likewise, must contain at least eight carbon atoms and may be straight chain or branched. Examples are lauric, myristic, oleic or stearic acids, mixed fatty acids from coconut oil, palm oil, palm kernel oil, babasu nut oil, olive oil, tallow, rosin or abietic acid, montanic acid and acids from the oxidation of paraffin.

It is not known definitely in how many ways the boric acid may be combined with ethers or esters of these polyhydroxy compounds. It appears, for instance, that ortho-boric acid may

not only be combined with a compound containing one hydroxyl to yield a derivative of the type:



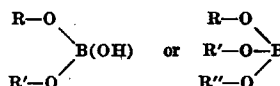
with two hydroxyls to give a compound of the type:



or with three or more hydroxyls giving the type:



but also that two or three linkages of the boric acid residue may be attached to hydroxyls of separate and distinct organic residues giving a compound of the type:



where R, R' or R'' may represent either the same or different kinds of radicals or residues. It is seen that the compounds formed according to the invention may be quite complex and of high molecular weight, a possibility that may explain the excellent emulsifying action of the compounds.

Similarly, by variation in operating conditions and choice of solubilizing agent, it is possible to attach one or more than one solubilizing group to the organic boron compound, and mixed derivatives may be formed in which the boric acid residue links two or more alkyl or acyl poly-hydroxy derivatives, with the sulfate, phosphate or other solubilizing group occurring in ratio of one or less than one with respect to the poly-hydroxy alcohol residue. Since the compounds formed may be quite complex, it is not my intention to limit the invention by illustration with formulas, but only to the alkyl or acyl derivatives of a poly-hydroxy compound in which the alkyl or acyl group contains not less than eight carbon atoms, the derivatives containing a boric acid residue and if desired in addition a solubilizing group such as a sulfuric acid, or phosphoric acid residue.

In the treatment with a sulfonating agent, an aromatic compound such as naphthalene or phenol or cresol may be added in which case the

ring compound is inserted between the poly-hydroxy borate residue and the sulfuric acid residue, and a substituted aromatic sulfonate is formed. Or mixed ring compounds obtained by the liquid SO_2 , or other known method of extraction of a fraction of petroleum, particularly from Gulf Coast or California crudes may be employed in place of aromatic compounds of known structure. Also, olefins, such as decene, octadecene, isobutylene or its polymers, or other olefins obtained by separation from or cracking of petroleum or a fraction of petroleum, may be introduced with the ring compounds during sulfonation, these attaching themselves to the ring as alkyl substituents.

Certain of the boric acid derivatives of alkyl or acyl derivatives of poly-hydroxy alcohols are water soluble, as for example the borates of the ethylene oxide derivatives of alkyl ethers or acyl esters of sorbitol. Others form emulsions with water but for solubility in water require the presence in the compound of a solubilizing group such as sulfuric or phosphoric acid residue or an aromatic sulfonic group.

All of the sulfated compounds of the general class described above that have been prepared are water soluble and possess marked wetting and detergent properties. The alkali, alkaline earth and heavy metal salts are water soluble. By variation in the choice of poly-hydroxy alcohol and the proportion of boric acid and conditions of its reaction, it is possible to vary the emulsifying characteristics of the product formed. Furthermore, boric acid possesses a preservative action toward bacterial decomposition and compounds of the type described are quite soluble derivatives of boric acid in a form that in aqueous solution have exceptional penetrating power. The un-sulfated boric acid esters are excellent emulsifying agents.

Borates of the poly-hydroxy alkyl or acyl derivatives are easily prepared by heating them with ortho or meta-boric acid in the molal ratio desired under a vacuum to promote removal of water. In addition, the acyl derivatives may be formed by reacting the preformed poly-hydroxy borate with a fatty acid, or fatty oil.

Boro-sulfates of the alkyl or acyl derivatives of poly-hydroxy alcohols may be prepared in several ways:

