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## DETERGENT COMPOSITION

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This invention relates to a detergent composition and material for use therein, and particularly to such a composition including a special type of boron compound and a surface-active agent of kind to be described.

The industry of soap detergents is very old. Also, there has been intense activity in this field in recent decades, with the result that a very large number of compositions including soap and soap builders have been proposed for use in washing dishes in hotels and restaurants, in laundering, and in other large establishments. Many of the best of such soap compositions involve the addition of sodium carbonate, sodium metasilicate, or trisodium phosphate.

Borates have been considered unsatisfactory as additions to soap compositions to increase the detergent effect. Instead of being helpful in their effects on the soap composition, the borates available on the market for the purpose are generally found to be seriously detrimental, the mixture including the borates being less effective than the soap alone. The exceptions to this, when other soap builders are not added, is in the case of very slightly soiled garments or what detergent chemists know to be alkaline or only very slightly acid forms of soil.

Thus, it is commonly understood that borax, the most readily available of the borates, is unsatisfactory as a soap builder in comparison with the merits of trisodium phosphate, sodium carbonate, sodium metasilicate and another class of compounds often called soap builders but depending on sequestration of calcium and magnesium, this class comprising sodium metaphosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, and their homologues and mixtures. Considering soap as the surface-active agent, for the purpose of illustration, it has been the opinion of experts in this art, that a soap builder must either increase the pH of the soap solution or belong to this latter class of so-called builders, the complex phosphates.

I have now found that the special sodium borate to be described herein gives a highly effective action with soap, even though it neither increases the pH of the solution appreciably nor belongs in the class of the complex phosphates. Further effectiveness is obtained by modifications which do increase the pH of the compositions containing my special borate, effectiveness so obtained being greater than that obtained by usual builders at the same pH.

With soap as the surface-active agent, for example, I have now discovered that, by the use of my new sodium borate, a very effective detergent composition may be made without substantial modification of the pH of soap solutions of concentrations commonly used in dish washing and laundering and that a particularly satisfactory detergent is made when the borate as made is dried to a moisture content not substantially above 50 per cent. I have found also that there is further improvement if the product is made to contain a moderate excess of sodium oxide over that required to combine with boric oxide to form sodium metaborate, which may be written for convenience in this connection as

$$Na_2O.B_2O_3$$

My new sodium borate is not the sodium borate of commerce which is commonly sodium tetraborate. Instead it is a more alkaline compound containing metaborate and prepared by combining the boron oxide with alkali in ratios to each other calculated to produce a series of materials having compositions in the range represented by the formulas $NaBO_2$ to $Na_3BO_3$ but not necessarily being pure chemical compounds or corresponding exactly to these formulas. The borate has new and desirable properties when used as an adjunct with surface-active agents and more particularly with soap.

While I have found my new sodium borates to be highly efficient in conjunction with soap as the surface tension or interfacial tension reducing agent, the invention is not limited to the use of soap as it is well known that builders which are useful with soap are also useful with other such agents. Thus the sodium metaborate may be used in conjunction with the sodium salts of "keryl" benzene sulfonate, succinic ester sulfonates, Igepon T, and other such surface tension reducing agents that are stable in alkaline solution. It cannot be used to obtain favorable results with surface or interfacial tension reducing agents that are unstable in alkaline solution, or with those which depend on a cation-active rather than an anion-active part of the molecule, even though the latter may be stable in alkaline solution, or with such agents that are not ionized in aqueous solution.

The invention comprises the new detergent composition including sodium metaborate material of the kind described and soap or other water-soluble surface tension and interfacial tension reducing agent that is stable at all pH's within the range of about 7 to 13 and that in water gives an anion upon which surface tension lowering depends.

The invention comprises also the improved sodium borate and the method of making it.

In making the new detergent composition there is first made the new borate and there is formed a mixture of the surface tension and interfacial tension reducing agent and the new borate.

The composition may be mixed dry, for addition to the water to be used in washing. The composition may be left in granular or powder form or pressed into a tablet, bar, or cake, as by mixing the soap and sodium borate in selected proportions and then forming the mixed composition in a type of press and with technique that is usual in the pressing of such tablets, cakes or bars of soap and other detergents. To facilitate the bonding of the composition by pressing, there may be admixed any desired water-soluble binder such as dextrine, casein, or other conventional binder for soap bars. The composition may also be prepared as a more or less homogeneous solid mass and ground to a suitable size of granules to produce the finished product. Or the composition may be prepared as a concentrated solution in hot or cold water, with or without some of the ingredients in suspension, because of their use in proportions above that which is soluble in the water present, and then converted to either granules or beads, as by spray congealing or spray drying by methods that are commonly employed in forming granules or beads of soap.

