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WETTING, DISPERSING AND WASHING AGENT

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The present invention relates to the production and the use of a wetting, dispersion and washing agent which is obtained by the condensation of a carboxyl compound e. g. a carboxylic acid or its ester with a boric compound e. g. boric acid or boric anhydride and a polyvalent alcohol and subsequent sulphonation. The product may be employed as a wetting, dispersion, reviving and washing agent in the textile industry, and also in the paper and leather industry and in the cosmetic industry, this both in the form of the free sulphonic acid and also in the form of its neutral salt.

It is certainly known that valuable products are obtained by the esterification of carboxylic acids with polyvalent alcohols and subsequent sulphonation. These products, however, are resistant towards acids and alkalis to a restricted extent only, since they are split up again into carboxylic acids upon heating. Moreover, they are affected by concentrated alkalis. It has now been found that, by the condensation of carboxylic acids or their esters with polyvalent alcohols with the use also of boric acid or boric anhydride, products of an entirely different kind are obtained which, unexpectedly, are much more resistant towards acids and, in particular, towards alkalis.

In accordance with the invention, the new products may be produced in the following fashion:

One molecule of a carboxylic acid or one molecule of a carboxylic-acid ester is heated with two molecules of a polyvalent alcohol and one half molecule of boric acid H_3BO_3 or one half molecule of boric anhydride. In some cases, heating may be performed under pressure and at correspondingly higher temperature, or in vacuo at a correspondingly lower temperature, or in the presence of an inert gas. In some circumstances, it is more advantageous to carry out this process in the presence of a high-boiling solvent. It is then quite immaterial whether the boric acid is first brought into reaction with the polyvalent alcohol or whether a mixture of the three components all together is heated. The volatile substances formed in this reaction, such as water, excess polyvalent alcohol and decomposition products are distilled off.

The condensation product may be used by itself as a softening agent in the textile and leather industry. It may further be employed as a foam-preventing agent.

Particularly valuable are the sulphonation products of these new condensation substances and the salts produced therefrom. The neutral products have soap-like properties without exhibiting the disadvantages of such soaps. They are soluble in water in completely neutral fashion, are not affected by sulphuric acid up to 6° Bé, and give no separation with concentrated common-salt or Epsom-salt solution. They are extremely resistant towards the hardness-producing substances in water, remaining perfectly clear even with water of over 100° DH. In conjunction with soaps, they prevent the formation of lime soaps to a certain extent. Precipitated lime soaps are dispersed by the products in accordance with the invention, so that the lime soaps are brought into a form in which they can be readily washed away. Even salt solutions of the heavy metals have no effect upon the new sulphonated products. Unexpectedly, however, the products are also very resistant towards alkaline substances without being subject at the same time to saponification. Clear solutions are obtained which remain clear, with the addition of up to 5% of phenol even with concentrations of up to 50° Bé of potash lye without turbidity or separation taking place after days. Consequently, these new products are particularly suitable for mercerisation and discharge printing. They are, moreover, also good emulsifying agents which are capable of converting comparatively large quantities of fatty acids, neutral fats, liquid and solid hydrocarbons and other substances insoluble in water into a water-soluble form, for which reason they can also be employed in the metal industry for the production of boring, grinding, and cooling agents. The new products are also suitable for the production of cosmetic and pharmaceutical products. Due to their good wetting powers, they are suitable, in combination with insecticide agents, for the extermination of vermin and vegetable pests.

The saturated and unsaturated fatty acids, their esters or their natural neutral oils are suitable as the carboxylic acids, also the resinic acids and their mixtures with fatty acids such, for example, as tall oil, further the naphthene acids, wool-fat acids and their natural wax-like cholesterides.

Glycol, di-glycols and polyglycols, glycerine and polyglycerines, erythritol, penta-erythritol, mannitol, sorbitol and the varieties of sugar are suitable as the polyvalent alcohols.

Concentrated commercial sulphuric acid and the maintenance of sulphonation temperature of less than 40°C suffice for the sulphonation. However, with appropriate precautions, sulphonation may also be performed with monohydrate, oleum

or chloro-sulphonic acid. In some cases, also, sulphonation may be effected in the presence of solvents which, as desired, may be left or distilled off. The sulphonation products may be neutralised with alkaline lyes, alkali carbonates, ammonia or organic bases such as triethylamine, triethanolamine, ethylenediamine or pyridine. Preferably the excess sulphuric acid is first washed out. However, it is then possible also to separate the acid sulphonation product from the washing water by suitable solvents such, for example, as hydrocarbons and then to neutralise and, in some cases, to distil off the solvent. Particularly concentrated products up to 60% content (calculated with reference to the content of condensation product) are obtained in this fashion. The final product may be produced in liquid form, in jelly-like and paste form with or without Glauber's salt. However, it is also possible to obtain a product, containing Glauber's salt, in powder form. The new product may be worked into soaps to which it imparts an increased resistance to lime.