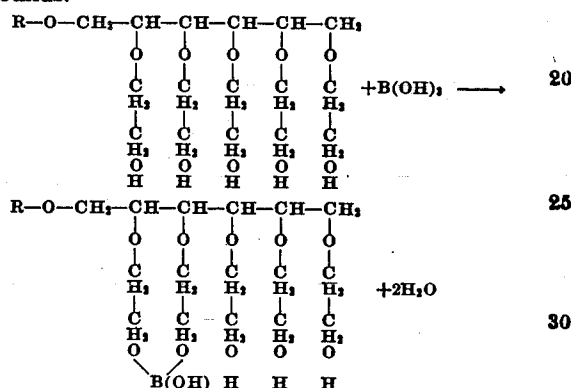
1. The poly-hydroxy alcohol may be reacted with ortho- or meta- boric acid under conditions that cause removal of water of reaction and the alcohol borate treated with fatty alcohols or fatty acids or their glycerides or other esters in such a manner as to result in the formation of the corresponding ether or ester of the poly-hydroxy alcohol borate. The compound is then sulfated by suitable reagents, such as sulfuric acid, oleum, chlorosulfonic acid, SO_3 in liquid SO_2 . The order of introduction of the fatty acid or alcohol and sulfuric acid may be reversed.

2. The ether or ester derivatives of poly-hydroxy alcohols may be prepared by known methods and converted into boric acid derivatives under conditions that result in the removal of water of reaction, after which the compound may be sulfated by the reagents indicated in 1.

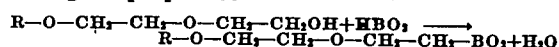
3. A mixture of fatty acid or its glyceride, the poly-hydroxy alcohol, boric acid or its anhydride and sulfuric acid or fuming sulfuric acid may be heated to about 50°C . until the reaction product is entirely miscible with water, attention being paid to proportioning the ingredients in the molal relationship desired in the product, and with sulfuric acid of sufficient strength and quantity to

form the sulfate and absorb the water of reaction. Sulfuric acid in this case acts to hydrolyze the tri-glyceride if used, to esterify the poly-hydroxy alcohol with fatty acid present or formed by hydrolysis, to bring about ester formation with the boric acid, to sulfate the compound and to absorb the water of reaction.

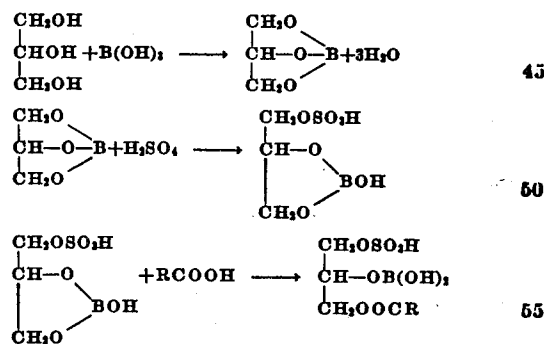
Illustrative equations are given below. The equations are not intended, however, to limit the scope of the invention. More particularly, is it not intended to limit the invention to compounds of the simple structure indicated. As discussed above, it is probable that more complex compounds are formed by the attachment of more than one organic residue to a single boric acid residue, and specific claim is made to such compounds.



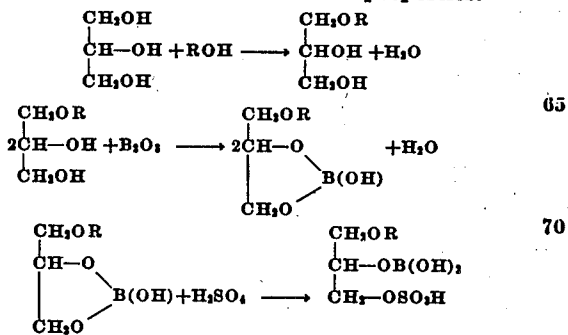
The borate of the penta- hydroxyl ethyl ether of sorbitol fatty alcohol ether is soluble in water and exhibits marked emulsifying, wetting and detergent properties.



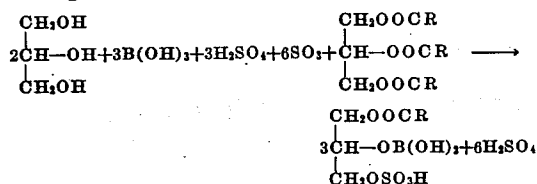
The meta-boric acid ester of the fatty ether of di-ethylene glycol is an excellent emulsifying agent.



The boro-sulfate of fatty acid mono-glyceride is soluble in water and has marked wetting, emulsifying and detergent properties in aqueous solution. The salts exhibit the same properties.



The boro-sulfate of the fatty ether of glycerine is water soluble and as such or in form of its alkali, alkaline earth, ammonium amine salts exhibits marked emulsifying, wetting and detergent characteristics.



Neutralization may be carried out to form the mixed salt of the organic compound and the excess sulfuric acid.