In a modification of the method of mixing, one of the ingredients in a somewhat moist condition, as for example the sodium borate, is tumbled in a rotated drum with the other ingredient in a dry condition; the other ingredient is thus caused to adhere to and coat the granules. For best results, the central or core ingredient of such tumbled product should be the one which it is desired to protect from air and moisture. When sodium hydroxide, for instance, is used in a composition with soap and borax or boric acid, in proportion of the sodium hydroxide to the boron oxide stated elsewhere herein, the sodium hydroxide in the form of moist granules is tumbled with the other ingredients, so that the sodium hydroxide becomes the core of the final particles. However, I do not prefer this method of making the composition because of the danger of non-uniformity of the borate composition when the borax or boric acid and sodium hydroxide have not been prereacted, to form the borate.

In another modification of the invention that is satisfactory for most purposes, the surface-active agent and the borate are added separately to the water which is to be used for washing dishes, clothes, or other articles.

In the above compositions other ingredients may be added without departing from the spirit of my invention. Thus there may be added an additional alkaline material such, for example, as sodium metasilicate, a calcium and magnesium sequestration agent such as sodium tripolyphosphate or one of such agents previously mentioned, or other ingredients conventionally added to detergent compositions an example of which is the color indicator of a dish-washing compound.

For best results under widely differing conditions of use, the proportion of the sodium borate composition should be at least 1 part and suitably 1 to 5 parts for each part of the surface-active agent or agents used. Larger proportions of the borate are allowable so long as a substantial proportion of surface-active agent is present, but such larger proportions are uneconomical.

When the borate is of a composition which approaches the metaborate, $Na_2O,B_2O_3$, as a lower limit and is used in about the proportion of 1 to 5 parts to 1 part of the surface-active agent, the borate does not seriously alter the pH of a soap solution and causes the solution of other useful surface-active agents to approach that pH. When the composition tends more toward the orthoborate, $3Na_2O,B_2O_3$, it raises the pH of the entire solution, regardless of the surface-active agent to the range of pH 10.0 to pH 12.0 which is found to be the desirable pH range for use of these cleaning mixtures containing the new borate. At the same time, the composition is more effective in cleansing of dishes and brightening of fabrics than usual compositions that are of comparable or even somewhat higher pH than my composition and that include soap or other surface-active agent and a conventional detergent salt.

Using standardized procedures for testing the effectiveness of detergent compositions for laundry use, I have made a number of determinations of the comparative merits of my new borate composition with soap and with soap and phosphate compositions of kind widely used. The determinations were made in a standard launderometer and the brightness of the laundered specimens of fabric, which were initially the same, was read with a photometer. The results follow.

Using an ordinary sodium soap solution of concentration 0.1%, I have found the increase in brightness of a standard soiled fabric to be but 2.0 units when washed in a standard launderometer for 15 minutes. The addition of 0.1 per cent on the weight of the soap solution of my sodium borate of moisture content 50 per cent gave an increase in brightness of 9 units when run in the same machine, in spite of the fact that the borate had little effect on the pH, the pH of the soap and borate solution being 10.2 as compared to 10.1 for the soap alone.

The detergent effect was greater for the new soap and borate composition in every case than for a soap and usual builder combination in equal concentration and of similar pH. For example, in 30 minutes the above soap and borate composition of pH 10.2 gave an increase of brightness of 16 units as compared with 15.5 units for soap and sodium carbonate solution of identical concentration at the much higher pH of 10.9.

It is important also that the 0.1 per cent of sodium carbonate added was anhydrous whereas the 0.1 per cent of the new sodium borate contained 50 per cent of water.

This effect of the sodium borate as a builder with soap is not involved with an increase of pH, as with usual soap builders, as the degree of alkalinity, in terms of hydroxyl ion concentration, of the less effective soap-sodium-carbonate mixture at pH 10.9 is about five times as great as that of the soap-borate at pH 10.2. In any use of detergents involving immersion of the hands of the operator, multiplication of the degree of alkalinity by about 5 is highly objectionable. With my new borate composition, a soap may be built with very large amounts of the borate that would still be comparatively mild to the skin.