No certain information can be given as to the chemical constitution of the new products. By comparatively detailed investigation, it has been determined that, for example, upon the condensation of ricinoleic acid with glycerine and boric acid, simple glycerine-monoricinoleate is not formed, but a product which contains two molecules of glycerine and one half molecule of boric acid to one molecule of ricinoleic acid. If the condensation product is washed with hot water a product is obtained which consists of one molecule of ricinoleic acid, one and a half molecules of glycerine and one sixth of a molecule of boric acid. The boric-acid content is maintained even after the sulphonation. If, in this condensation reaction, the boric acid is omitted, then the known glycerine-monoricinoleate is obtained which, after the sulphonation, does not exhibit the favourable properties like the condensation product obtained with the employment of boric acid. In a further experiment, distillation flasks respectively containing one molecule of stearic acid and two molecules of glycerine were set in the same heating bath. One half molecule of boric acid was added to one of the distillation flasks. Both preparations were heated to 340°C and thereafter washed with hot water. From the experiment with the boric acid, a product was obtained having 72.03% of stearic acid and 2.9% of boric acid. From the experiment without boric acid, a product having a 79.23% content of stearic acid was obtained.

Example 1

A mixture consisting of 298 parts of anhydrous ricinoleic acid, 184 parts of anhydrous glycerine and 31 parts of boric acid is heated in a distillation apparatus. The boric acid disappears between 120 and 130°C and two sharply separated layers are formed. A homogeneous clear liquid is obtained upon further heating up to 310°C. Approximately 51 parts of water, 47 parts of excess glycerine and 8 parts of an oily decomposition product are distilled off. The yield amounts to 407 parts, or 79% of the originating material. The cool oil is stirred gradually in a suitable apparatus at between 30–35°C with 450 parts of concentrated sulphuric acid until a sample is clearly soluble in water. After 2–3 hours further stirring, 1200 parts of the ice water are added and the excess sulphuric acid is washed out therewith. After the removal of approximately 950 parts of acid water, there remain approximately 1100 parts of the sulphonated product. These are neutralised with approximately 310 parts by weight of soda lye of 40° Bé, 360 parts of Glauber's salt solution separating out again. 1050 parts of neutral product are obtained with a content of 28.8% of organic substance and 0.93% of boric acid.

The completely neutral product is suitable as a wetting agent in the dyeing industry and a solution of 3°/00 at 18°C gives a wetting period of 4 seconds, whereas 12 seconds was determined in a similar experiment with 50% Turkey-red oil. Moreover, the product, due to its softening and dispersive properties in the various finishing processes, is suitable also as a washing agent for artificial silk, cellulose wool, cotton, wool and coloured fabrics. It may be employed, as required, in acid, neutral or alkaline dye-baths. Due to its fat content, it imparts a soft feel to the goods. In combination with fat solvents or alcohols, the product may be employed as a cleaning or purifying agent or a conditioning agent, since it is weakly hygroscopic.

Example 2

141 parts of olein, 62 parts of glycol and 15.5 parts of boric acid are heated to 215°C, carbon dioxide being passed through. 28 parts of water, 4 parts of glycol and 8 parts of oil are thereby distilled off. The yield amounts to 178 parts. The product is sulphonated and worked up as in Example 1. A bright yellow oil is formed which is particularly suitable as a washing agent due to its dense and stable foam.

Example 3

A mixture of 142 parts of stearic acid, 92 parts of glycerine and 15.5 parts of boric acid are heated in vacuo at 16 mm. pressure to 240°C. 28 parts of water, 3 parts of glycerine and 3.5 parts of fatty acid are thereby distilled off. The yield amounts to 215 parts. The product is dissolved in 400 parts of carbon tetrachloride, sulphonated with 200 parts of 100% sulphuric acid and thereafter washed with 300 parts of ice water. The sulphonation product remains dissolved in the carbon tetrachloride and, after the separation of the acid water, is neutralised with 81 parts of triethanolamine. A bright yellow solution is obtained which completely emulsifies in water. The product may advantageously be employed as a spot-cleaning agent.

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