It is specifically within the scope of this invention to produce and employ as cleansing, preserving, wetting, deterring and emulsifying agents, the boro-sulfuric acid derivatives as such or their compounds with alkalis or alkaline earths, ammonia, an ethanolamine, or other basic substance, whether organic or inorganic.

EXAMPLES OF PREPARATION

1.—Coconut oil fatty acid monoglyceride borate

94.7 gms. of coconut oil fatty acid monoglyceride and 6.9 gms. of ortho-boric acid were mixed in a distilling flask and warmed. Above 100° C. water was evolved and at 125° C., solution of the boric acid was complete. The flask was placed under vacuum to assist in withdrawal of water and the product heated to 150° C. under 1" pressure. The loss in weight amounted to 6.5 gms. whereas theory would require 6.0 gms. The product was a clear straw colored liquid slowly solidifying at about 28° C. No boric acid separated on standing.

2.—Sulfation of coconut oil monoglyceride borate

43.0 gms. of coconut oil monoglyceride borate prepared as above was warmed to 47° C. and 69.8 gms. of sulfuric acid (102.8%) was added dropwise. Within a short time after the acid had been added, a sample of the product was completely soluble in water. The mixture of the organic boro-sulfuric acid with the excess sulfuric acid was stirred into ice water and neutralized with 30% caustic soda. The product formed a perfectly clear 1% solution in water, whether soft or hard, and exhibited excellent foaming, wetting and washing properties.

3.—Coconut oil fatty acid monoglyceride boro-sulfate

43.2 gms. of coconut oil, 12.8 gms. of 99.3% glycerine, and 4.0 gms. of ortho-boric acid were taken with 105.2 gms. of sulfuric acid. The sulfuric acid was of 102.84% strength, containing 11.9% of free SO₃. The boric acid was added to the sulfuric acid and the mixture placed in an ice bath, after which with stirring, the glycerine was added dropwise. The mixture was warmed to 45–50° C. and at this temperature with stirring, the oil was added slowly. After holding the batch at this temperature for 35 minutes, a test sample was perfectly clear on dilution with water. The batch was now dumped into a mixture of ice and water and neutralized with 30% caustic soda.

4.—Fatty acid hydroxyethyl sorbitol borate

260 grams of the esters derived from coconut oil fatty acid and the hexahydroxyethyl ether of sorbitol were converted into the ortho-boric acid

ester by heating in vacuo with 10.3 grams of ortho-boric acid until the water of reaction was removed.

5.—Boro-sulphate of lauryl glycerine ether

138 grams of the ether of glycerine and lauryl alcohol were heated in vacuo with 28 grams of meta-boric acid at a temperature up to 150° C. until the reaction was completed by removal of the water liberated. The product was then treated with 275 grams of 20% oleum (104.5% H₂SO₄) at a temperature of 30 to 40° C. for one hour. The reaction mixture was then poured into ice and water and neutralized with monoethanolamine to a pH of 7.0.

6.—Boro-sulphonate of cocoanut oil monoglyceride and Edeleanu extract of petroleum

284 grams of the monoglyceride of cocoanut oil fatty acids were converted into the ortho-boric acid ester as described in Example 1. This was mixed with 100 grams of Edeleanu extract of California lubricating oil and the whole treated with 500 grams of 20% oleum at 80° C. for about 2 hours. The reaction mixture was then poured into ice and water and neutralized with ammonium hydroxide.

7.—Boro-sulphonate of cocoanut oil monoglyceride, olefin and naphthalene

284 grams of cocoanut oil fatty acid monoglyceride were converted into the meta-boric acid ester by heating in vacuo with 28 grams of meta-boric acid. The product was mixed with 125 grams of naphthalene and 100 grams of decene and heated at 75° C. with 500 grams of 20% oleum for 2 hours. The reaction mixture was then extracted with butyl alcohol and the alcoholic solution neutralized with an aqueous solution of sodium bicarbonate, after which the alcohol solution was removed by distillation.

Having described my invention, I claim:

1. A process for preparing boric acid esters of fatty acid monoglycerides which comprises heating at least one fatty acid monoglyceride and boric acid under conditions to remove the water of reaction.

2. The process which comprises preparing a boric acid ester of a polyhydroxy alcohol, condensing said ester with at least one compound of the class consisting of fatty alcohols, fatty acids, and esters thereof, to form a boric acid ester of a compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, sulphating the condensation product and neutralizing the resulting material.

3. The process which comprises preparing a boric acid ester of a polyhydroxy alcohol, treating said ester with a sulphating agent, condensing the product with at least one compound of the class consisting of fatty alcohols, fatty acids and esters thereof, to form an inorganic acid ester of a compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, and neutralizing the resulting inorganic acid ester.