Additional compositions have been made containing sodium oxide and boron trioxide respectively in the ratios of 1 to 3 mols of the former to 1 mol of the latter, the resulting borate com-

position being dried down to the moisture content which remains at 230° F., and then granulated, that is, milled either to small particles of such size as to be individually visible to the eye or milled to a fine powder. With the soap and borate containing an excess of the sodium oxide over that required to form metaborate with the boron trioxide, the cleansing effect was very high for each proportion of the alkali as compared to the cleansing power of present detergent mixtures of the same pH when dissolved in water.

Various comparisons show the superiority of the borate over comparable sodium carbonate and sodium metasilicate as soap builder at similar pH values, as is the case in the following example with sodium metasilicate, a builder which is commonly used for the higher pH levels of detergency as in power laundry work where the solution does not come into contact with the hands of the operator. In each case, washing of the fabric was conducted for 15 minutes and there was used an aqueous 0.1% soap solution containing in one instance 0.1% of metasilicate and in the other 0.1% of a sodium borate in which the sodium oxide is present in a ratio to boron trioxide of approximately 2:1. The two solutions were of pH's 11.9 and 11.8, respectively. The increase in brightness due to the laundering with the sodium borate and soap composition was 14 units as compared to only 12 units with the soap and metasilicate. It is found that at these higher pH levels the advantage of the sodium borate compositions is somewhat less relatively than at lower levels but nevertheless definitely better than that of other alkaline builders of comparable or even somewhat higher pH.

In addition to the greater effectiveness of the borate and soap composition of a given pH, the new sodium borate contains a larger proportion of sodium oxide to the total weight of the material on the anhydrous basis than any of the other salts which will give a comparable pH in the same concentration. Thus a solution of the borate composition which in 0.1% concentration of anhydrous borate will give the same pH as a 0.1% solution of sodium carbonate contains more sodium oxide and has greater buffer value. The same is true of a borate composition which in 0.1% solution will give the same pH as a 0.1% solution of sodium metasilicate, the two being present in the same content of anhydrous builder. Therefore, the new borate composition will have a greater effect in uses where the detergent must neutralize acidity in the soil being removed. Generally it may be said that the borate composition will stand more abuse (unfavorable conditions of use) without losing its effectiveness than will any other known soap builder.

In the manufacture of the borate, I form a solution including the relatively inexpensive commercial borax and sodium hydroxide in proportion at least equal to the amount required theoretically to convert the borax to sodium metaborate according to the following equation:

$$Na_2B_4O_7+2NaOH=4NaBO_2+H_2O$$

This reaction requires at least 2 mols of sodium hydroxide for 1 mol of the borax and gives a product containing sodium and boron in the ratio corresponding approximately to 1 mol of sodium oxide ($Na_2O$) to 1 mol of boron trioxide ($B_2O_3$). Particularly satisfactory results in detergent compositions are obtained, however, when the ratio of sodium hydroxide to borax is increased to a higher ratio up to 3 mols of sodium oxide to one of boron trioxide. In these higher ratios, I find my new detergent builder to be definitely superior to others on the market but not in as great a ratio for a given pH of the solution as when the molecular ratio of boron trioxide to sodium oxide is about 1:1. The most desirable range is from about 1.1 to 2 mols of $Na_2O$ to 1 $B_2O_3$, borates with higher ratios of sodium oxide being more alkaline and of somewhat limited applicability although useful when such relatively highly alkaline detergents are permissible.

Instead of commercial borax, it is advantageous from the standpoint of cost for a given effectiveness to use crude borate ore. Thus ores representing crude forms of soluble boron compounds may be used, provided the proper ratio of alkali to boron obtains and insoluble matter in the crude is filtered out. The amount of sodium hydroxide to add in establishing the proper ratio must be determined by analysis of the particular lot of raw boron material to be treated, to give the stated $M_2O:B_2O_3$ ratio. It is understood that the sodium oxide and boron trioxide are combined in the finished product but the ratios of the sodium and boron are most conveniently stated in the form of the ratios of their two oxides which may be considered as jointly forming the molecule of the borate. Thus in sodium metaborate, the molar ratio would be 1:1, in sodium sesquiborate 2:1, and in sodium orthoborate 3:1.