4. The process which comprises reacting at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, with boric acid to form the corresponding boric acid ester, sulphating said boric acid ester and neutralizing the resulting product.

5. The process which comprises reacting a mixture of a polyhydroxy alcohol, boric acid, sulphuric acid, and a compound of the class consisting of fatty acids and esters thereof by warming

until the reaction product is miscible with water, and neutralizing the resulting product.

6. The process which comprises warming a mixture containing in molecular proportions about one part of coconut oil, about two parts of substantially anhydrous glycerine, from about one to three parts of boric acid, and more than three parts of sulphuric acid at from 30° to 90° C. until the product is miscible with water, and neutralizing the reaction product.

7. The process of producing a wetting agent and detergent which comprises reacting at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, with boric acid, an aromatic compound, and fuming sulphuric acid.

8. The process of producing a wetting agent and detergent which comprises reacting an olefin and at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, with boric acid, an aromatic compound, and fuming sulphuric acid.

9. The process of producing a wetting agent and detergent which comprises reacting boric acid and at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, with a liquid sulphur dioxide extract of a fraction of petroleum, and fuming sulphuric acid.

10. The process which comprises reacting a partial ether of a polyhydroxy alcohol and a high molecular weight aliphatic alcohol, with boric acid under conditions to remove the water of reaction.

11. The process which comprises reacting a partial ester of a polyhydroxy alcohol and a high molecular weight fatty acid, with boric acid under conditions to remove the water of reaction.

12. The process which comprises reacting a mixed ether of a polyhydroxy alcohol and a high molecular weight aliphatic alcohol, with boric acid, and with a sulphonating agent.

13. The process which comprises reacting a partial ester of a polyhydroxy alcohol and a high molecular weight fatty acid, with boric acid, and with a sulphonating agent.

14. The process which comprises reacting a polyhydroxy alcohol with a high molecular weight fatty acid, and with boric acid under conditions to remove the water of reaction.

15. The process which comprises reacting at least one high molecular weight aliphatic compound selected from the group consisting of partial ethers and esters of polyhydroxy alcohols, with boric acid, and with a sulphonating agent.

16. A compound of the class consisting of boric acid esters, boric acid-sulphuric acid esters, boric acid-phosphoric acid esters, and salts of said esters, of at least one compound of the class con-

sisting of aliphatic partial ethers and esters of polyhydroxy alcohols, wherein the aliphatic substituent on the polyhydroxy alcohol contains at least eight carbon atoms.

17. A compound of the class consisting of boric acid esters, boric acid-sulphuric acid esters, boric acid-phosphoric acid esters, and salts of said esters, of coconut oil fatty acid monoglycerides.

18. The reaction product obtained by warming a mixture of tallow, glycerine, boric acid and sulphuric acid which contains a sufficient amount of sulphur trioxide to absorb the water of reaction.

19. A cleansing agent comprising as its essential ingredient a compound of the class consisting of boric acid esters, boric acid-sulphuric acid esters, boric acid-phosphoric acid esters, and salts of said esters of at least one aliphatic acid monoglyceride.

20. The product obtained by reacting at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols with boric acid, an aromatic compound and fuming sulphuric acid.

21. The product prepared by reacting boric acid, an olefin, and at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, with an aromatic compound, and fuming sulphuric acid.

22. The product prepared by reacting boric acid and at least one compound of the class consisting of partial ethers and esters of polyhydroxy alcohols with a liquid sulphur dioxide extract of a fraction of petroleum and fuming sulphuric acid.

23. A boric acid ester of a compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, the organic substituent on the polyhydroxy alcohol having at least eight carbon atoms.

24. A boric acid ester of a compound of the class consisting of partial ethers and esters of polyhydroxy alcohols, the organic substituent on the polyhydroxy alcohol having at least eight carbon atoms, and the polyhydroxy alcohol being glycerine.

25. Boric acid esters of monoglycerides of coconut oil fatty acids.

26. A compound of the class consisting of boric acid esters, boric acid-sulphuric acid esters, boric acid-phosphoric acid esters and salts of said esters, of a partial aliphatic ether of polyhydroxy alcohols wherein the aliphatic substituent on the polyhydroxy alcohol contains at least eight carbon atoms.

27. An emulsifying agent comprising as the essential ingredient a boric acid ester of a fatty acid monoglyceride.

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