In treating the ore or boron-containing raw material, I dissolve the said material in water with the selected proportion of sodium hydroxide, filter if necessary to separate undissolved foreign matter, evaporate the clear solution, heat the resulting residue, and then mill it to particles of desired size that are substantially non-caking and free-flowing. This requires that the moisture content be not appreciably above 50 per cent in any case. I have found it desirable to dry at 230° F., and get a much lower moisture content with a resulting greater concentration of active agent and greater stability against caking.

In a typical preparation of the sodium borate of kind described, there were dissolved in 100 parts of water 20.2 parts by weight of borax ($No_2B_4O_7.10H_2O$) and 9 parts of sodium hydroxide calculated on the anhydrous basis. After the solution was made uniform, it was subjected to evaporation to produce a residue of the desired sodium borate. This was then further heated until the moisture content of the borate was 50 per cent or less. The resulting material was then sent through a hammer mill and formed to particles predominantly finer than 20 mesh in which form the material is ready for use in the detergent composition. When it is desired that the finished detergent composition be more alkaline, the amount of sodium hydroxide in the above example is increased to as much as 40 parts of sodium hydroxide to 20.2 of the borax. For most practical uses the amount of sodium hydroxide used should be between 9 and 24 parts.

If soap is used as the surface-active agent, there is selected a water-soluble soap such as any of the common sodium soaps including the sodium stearate, palmitate, oleate, laurate or like sodium salts of higher fatty acids, either alone or mixed with each other, a mixture ordinarily being selected. For purposes of economy and also to produce profuse lathering, sodium abietate may be included or even substituted entirely for the other soaps. The soap may contain alkali salts of the fatty acids present in coconut and similar oils of relatively low average molecular weight of acids present.

Examples of surface-active agents that may be used in place of soap are sodium lauryl sulfate; sodium keryl benzene sulfonate; sodium dialkyl succinyl sulfonate, the size of the alkyl radical selected being reduced as the desired degree of alkalinity of the borate solution is increased; fatty acid derivatives of N-phenyl taurine or N-phenyl methyl taurine such as Igepon T; and like agents that are stable in alkaline solutions. I do not find it advantageous to add my borate to cation-active agents or to the non-ionizing types such as the polyethylene oxide compounds.

In addition to the surface-active agent and sodium borate there may be incorporated also other materials. Various calcium and magnesium sequestration agents may be added to advantage to soap. Such calcium sequestration agents that may be used are tetrasodium pyrophosphate, sodium hexametaphosphate, and sodium tripolyphosphate, the calcium and magnesium sequestration agent being often used to advantage in about the same proportion as the sodium borate but for special uses, as with very hard water, it is desirable to increase the relative proportion of such sequesterer. In very soft water such as one containing only around 2–3 grains of hardness, on the other hand, it is desirable to decrease the sequesterer to an amount substantially below the proportion of the borate. When the sequestration agent is used, then the effectiveness of the detergent composition in hard water is increased because of the protection afforded by the agent against precipitation of the soap and borate by hardness of the water used.

While I find it advantageous to use these sequesterers with soap and the new borate they are not as advantageous with other surface-active agents and my borate, although they can be used without detriment and offer some advantage. Similarly inexpensive neutral salts such as sodium chloride, sodium sulfate, etc. when added to a surface-active agent give advantages that more than offset their cost when the amount of such salts used is substantially less than that of the combined weight of borate and surface-active agent.

It will be understood that certain details that have been given are for the purpose of illustration, not restriction, and that variations within the spirit of the invention are intended to be included within the scope of the appended claims. Thus while these compositions have been described in relation to dishwashing or home laundering they are also effective for such diverse purposes as bottle washing; metal cleaning, particularly before plating; floor, wall and tile cleaning, the composition to be selected in accordance with the intent to clean by hand or by machine; and other analogous and related purposes. In some of its forms it is a desirable packaged soap composition for sale to the public for general home use.

1. A cleansing composition in dry form comprising an intimate mixture of a water soluble fatty acid soap and a soap builder consisting of a sodium borate having 1.1 to 2 mols of sodium oxide to one mol of boron trioxide, the proportion of sodium borate being substantial but not above 5 parts of the borate to one part of the soap.

2. The cleansing composition described in claim 1 including a molecularly dehydrated sodium phosphate serving as a calcium sequestration agent.

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